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ORIGINAL PAPER

Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska

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Abstract Understanding how the concentration and chemical quality of dissolved organic matter (DOM) varies in soils is critical because DOM influences an array of biological, chemical, and physical processes. We used PARAFAC modeling of excitation–emission fluorescence spectroscopy, specific UV absorbance ($SUVA_{254}$) and biodegradable dissolved organic carbon (BDOC) incubations to investigate the chemical quality of DOM in soil water collected from 25 cm piezometers in four different wetland and forest soils: bog, forested wetland, fen and upland forest. There were significant differences in soil solution concentrations of dissolved organic C, N, and P, DOC:DON ratios, $SUVA_{254}$ and BDOC among the four soil types. Throughout the sampling period, average DOC concentrations in the four soil types ranged from 9–32 mg C l^{-1} and between 23–42% of the DOC was biodegradable. Seasonal patterns in dissolved nutrient concentrations and BDOC were observed in the three wetland types suggesting strong biotic controls over DOM concentrations in wetland soils. PARAFAC modeling of excitation–emission fluorescence spectroscopy showed that protein-like fluorescence was positively correlated ($r^2 = 0.82$; $P < 0.001$) with BDOC for all soil types taken together. This finding indicates that PARAFAC modeling may substantially improve the ability to predict BDOC in natural environments. Coincident measurements of DOM concentrations, BDOC and PARAFAC modeling confirmed that the four soil types contain DOM with distinct chemical properties and have unique fluorescent fingerprints. DOM inputs to streams from the four soil types therefore have the potential to alter stream biogeochemical processes differently by influencing temporal patterns in stream heterotrophic productivity.

Keywords Biodegradable dissolved organic carbon · Dissolved organic matter · Fluorescence · PARAFAC · Peatland · Soil biogeochemistry

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Introduction

Dissolved organic matter (DOM) is a mixture of soluble organic compounds derived from both terrestrial and aquatic sources and in soils, plays an important role in the cycling of C, N and P. DOM controls the nutrient balance in terrestrial ecosystems by acting as a vector for dissolved losses of N, P and C (Qualls

et al. 1991). DOM also provides a substrate for microbial metabolism, facilitates the transport of metals and plays an important role in soil formation (Kalbitz et al. 2000). These qualities of DOM differ in relation to the precursor organic material; thus, understanding how the chemical composition of soil DOM varies spatially and temporally is important for elucidating the biogeochemical role of DOM within the soil profile and along the soil-stream continuum.

Wetlands are an important source of dissolved organic carbon (DOC) to aquatic ecosystems (Mulholland 1997). As a result, wetland inputs of DOM to streams can have a profound impact on the chemistry (Billett et al. 2006) and biology (Sun et al. 1997) of aquatic ecosystems. Aquatic DOC concentrations have been shown to be significantly correlated with peatland coverage (Aitkenhead et al. 1999), wetland area (Gorham et al. 1998) and wetland type (Xenopoulos et al. 2003). Despite the recognition that wetlands are a substantial source of DOC to surface waters, the chemical quality of DOC from different wetland types and how it varies seasonally is not well understood. Moreover, the importance of wetlands as a potential source of biodegradable DOC to support stream heterotrophic productivity has received little attention.

The biodegradation of DOC (BDOC) is an important process controlling DOC dynamics in soils, and controls on BDOC to a large extent are still poorly understood in soils (Kalbitz et al. 2000). In particular, DOM derived from wetland soils contains high concentrations of dissolved humic substances that have conventionally been considered recalcitrant and largely unavailable for bacterial degradation (Geller 1986). However, evidence suggests that this recalcitrant DOM may be more available than previously presumed and that terrestrially-derived humic substances might represent an important component of the streamwater BDOC pool (Moran and Hodson 1990; Volk et al. 1997). Since DOM is an important source of C and energy for microbial heterotrophs and given its heterogeneous nature, scientists have developed a variety of simple indicators for BDOC in natural ecosystems.

One common approach is to use elemental ratios, such as C:N, H:C or O:C, as an indicator of the biodegradability of DOM (Meyer et al. 1987; Hunt et al. 2000). Another approach is the use of specific UV absorbance ($SUVA_{254}$), an indicator of aromatic C content, which has been shown to be negatively correlated with BDOC (Kalbitz et al. 2003a; Saadi et al. 2006). However, Marschner and Bredow (2002) found no relationship between $SUVA_{254}$ and BDOC and suggested BDOC of non-aromatic compounds varied greatly. A third approach uses molecular weight as determined by ultrafiltration (Meyer et al. 1987). The traditionally accepted model of biodegradation is that as the size of the molecule increases, the degree of recalcitrance to bacterial breakdown decreases (Saunders 1976). This view is no longer widely accepted since studies indicate high molecular weight compounds can be readily utilized by microbes (Amon and Benner 1996). These findings suggest there are multiple factors controlling the biodegradability of DOM and that more advanced techniques for assessing BDOC in natural environments are necessary.

Recent advances in fluorescence spectroscopy enable the rapid and precise characterization of DOM and provide an alternative to the traditional approaches for predicting BDOC. Laboratory incubation studies have shown fluorescence spectroscopy can be used successfully to obtain information about the biodegradability of DOM (Kalbitz et al. 2003a; Wu et al. 2003; Saadi et al. 2006). Excitation–emission fluorescence spectroscopy (EEMs) can also be analyzed using the multivariate modeling technique parallel factor analysis (PARAFAC), a three-way decomposition method similar to principal component analysis (Stedmon et al. 2003; Stedmon and Markager 2005; Cory and McKnight 2005). PARAFAC decomposes the fluorescence spectra of DOM into independent components whose abundance can be related to differences in composition and source material. PARAFAC analyses have been used successfully in soil DOM studies to differentiate between different terrestrial sources (Ohno and Bro 2006) and to investigate the sorption of DOM onto mineral soils (Banaitis et al. 2006).

We used PARAFAC modeling of fluorescence EEMs, $SUVA_{254}$ measurements and BDOC incubations to investigate the chemical quality of DOM from four different forest and wetland soil types in coastal temperate watersheds of southeast Alaska. Our goal was to understand how the chemical quality and biodegradability of soil solution DOM varies between the different soil types. This, in turn, provides an improved understanding of the potential for

different soils to contribute labile DOM to aquatic ecosystems. We further evaluate the use of PARAFAC modeling of fluorescence EEMs as a tool to identify unique terrestrial sources of DOM from coastal temperate watersheds in southeast Alaska.

Methods

Site descriptions and experimental design

DOM was examined in soil solution samples collected near Juneau, Alaska (58.2°N, 134.2°W). Juneau has a maritime climate with a mean annual precipitation of 1,400 mm and a mean monthly temperature ranging from −2 to 14°C at sea level. The heavily glaciated, mountainous terrain of southeastern Alaska, the cool climate and the abundant precipitation create a landscape mosaic of carbon-rich peatlands mixed with coniferous forests dominated by *Picea sitchensis* and *Tsuga heterophylla*. Overall, wetlands account for approximately 30% of the land area in the Tongass National Forest (USDA 1997).

Three replicate field sites were established for four different forest and wetland soil types (bog, forested wetland, fen and upland forest) during the spring of 2006, yielding a total of 11 sites (only two replicate upland forest sites). The bog and forested wetland sites were selected because these wetlands represent the most typical mapped wetland communities in southeast Alaska (USDA 1997). The fen sites were included to represent the wetland diversity present in southeast Alaska, and the upland forest sites were selected to provide a mineral soil contrast to the three wetland types. All three wetland types are peatlands, characterized by the accumulation of organic matter due to frequent near-surface soil saturation.

The bog sites were mapped as a complex of deep, moderate to well decomposed peat (>1 m deep) that has accumulated over glacial till and were typical of the slope bog wetland type (NWWG 1988). Water and nutrient supply to the bog is dominated by atmospheric inputs although groundwater and surface runoff can be locally important. The forested wetland sites were typical of the raised peatland swamp (NWWG 1988) with 0.5–0.75 m deep peat overlaying glacial till. Forested wetland sites have formed on the same deposits as the bog, although forested wetlands maintain a different hydrologic regime where soil hydraulic conductivity is greater than in the bog but soil saturation is sufficient to create anoxic conditions.

Fen sites were typical of the rich fen (NWWG 1988) wetland type and have greater graminoid and forb diversity as well as more robust growth. Nutrient and water supply to the bog and fen sites are typified by extremes since fens receive large inputs through surface water and groundwater from the surrounding uplands as well as via precipitation. These hydrologic and geochemical inputs are responsible for the more neutral pH in fens. Upland forest sites are spodosols (Typic Humicryod) where soils are moderately deep and moderately well-drained, due to the steep slope present at the sites. The soils are colluvial material derived from bedrock dominated by igneous intrusive material. The soils at all sites were characterized by soil profile descriptions to 1 m, although we present data from the top 25 cm (Table 1).

Field sampling

Soil solution samples were collected eight times for each site from May 9, 2006 until October 17, 2006. This period of time corresponds to the approximate length of the snow free season. Soil solution samples were collected from four, 25 cm deep piezometers and combined, yielding one sample from each of the sites per sample date. Piezometers were constructed from 3.1 cm PVC pipe and inserted in a small grid across the site. The 25 cm piezometer depth corresponds to the approximate acrotelm/catotelm boundary for all wetland sites. Piezometers were used to sample soil solution in the mineral soils because our interests were in collecting a bulk sample that is representative of the upland forest. Therefore, the soil solution in the upland forest represents a composite of DOM from the O (0–15 cm), E and upper B horizons (15–25 cm). All soil solution samples were field-filtered using pre-combusted, Gelman A/E glass fiber filters (nominal pore size 0.7 μm) and stored in the refrigerator until analysis, which occurred within 48 h.

Dissolved C, N and P analyses

Concentrations of DOC (determined by non-purgeable organic carbon analysis) and total dissolved N (TDN) from soil solution samples were determined

Table 1 Characteristics for the four soil types

Site	Total N (%) Mean (SE)	Total C (%) Mean (SE)	Soil pH ($CaCl_2$) Mean (SE)	Dominant vegetation
Bog	1.6 (0.3)	50.3 (1.5)	3.3 (0.3)	*Sphagnum* spp., ericaceous shrubs, *Pinus contorta* var. contorta
Forested wetland	1.4 (0.3)	43.1 (5.6)	3.2 (0.2)	*Sphagnum* spp., *Lysichiton americanum*, *Tsuga heterophylla*
Fen	2.4 (0.3)	44.2 (2.4)	5.5 (0.3)	*Carex* spp., *Alnus* spp., *Lysichiton americanum*
Upland forest (org) 0–15 cm	0.9 (0.1)	45.1 (7.1)	3.0 (0.2)	*Tsuga heterophylla*, *Vaccinium* spp., *Oplopanax horridum*
Upland forest (min) 15–25 cm	0.3 (0.1)	7.2 (1.6)	a	

Soil horizons down to 25 cm (depth of piezometer) were averaged for the bog, forested wetland and fen sites and then averages and standard errors (±1) were taken of sites within each soil type ($N = 3$). For all wetland sites, the depth of the peat extended below 25 cm

[a] Indicates missing values

by high-temperature combustion using a Shimadzu TOC-V Organic Carbon and Total Nitrogen Analyzer with lower detection limits of 0.4 mg C l^{-1} for DOC and 0.1 mg N l^{-1} for TDN. Ammonium (NH_4-N) and nitrate (NO_3-N) were measured on a Dionex Ion Chromatograph (cation ICS-1500; anion DX-600), and dissolved organic N (DON) was calculated as the difference between TDN and inorganic N (NH_4-N and NO_3-N). The calculated error or lower quantification threshold for DON values during analytical runs was 0.2 mg N l^{-1} (square root of the sum of the squared analytical errors of TDN, NH_4-N and NO_3-N).

Soluble reactive phosphorus (SRP) was measured using the ascorbic acid method (Murphy and Riley 1962), total dissolved phosphorus (TDP) was measured using a persulfate digestion (Valderrama 1981) in conjunction with the ascorbic acid method, and dissolved organic phosphorus (DOP) was calculated as the difference between TDP and SRP. A 10 cm quartz flow through cell was used for both SRP and TDP analyses to enable the detection of low P concentrations (1.0 μg P l^{-1}).

Spectroscopic analyses and PARAFAC modeling

Specific UV absorbance ($SUVA_{254}$) was measured using a 1.0 cm quartz cell on soil solution DOM following the procedures of Weishaar et al. (2003). Samples were allowed to warm to room temperature, analyzed on a Genesys 5 spectrophotometer and $SUVA_{254}$ was calculated as the UV absorbance at 254 nm per 1 mg-C^{-1} m^{-1}. Fluorescence excitation–emission matrices (EEM) of DOM were measured on a Fluoromax-3 (Jobin Yvon Horiba) fluorometer with a xenon lamp following the procedures of Hood et al. (2007). EEMs were created by measuring fluorescence intensity across excitation wavelengths ranging from 240–450 nm and emission wavelengths ranging from 300–600 nm. Samples were diluted to avoid inner filter effects by adding Milli-Q water to soil solution samples to provide an optical density of 0.02 at 300 nm (Green and Blough 1994). EEMs were corrected for instrument bias and Raman normalized using the area under the water Raman peak at excitation wavelength 350 nm.

PARAFAC modeling of fluorescence EEMs was conducted with MATLAB using the PLS_toolbox version 3.7 (Ohno and Bro 2006) following the procedures described in Stedmon et al. (2003; Stedmon and Markager 2005). PARAFAC can take overlapping fluorescence spectra and decompose the data into score and loading vectors that are quantitative estimates of the relative concentrations of the components. If the correct number of fluorescent components is selected using the PARAFAC model, the components can be compared for each sample by determining the relative contribution of each component to the total DOM fluorescence. Since DOM is a complex mixture of organic compounds, it is doubtful that each component represents a pure or specific fluorophore; rather, each component more likely represents a group of fluorophores with very similar fluorescence characteristics (Stedmon and Markager 2005). We therefore refer to fluorescence components

in this study as "humic-like, fulvic-like or protein-like" since these components are likely a mixture of similar fluorophores rather than pure fluorophores.

Using PARAFAC modeling, we identified a total of nine unique components within the fluorescence EEMs (Table 2). We validated our PARAFAC model using core consistency diagnostics (Ohno and Bro 2006) followed by a split plot analysis (Stedmon and Markager 2005). The core consistency provides a quantitative measure of how well the spectral loadings represent variation in data. If the core consistency is not close to 100%, a different number of components should be selected. The core consistency score in our nine component model was 98.1% and the model explained 99.7% of the variability in the dataset. To perform a split plot analysis, we randomly divided our data array into two separate halves of 165 EEMs each (total dataset of 330 EEMs), applied the PARAFAC model to each half separately and repeated the analysis stepwise from 7 to 10 components. We selected nine components as the best model fit since we found good agreement in the spectral loadings for each dataset.

The percent contribution of each of the components was determined by quantifying the relative abundance of each component in comparison to the other components identified by the PARAFAC model. All nine components identified by our model have been previously identified as either part of a PARAFAC model (Stedmon et al. 2003; Stedmon and Markager 2005; Ohno and Bro 2006) or through visual analysis of EEMs (Coble 1996; Baker 2001). Of the nine components identified by the PARAFAC model, we focused our analyses on the following four components: component 1 (humic-like fluorescence), component 4 (fulvic-like fluorescence), component 8 (tryptophan-like fluorescence) and component 9 (tyrosine-like fluorescence). These four components were selected because they are commonly observed fluorophores in other studies and on average, the relative contribution of the four components taken together accounted for approximately 51% (average of four soil types) of the total DOM fluorescence.

Biodegradable DOC incubations

In this study, we refer to BDOC as the DOC utilized by heterotrophic microbes through two different processes: (1) complete mineralization of C to obtain energy, and (2) incorporation of C into microbial biomass. BDOC was measured following a slightly modified protocol described in Qualls and Haines (1992). Soil solution samples were initially analyzed for DOC concentrations and then filtered through a 0.2 μm filter

Table 2 Characteristics of the nine different components identified by the PARAFAC model in this study

Component	Excitation maxima (nm)	Emission maxima (nm)	Comps. identified from previous studies	Description
1	<250	450–460	Stedmon and Markager (2005) Comp. 1	Humic-like fluorophore
2	330	460–480	Ohno and Bro (2006) Comp. 1	Humic-like fluorophore
3	<250 (370)	440	Stedmon and Markager (2005) Comp. 4	Fulvic-like fluorophore
4	340	410	Baker (2001) Comp. B	Fulvic-like fluorophore
5	290	414	Coble (1996) Comp. M	Humic-like fluorophore
6	240 (300)	416	Stedmon and Markager (2005) Comp. 3	Humic-like fluorophore
7	240 (315)	400	Stedmon and Markager (2005) Comp. 6	Humic-like fluorophore
8	280	330–340	Stedmon and Markager (2005) Comp. 7	Tryptophan-like fluorescence
9	275	304–306	Stedmon and Markager (2005) Comp. 8	Tyrosine-like fluorescence

Secondary maxima are shown in parentheses

to remove the majority of microbial biomass. After filtration, 23 ml of the filtrate was transferred to ashed amber glass bottles and 2 ml of a bacterial inoculum was added. Caps were placed loosely on the bottles to allow air movement, and samples were incubated at 25°C for 30 days in the dark. After 30 days, the solution was re-filtered through a 0.2 μm filter, DOC was measured, and BDOC was calculated as the difference in DOC before and after the 30 day incubation. DOC analysis was also performed on the bacterial inoculum and additional DOC provided to the soil water sample (ranged from 0.1 to 0.3 mg C l^{-1}) was added to the initial sample DOC concentration.

The bacterial inoculum was prepared by first collecting soil from the riparian zone at one of the study sites. Approximately 10 g of sieved, moist soil was combined with 50 ml of deionized water, gently shaken for 10 min, and allowed to settle over night. The bacterial inoculum was next filtered through a pre-combusted, Whatman GF/D filter, transferred to a pre-combusted glass bottle, diluted 1:1 with deionized water and incubated at 25°C for 24–48 h before addition to the sample solution.

Statistical analyses

We used a mixed-model (Proc Mixed; SAS Institute, Inc. 2003), repeated measures analysis of variance (ANOVA) with a compound symmetry (CS) covariance structure in conjunction with a Tukey's pairwise differences test to evaluate the effects of soil type on nutrient concentrations, BDOC and the relative contribution of PARAFAC components. All values for different sample dates were considered as repeated measurements. Because we were only interested in statistically comparing the four soil types, we did not statistically evaluate the temporal patterns within each soil type. Linear regression models were used to evaluate relationships between BDOC and the chemical characteristics of DOM using Proc GLM, SAS (SAS Institute, Inc. 2003).

Results

Dissolved C, N and P concentrations

For all sample dates taken together, average soil solution concentrations of C, N and P varied by more than 100% across the four different soil types (Table 3). Average DOC concentrations ranged from 9 mg C l^{-1} in the upland forest to 32 mg C l^{-1} in the forested wetland and were not significantly different between the forested wetland and bog ($P > 0.05$). Concentrations of DOC in the fen and upland forest were significantly less than in the bog and forested wetland ($P < 0.05$). There was no significant difference in DON concentrations between the three wetland types, whereas DON concentrations for the upland forest were significantly less than in the three wetland types ($P < 0.05$). The DOC:DON ratio in the forested wetland was significantly greater than those for the other three soil types ($P < 0.05$), while the fen had the lowest DOC:DON ratio and was significantly less than in the forested wetland and bog ($P < 0.05$). Despite possessing significantly lower DON concentrations than the other soil types, the DOC:DON ratio in the upland forest was lower than the bog and significantly lower than in the forested wetland. DOP concentrations in the fen were significantly greater than in the bog and the upland forest but did not differ from those in the forested wetland ($P < 0.05$). DON and DOP were the dominant fractions of total dissolved N and P for all soil types and NH_4-N dominated the pool of DIN. Concentrations of NH_4-N and SRP were significantly greater in the fen than those in the other soil types ($P < 0.05$), while both NH_4-N and SRP were significantly less in the upland forest than in the other soil types ($P < 0.05$). Similar to DOC,

Table 3 Mean ($N = 3$) and standard error (± 1) of dissolved nutrient concentrations for each of the four soil types

	DOC (mg C l^{-1})	DON (mg N l^{-1})	DOC:DON ratio	NH_4-N (μg N l^{-1})	NO_3-N (μg N l^{-1})	SRP (μg P l^{-1})	DOP (μg P l^{-1})
Bog	27.1 (2.0)	0.8 (0.1)	34.1 (3.9)	38.3 (5.2)	4.2 (1.1)	18.2 (2.1)	24.7 (4.3)
FW	32.1 (2.8)	0.7 (0.1)	49.7 (4.5)	62.5 (5.8)	5.9 (2.2)	20.6 (3.2)	31.3 (4.2)
Fen	14.6 (1.2)	0.6 (0.1)	24.6 (2.6)	200.9 (9.9)	7.5 (2.9)	46.2 (5.3)	51.2 (7.3)
Upland	9.2 (1.1)	0.3 (0.1)	30.3 (3.4)	16.4 (3.8)	6.9 (2.3)	8.5 (1.9)	12.7 (1.8)

FW, forested wetland and Upland, upland forest

the upland forest had the lowest average N and P concentrations observed.

Concentrations of soil solution DOC in the bog and forested wetland exhibited minima in the spring and fall and peaked at greater than 35 mg C l^{-1} during the mid-summer growing season (Fig. 1a). The upland forest showed a contrasting seasonal pattern where the greatest DOC concentrations (15–17 mg C l^{-1}) were observed during the spring/early summer and fall months. DON concentrations were high for all soil types during the spring sampling, decreased during the summer growing season to a low of 0.1 mg N l^{-1} in the upland forest and gradually increased during the autumn wet season (Fig. 1b). DOP concentrations for all soil types were greatest during the spring followed by a gradual decrease throughout the remainder of the growing season (Fig. 1c). DOC:DON ratios in the bog and forested wetland were lowest during the spring and fall months compared to the summer growing season, while seasonal variation in DOC:DON ratios was small in the fen and upland forest (Fig. 1d). Seasonal variation in DIN and SRP concentrations was small in the bog, forested wetland and upland forest, whereas NH_4-N and SRP concentrations in the fen were greater during the summer compared to the summer and fall (data not shown).

Spectroscopic properties of DOM and PARAFAC modeling

$SUVA_{254}$ of DOC proved to be a good indicator of differences in the chemical quality of soil DOM between soil types (Fig. 2a). Average $SUVA_{254}$ values ranged from 3.5 l mg-C^{-1} m^{-1} in the fen to 4.4 l mg-C^{-1} m^{-1} in the forested wetland and were significantly lower for the fen than those for the other soil types ($P < 0.05$). This range in $SUVA_{254}$ values corresponds to an aromatic C content of approximately 25–34% according to the linear model devel-

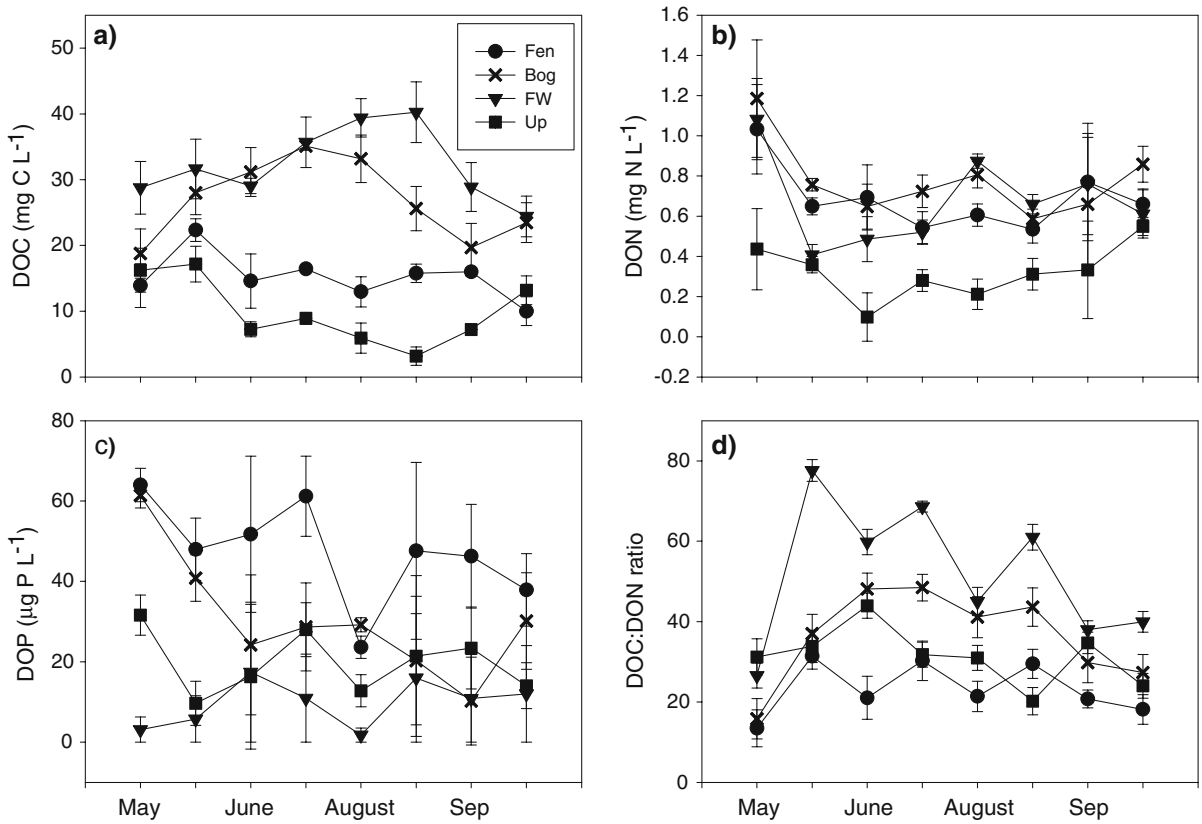

Fig. 1 Time series of average DOC, DON and DOP concentrations and DOC:DON ratios for the four soil types collected across the range of sample dates. Error bars indicate ±1 SE and $N = 3$ for all soil types. Abbreviations are: FW, forested wetland and Up, upland forest

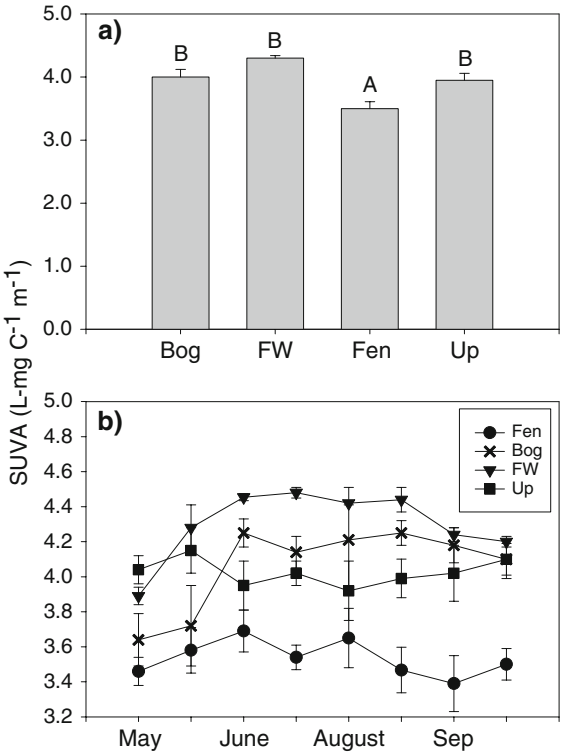

Fig. 2 (**a**) Average soil solution $SUVA_{254}$ values and (**b**) Time series for the four soil types collected across the range of sample dates. Significant differences among soil types are indicated by different capital letters above the columns, error bars indicate ±1 SE and $N = 3$ for all soil types. Abbreviations are: FW, forested wetland and Up, upland forest

oped by (Weishaar et al. 2003). In evaluating the temporal patterns in $SUVA_{254}$, there was very little variation in $SUVA_{254}$ in the upland forest and fen (Fig 2b). However, $SUVA_{254}$ in the bog and forested wetland was lowest during the spring, increased during the summer months and decreased slightly during the fall as $SUVA_{254}$ values returned to 4.1 l mg-C^{-1} m^{-1} in the bog and 4.2 l mg-C^{-1} m^{-1} in the forested wetland.

Visual analysis of the fluorescence EEMs for soil solution samples collected on June 17 revealed both similar and unique fluorophores among the different soil types (Fig. 3). In particular, all four soil types had a primary fluorescence peak at approximately 240 nm excitation and 450–460 nm emission. This fluorophore, which has been attributed to humic-like material of terrestrial origin (Stedmon et al. 2003) was very prominent at the bog while it was less well developed in the other soil types. Moreover, the fen had a fluorescence peak at approximately 280 nm excitation and 334 nm emission. This fluorophore, which has been linked to the amino acid tryptophan (Coble 1996), was very prominent at the fen but it was less well developed at the bog and upland forest and non-detectable in the forested wetland EEM.

The humic-like component 1 (determined by PARAFAC modeling) was the dominant fluorescent component in soil solution DOM for all soil types and was significantly greater in the bog than in the other three soil types ($P < 0.05$; Fig. 4). In contrast, the fulvic-like component 4 was significantly greater in the forested wetland than in the other soil types ($P < 0.05$). The ratio of the humic-like component 1 and the fulvic-like component 4 varied across the four soil types and was 1.7 for the forested wetland, 2.6 for the upland forest, 10.2 for the fen and 22 for the bog. Component 8, tryptophan-like fluorescence, was significantly greater than the tyrosine-like component 9 for the fen, upland forest, and forested wetland sites ($P < 0.05$); whereas, there was no significant difference between the two components in the bog ($P > 0.05$). The contribution of the protein-like fluorescence (the sum of tyrosine and tryptophan-like components) was significantly greater for the fen (23.4%; $P < 0.05$) than for all other soil types, and the bog (10.4%) was significantly greater than the forested wetland (4.6%; $P < 0.05$), but did not differ from the upland forest (10.1%; $P > 0.05$).

Biodegradability of DOC

Consistent with the low DOC:DON ratios and low $SUVA_{254}$ values, soil solution BDOC was significantly greater for the fen than in the other three soil types ($P < 0.05$; Fig. 5a), while BDOC was significantly greater in the bog than in the forested wetland but did not differ from the upland forest ($P < 0.05$). During the incubations, an average of 6.2, 7.3 and 2.7 mg C l^{-1} was consumed for the fen, bog and upland forest sites, respectively. Average BDOC concentrations in the forested wetland (7.2 mg C l^{-1}) were greater than in the fen, although the fraction of BDOC was nearly half (23%) that reported for the fen (42%). Similar to $SUVA_{254}$, there was very little temporal variation in BDOC for the upland forest; however, BDOC was greatest in the spring and fall compared to the summer months in the three wetland types (Fig. 5b). DOC:DON ratios, $SUVA_{254}$ values

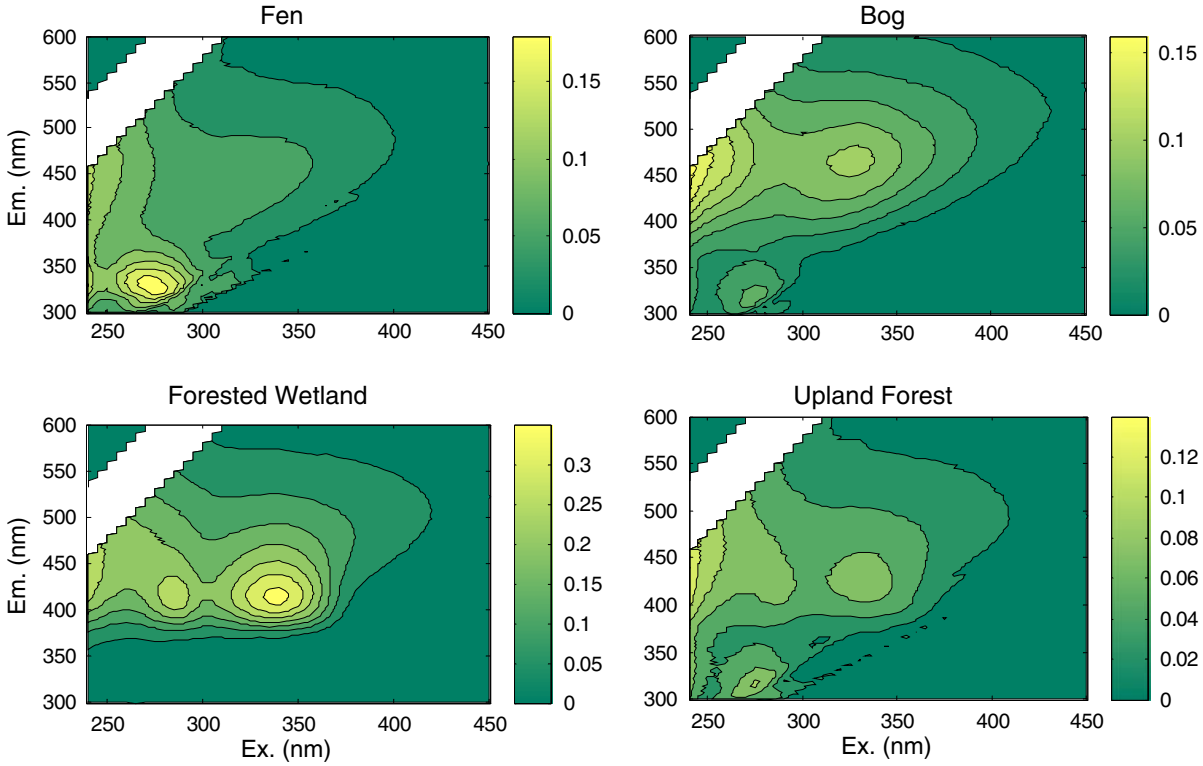

Fig. 3 Excitation–emission matrices of soil solution collected on June 17, 2006 from one replicate for each of the four soil types. Fluorescence intensities are in Raman units

and the contribution of the humic-like component 1 were all negatively correlated with soil solution BDOC for all sites taken together (Fig. 6a–c). Therefore, as the C:N ratio and the aromatic C content of the DOM increased, the biodegradability of DOM decreased. In addition, protein-like fluorescence was a strong predictor of DOC biodegradability for all soil types taken together (Fig. 6d).

Discussion

Dissolved C, N and P concentrations

The organic C, N and P concentrations reported in this study fall within the range reported in other studies of forested (Qualls and Haines 1991; Michalzik et al. 2001) and wetland soils (Fraser et al. 2001; Blodau et al. 2004), which supports the idea that DOM concentrations in wetland soils are significantly greater than in upland forest soils. The organic forms of N and P dominated soil solution for all soil types and suggests that DON and DOP are an important component of nutrient cycling in coastal temperate soils. The significantly lower concentrations of DOM in the upland forest are not surprising given the shallow depth of the O horizon as well as the potential for sorption of DOM by underlying mineral horizons (McDowell and Likens 1988; Qualls and Haines 1991). The different organic C, N and P concentrations observed between the wetland types are likely a function of distinct ecosystem nutrient dynamics caused by differences in site characteristics (i.e. soil properties), hydrologic inputs, and dominant vegetation. For example, the greater DOC concentrations in the bog and forested wetland could result from seasonal water table drawdown in combination with greater rates of organic matter decomposition and subsequent DOC production in the aerobic surface horizons (McKnight et al. 1985; Fraser et al. 2001). The fen in contrast had significantly lower DOC concentrations than the bog and forested wetland and suggests that continuous soil flushing in fens results in low pore water DOC concentrations (Urban et al. 1989).

Seasonal changes in DOC and DON concentrations have been previously documented in both

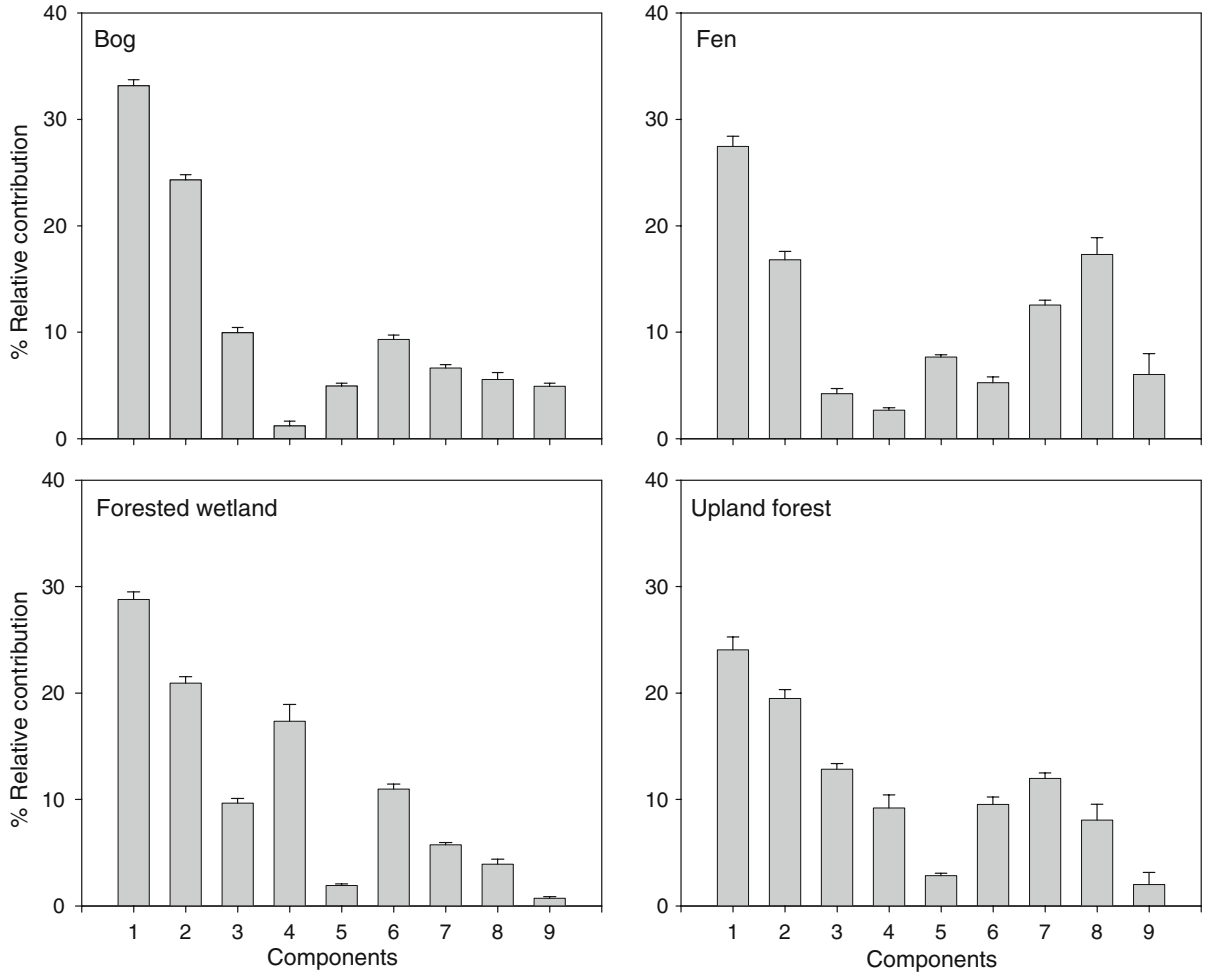

Fig. 4 Relative percent contribution of the nine components identified by the PARAFAC model for the four soil types. Refer to Table 2 for component descriptions

wetland (Devito et al. 1989; Fraser et al. 2001) and forested landscapes (Qualls and Haines 1991; Yano et al. 2004). Concentrations of DOC and DON exhibited contrasting seasonal patterns in the bog and forested wetland suggesting controls on DOC production and/or removal may be different than those for DON. During the spring snowmelt period, low wetland DOC concentrations can be attributed to prolonged soil saturation and subsequent dilution of soil pools of DOC (Fraser et al. 2001; Worrall et al. 2002). However, DOP and DON concentrations exhibited maxima during the spring which suggests that decreased biotic demand (Devito et al. 1989) in combination with soil freeze thaw events (Fitzhugh et al. 2001) can result in a pool of DON and DOP in soil solution that is potentially available to flush to streams. As a result, DOC:DON ratios exhibited minima during the spring. With the onset of the summer growing season, biotic demand for DON and DOP increases, water table drawdown occurs followed by higher rates of DOC production, which results in DOC:DON ratios typically greater than 40 in the bog and 50 in the forested wetland. DOC concentrations once again decrease during the late summer/fall wet season as the supply of DOC becomes exhausted and DOC:DON ratios approach near spring values. Our findings suggest strong biotic control over DOM concentrations in wetland soils, which is similar to previous research in five Canadian peatlands that found N and P retention during the summer growing season and net N and P export during the spring (Devito et al. 1989).

For upland forest sites, temporal patterns in DOM concentrations were similar indicating similar controls on the production and/or retention of DOM in

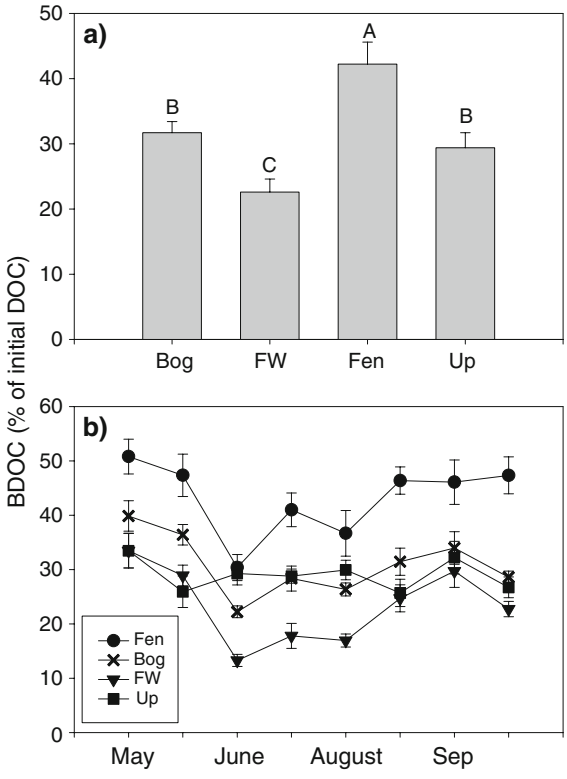

Fig. 5 (**a**) Average soil solution BDOC and (**b**) Time series for the four soil types collected across the range of sample dates. Significant differences among soil types are indicated by different capital letters above the columns, error bars indicate ±1 SE and $N = 3$ for all soil types. Abbreviations are: FW, forested wetland and Up, upland forest

forest soils (Neff et al. 2000). The greater DOM concentrations during the spring and fall months can be attributed to rising water tables associated with snowmelt and large precipitation events. When these events occur, water infiltrates into the soil causing water tables to rise into the organic horizons. Soluble organic material that has built up in the organic layers can be solubilized and potentially leached from the soil. These findings suggest concentrations of DOM are not tightly controlled by microbial demand for N and P in the soil but rather both production/degradation and physical removal processes interact to control DOM concentrations in upland forest soils.

Biodegradable DOC

The biodegradable fraction of DOC in the upland forest reported in our study (30%) was similar to values reported previously for pine and hardwood forest soils in central Massachusetts (10–45%; Yano et al. 2000) as well as for mixed hardwood soils in the southern Appalachians (20–30%; Qualls and Haines 1992). In evaluating BDOC in wetland soils, approximately 40% of the initial DOC was consumed during incubations in Japanese mountain bog pools (Satoh and Abe 1987) and an average of 45% was consumed from freshwater marshes (Mann and Wetzel 1995). Moreover, 22% of the initial DOC was consumed from two cedar bogs in the Pine Barrens region of New Jersey (Wiegner and Seitzinger 2004); thus, our estimates of BDOC in wetlands (23–42%) fall within the range of other incubation studies. In our study, the amount of DOC consumed from the forested wetland (7.2 mg C l^{-1}) was greater than in the fen (6.2 mg C l^{-1}), although the percentage of DOC consumed in the forested wetland was nearly half than reported for the fen. This suggests that both the percentage and the amount of DOC consumed could be equally as important when evaluating BDOC in soils.

Seasonal patterns in BDOC were observed in the three wetland types which is consistent with other studies of wetlands soils that have found BDOC to be greatest during the spring and fall compared to the summer (Wiegner and Seitzinger 2004). Similar to the seasonal patterns observed in $SUVA_{254}$ values and DOC:DON ratios, concentrations of BDOC strongly reflect biotic controls in wetland soils. In contrast, we observed no seasonal patterns in BDOC in the upland forest which is consistent with the results in other hardwood forests soils (Boyer and Groffman 1996). However, other studies in forest soils have found seasonal changes in BDOC (Qualls and Haines 1992; Yano et al. 2000). These findings suggest that in upland forest soils, multiple factors interact to control BDOC concentrations because labile DOC is actively removed by the heterotrophic community while at the same time, modified in its composition by the adsorption of recalcitrant fractions of DOM by mineral soils (Qualls and Haines 1992).

Effects of nutrients on biodegradable DOC

Many factors can affect the amount of BDOC in soil solution including temperature, nutrient availability, water stress, bacterial community composition and the chemical characteristics of DOM (Del Giorgio and Cole 1998). As a result, BDOC is determined by

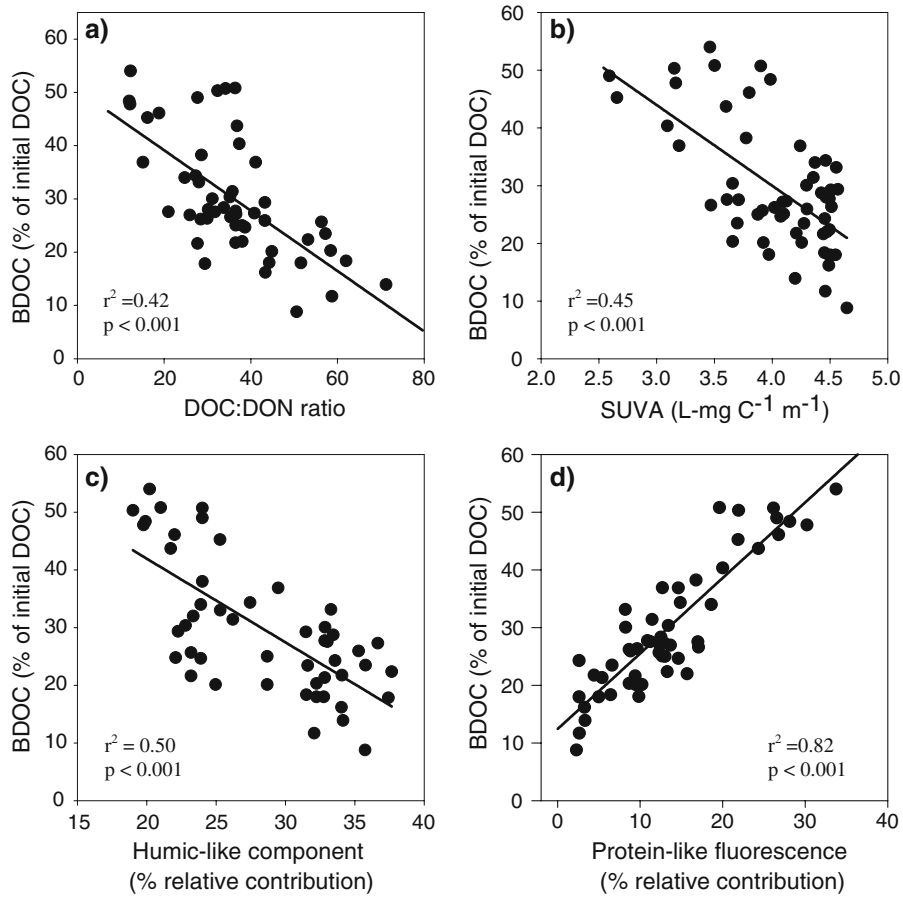

Fig. 6 Regression models describing the relationship between DOM properties and BDOC. Protein-like fluorescence is determined from the sum of tyrosine-like and tryptophan-like fluorescent components

the dynamic balance between the production and consumption of DOM in the soil. Previous BDOC experiments have shown N and P can limit bacterial growth efficiencies. In our study, BDOC was correlated with both DOC:DON ratios and protein-like fluorescence, which is consistent with laboratory trials that have shown amino acids to be a readily available source of C, N and energy for heterotrophic microbes (Ellis et al. 2000). We also found BDOC to be mildly correlated with concentrations of both DOP ($r^2 = 0.41$; $P < 0.05$) and DON ($r^2 = 0.35$; $P < 0.05$) but more importantly, BDOC was poorly correlated with DIN ($r^2 = 0.21$) and SRP ($r^2 = 0.25$). These results indicate microbes were predominantly using organic sources of N and P to satisfy growth demands. However, given that the total N and P concentrations were relatively low in comparison to the amount of DOC consumed during incubations (for every 1 mg C l^{-1} consumed, microbes require 40 μg N l^{-1} and 8 μg P l^{-1} to satisfy growth requirements using a bacterial growth efficiency of 0.4 and a bacterial molar ratio for C:N of 10 and C:P of 50), we suggest that much of the DOC consumed during incubations was not incorporated into biomass but rather was respired as CO_2 through waste respiration, as observed in Wiegner and Seitzinger (2004). Therefore, N and potentially P could have limited microbial uptake of DOC during incubations in the bog, forested wetland and upland forest soils, which is consistent with the idea that net primary production is frequently limited by N in freshwater wetlands (summarized by Aerts et al. 1999) and in temperate forests (Vitousek and Howarth 1991).

Indicators of biodegradable DOC

The ratio of DOC:DON in soil solution DOM proved to be a good predictor of biodegradable DOM supporting the idea that microbes grow more efficiently on DOM with low C:N ratios (Hunt et al. 2000; Wiegner and Seitzinger 2004). We also found a strong negative correlation between BDOC and

$SUVA_{254}$, consistent with other studies showing a relationship between aromatic C content and BDOC (Kalbitz et al. 2003a; Marschner and Kalbitz 2003; Saadi et al. 2006). These results suggest that seasonal changes in the N and aromatic C content of DOM can influence the biodegradability of DOM in soils.

PARAFAC components were good predictors of BDOC for all soil types taken together. The humic-like component 1 was negatively correlated with BDOC, which is consistent with previous studies showing that fluorophores with long emission wavelengths are highly conjugated and more aromatic in nature (Coble 1996; Stedmon et al. 2003). Therefore, the humic-like component 1 provides an independent indicator that aromatic C content can be used to predict BDOC in soil waters. The relative contribution of protein-like fluorescence was a very strong predictor of BDOC in soil solution. Previous studies have also used simple fluorescence indicators, such as a humification index (Kalbitz et al. 2003a) or tryptophan-like fluorescence intensities (Wu et al. 2003; Saadi et al. 2006), to study DOM biodegradation. However, there are several reasons why protein-like fluorescence may be a more useful predictor of BDOC compared to other fluorescent indicators. First, PARAFAC modeling determines the relative contribution of tryptophan and tyrosine-like fluorescence to the total pool of DOM fluorescence; and, even though fluorescence intensities may be used to predict total hydrolyzable amino acid concentrations (Yamashita and Tanoue 2003), protein-like fluorescence is a better indicator of more favorable C:N ratios for the microbial utilization of DOM.

Tyrosine and tryptophan-like fluorescence also appear to indicate differences in the form or degree of amino acid degradation. Tyrosine has been shown to fluoresce well in its monomer form or when tryptophan is present in low concentrations, suggesting that tyrosine-like fluorescence indicates more degraded peptide material (Mayer et al. 1999; Yamashita and Tanoue 2003, 2004). These same studies have also suggested that samples dominated by tryptophan-like fluorescence may indicate the presence of intact proteins or less degraded peptide material. Our findings suggest that using the combined fluorescent signal for both amino acids more effectively predicts the biodegradability of DOM than using tryptophan-like fluorescence alone. Overall, the strong positive relationship between protein-like fluorescence and BDOC in our study suggests that PARAFAC analysis of DOM may represent a substantial advancement over other optical measurements in the ability to predict the biodegradability of DOM in soil solution.

Relationships between soil types, BDOC and the chemical quality of DOM

The relative contribution of PARAFAC components differed between the four soil types suggesting there are distinct differences in the chemical properties and lability of DOM between the soil types. The fen sites had the greatest fraction of BDOC among the soil types, which is consistent with the high protein-like fluorescence, low C:N ratios and low aromatic C content. Minerotrophic fens have been shown to possess greater rates of primary production (summarized by Aerts et al. 1999), plant litter decay and enhanced rates of nutrient cycling than in bogs. As a result, the highly productive vascular plants, either through root exudates of carbohydrates and amino acids (Eviner and Chapin 1997) or litter decay (Yano et al. 2000), are likely the reason for the abundance of labile DOM present in the fen. This finding corroborates other studies (McDowell and Likens 1988; Yano et al. 2000) that suggest there is a significant contribution of recently fixed C to biodegradable DOM in the soil.

Significant differences in PARAFAC components also existed between the bog, forested wetland and upland forest. The humic-like component 1 is the dominant fluorescent component in the bog which is consistent with the idea that DOM in peat bogs is largely comprised of humic acids (Gondar et al. 2005). In the forested wetland and upland forest sites where organic horizons overlay mineral soils, the fulvic-like component 4 contributes greater to DOM fluorescence than in the bog and the humic-like to fulvic-like ratio is less than 3. This finding corroborates previous research in a northern hardwood forest showing that humic acids dominate the surface organic horizons and decrease with depth in the soil profile until the more mobile fulvic acids eventually became the dominant fraction in the lower horizons (Ussiri and Johnson 2003). Another possible reason for the greater fulvic acid content in the upland forest and forested wetland is the potential for lateral transport of DOM downslope through the soil, which has been suggested to occur in forested histosols of southeast Alaska (D'Amore and Lynn 2002). This type of

water movement would most likely transport fulvic-rich DOM because humic acids usually precipitate out and accumulate in organic horizons and fulvic acids tend to remain soluble and move downward with percolating water (Ussiri and Johnson 2003).

The significantly greater contribution of tryptophan-like fluorescence in comparison to tyrosine-like fluorescence in the upland forest, forested wetland and fen indicates that the protein containing DOM is of relatively recent origin or is relatively unaltered (Mayer et al. 1999; Yamashita and Tanoue 2003, 2004). This would suggest that the lability of this DOM is closely related to the chemical quality of the DOM precursor material. In particular, plant litter extraction experiments have shown that higher quality litter contributes more BDOC to soils than low quality litter (Boyer and Groffman 1996). Therefore, a potential reason for the low quality DOM at the forested wetland is the high lignin content and aromatic litter of *Tsuga heterophylla* (C:N ratio > 80; Prescott and Preston 1994), which is the dominant conifer in forested wetlands.

Tryptophan and tyrosine-like fluorescence were not significantly different in the bog in contrast to the other three soil types. This proportionally higher tyrosine-like fluorescence suggests greater degradation of amino acid containing DOM in the bog. Water movement in bogs has been shown to be predominantly in the vertical direction, rather than in lateral directions (McKnight et al. 1985). This long residence time for DOM in the bog soils could lead to a high degree of microbial modification of the original source material. Moreover, research from Mer Blue bog, Canada has shown that the fluorescent properties of soil solution DOM changed from plant-derived to more microbial-like with depth in the soil profile, which was attributed to the microbial consumption of available DOM (Fraser et al. 2001). We therefore propose the pool of DOM in bog soil waters reflects both substantial microbial modification of the original source material and subsequent production of more microbial-like DOM. Since this DOM released into bog soil solution can occur through the biodegradation of microbial cell walls as well as the release of microbial metabolites (Guggenberger et al. 1994; Kalbitz et al. 2003b), such as carbohydrates and proteins, we suggest the high protein-like fluorescence and labile DOM present in the bog is the result of the production of this microbial-like DOM.

We compared DOC:DON ratios with the ratio between the humic-like component 1 and the fulvic-like component 4 and found that as the DOC:DON ratio increases, there was a decrease in the humic:fulvic ratio ($r^2 = 0.46$; $P < 0.001$; data not shown). This finding indicates that the humic-like component 1 has a greater N content, which is consistent with the lower C:N ratios of extractable humic acids in comparison to fulvic acids (Ussiri and Johnson 2003; Gondar et al. 2005). Even though the contribution of DOM fluorescence to the total pool of DOM is still unknown, DOC:DON analysis reveals components 1 and 4 of our PARAFAC model resemble humic and fulvic acids extracted from soils. Our results suggest DOM fluorescence combined with PARAFAC analysis could be used as a proxy for tracing the dynamics of the bulk pool of DOM in natural ecosystems.

Conclusions

We found an average of 23–42% of the DOM in soil solution from the four soil types is biodegradable. Even though the bulk of the DOM pool (58–76%) was found to be refractory, 2.7–7.3 mg C l^{-1} of DOC was consumed during incubations from the four soil types. This suggests that the DOM derived from wetland soils could be an important component of the streamwater pool of BDOC. The temporal changes observed in DOM concentrations indicate DOM inputs to streams from the different soil types have the potential to alter stream biogeochemical processes differently by influencing stream heterotrophic productivity. We further suggest that DOM dynamics within the three different wetlands may respond differently to climate change or different management practices and that these wetland types should be evaluated separately in future assessments of wetland ecosystem function. Therefore, attempts to lump these wetlands into a homogenous ecosystem for climate models should be conducted with caution.

Coincident measurements of $SUVA_{254}$, BDOC and PARAFAC modeling of fluorescence EEMs confirmed that different terrestrial source pools contain DOM with distinct chemical properties and that these terrestrial source pools have a unique fluorescent fingerprint. Since PARAFAC modeling of DOM fluorescence is a precise and rapid technique for tracing DOM dynamics in soils, its application for intensive

temporal and spatial sampling protocols is possible. Taken together, our findings suggest that PARAFAC analysis of fluorescence EEMs has the potential to be used as an ecological tool to trace the movement of DOM from different terrestrial source pools along the soil-stream continuum.

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References

Aerts R, Verhoeven JTA, Whigham DF (1999) Plant-mediated controls on nutrient cycling in temperate fens and bogs. Ecology 80(7):2170–2181

Aitkenhead JA, Hope D, Billett MF (1999) The relationship between dissolved organic carbon in streamwater and soil organic carbon pools at different spatial scales. Hydrol Process 13:1289–1302

Amon RMW, Benner R (1996) Bacterial utilization of different size classes of dissolved organic matter. Limnol Oceanogr 41(1):41–51

Baker A (2001) Flourescence excitation–emission matrix characterization of some sewage-impacted rivers. Environ Sci Technol 35:948–953

Banaitis MR, Waldrip-Dail H, Diehl MS, Holmes BC, Hunt J, Lynch RP, Ohno T (2006) Investigating sorption-driven dissolved organic matter fractionation by multi-dimensional fluorescence spectroscopy and PARAFAC. J Colloid Inter Sci 304:271–276

Billett MF, Deacon CM, Palmer SM, Dawson JC, Hope D (2006) Connecting organic carbon in streamwater and soils in a peatland catchment. J Geophys Res 111, G02010. doi:10.1029/2005JG000065

Blodau C, Basiliko N, Moore TR (2004) Carbon turnover in peatland mesocosms exposed to different water table levels. Biogeochemistry 67:331–351

Boyer JN, Groffman PM (1996) Bioavailability of water extractable organic carbon fractions in forest and agricultural soil profiles. Soil Biol Biochem 28(6):783–790

Coble PG (1996) Characterization of marine and terrestrial DOM in seawater using excitation–emission matrix spectroscopy. Mar Chem 51:325–346

Cory RM, McKnight DM (2005) Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in DOM. Environ Sci Technol 39:8142–8149

D'Amore DV, Lynn WC (2002) Classification of forested histosols in southeast Alaska. Soil Sci Soc Am J 66:554–562

Del Giorgio PA, Cole JJ (1998) Bacterial growth efficiency in natural aquatic systems. Ann Rev Ecol Syst 29:503–541

Devito KJ, Dillon PJ, Lazerte BD (1989) Phosphorus and nitrogen retention in five Precambrian shield wetlands. Biogeochemistry 8:185–204

Ellis BD, Butterfield P, Jones WL, McFeters GA, Camper AK (2000) Effects of carbon source, carbon concentration, and chlorination on growth related parameters of heterotrophic biofilm bacteria. Microb Ecol 38:330–347

Eviner VT, Chapin FS III (1997) Plant–microbial interactions. Nature 385:26–27

Fitzhugh RD, Driscoll CT, Groffman PM, Tierney GL, Fahey TJ, Hardy JP (2001) Effects of soil freezing disturbance on soil solution N, P, and C chemistry in a northern hardwood ecosystem. Biogeochemistry 56:215–238

Fraser CJD, Roulet NT, Moore TR (2001) Hydrology and dissolved organic carbon biogeochemistry in an ombrotrophic bog. Hydrol Proc 15:3151–3166

Geller A (1986) Comparison of mechanisms enhancing biodegradability of refractory lake water constituents. Limnol Oceanogr 31:755–764

Gondar D, Lopez R, Fiol S, Antelo JM, Arce F (2005) Characterization and acid–base properties of fulvic and humic acids isolated from two horizons of an ombrotrophic peat bog. Geoderma 126:367–374

Gorham EJK, Underwood JA, Janssens B, Freedman W, Maass DH, Waller DH, Ogden JG III (1998) The chemistry of streams in southwestern and central Nova Scotia, with particular reference to catchment vegetation and the influence of dissolved organic carbon primarily from wetlands. Wetlands 18(1):115–132

Green SA, Blough NV (1994) Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters. Limnol Oceanogr 39:1903–1916

Guggenberger G, Zech W, Schulten HR (1994) Formation and mobilization pathways of dissolved organic matter: evidence form chemical structural studies or organic matter fractions in acid forest floor solutions. Org Geochem 21(1):51–66

Hood E, Fellman JB, Edwards RT (2007) Salmon influences on dissolved organic matter in a coastal temperate brownwater stream. Limnol Oceanogr 52(4):1580–1587

Hunt AP, Parry JD, Hamilton-Taylor J (2000) Further evidence of elemental composition as an indicator of the bioavailability of humic substances to bacteria. Limnol Oceanogr 45(1):237–241

Kalbitz K, Solinger S, Park JH, Michalzik B, Matzner E (2000) Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci 165(4):277–304

Kalbitz K, Schmerwitz J, Schwesig D, Matzner E (2003a) Biodegradation of soil-derived dissolved organic matter as related to its properties. Geoderma 113:273–291

Kalbitz K, Schwesig D, Schmerwitz J, Kaiser K, Haumaier L, Glaser B, Ellerbrock R, Leinweber P (2003b) Changes in properties of soil-derived dissolved organic matter induced by biodegradation. Soil Biol Biochem 35:1129–1142

Mann CJ, Wetzel RG (1995) Dissolved organic carbon and its utilization in a riverine wetland ecosystem. Biogeochemistry 31:99–120

Marschner B, Bredow A (2002) Temperature effects on release and ecologically relevant properties of dissolved organic carbon in sterilized and biologically active soil samples. Soil Biol Biochem 34:459–466

Marschner B, Kalbitz K (2003) Controls on the bioavailability and biodegradability of dissolved organic matter in soils. Geoderma 113:211–235

Mayer LM, Schick LL, Loder TC III (1999) Dissolved protein fluorescence in two Maine estuaries. Mar Chem 64:171–179

McDowell WH, Likens GE (1988) Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecol Monogr 58(3):177–195

McKnight DM, Thurman EM, Wershaw RL, Hemond H (1985) Biogeochemistry of aquatic humic substances in Thoreau's Bog, Concord, Massachusetts. Ecology 66(4):1339–1352

Meyer JL, Edwards RT, Risley R (1987) Bacterial growth on dissolved organic carbon from a blackwater river. Microb Ecol 13:13–29

Michalzik B, Kalbitz K, Park JH, Solinger S, Matzner E (2001) Fluxes and concentrations of dissolved organic carbon and nitrogen—a synthesis for temperate forests. Biogeochemistry 52:173–205

Moran MA, Hodson RE (1990) Bacterial production on humic and nonhumic components of dissolved organic carbon. Limnol Oceanogr 35(8):1744–1756

Mulholland PJ (1997) Dissolved organic matter concentration and flux in streams. J N Am Benthol Soc 16:131–141

Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal Chim Acta 27:31–36

National Wetlands Working Group (NWWG) (1988) Wetlands of Canada. Environment Canada, Sustainable development branch, Ottawa, Ontario, Canada. Ecological Land Classification Series 24

Neff JC, Hobbie SE, Vitousek PM (2000) Nutrient and mineralogical control on dissolved organic C, N and P fluxes and stoichiometry in Hawaiian soils. Biogeochemistry 51:283–302

Ohno T, Bro R (2006) Dissolved organic matter characterization using multiway spectral decomposition of fluorescence landscapes. Soil Sci Soc Am J 70:2028–2037

Prescott CE, Preston CM (1994) Nitrogen mineralization and decomposition in forest floors in adjacent plantations of western red cedar, western hemlock and Douglas fir. Can J For Res 24:2424–2431

Qualls GQ, Haines BL (1991) Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. Soil Sci Soc Am J 55:1112–1123

Qualls RG, Haines BL (1992) Biodegradability of dissolved organic matter in forest throughfall, soil solution, and stream water. Soil Sci Soc Am J 56:578–586

Saadi I, Borisover M, Armon R, Laor Y (2006) Monitoring of effluent DOM biodegradation using fluorescence, UV and DOC measurements. Chemosphere 63:530–539

Satoh Y, Abe H (1987) Dissolved organic matter in colored water from mountain bog pools in Japan II. Biological decomposability. Arch Hydrobiol 111(1):25–35

SAS Institute (2003) Version 9.1, SAS Institute Inc., Cary, NC, USA

Saunders G (1976) Decomposition in fresh water. In: Anderson J, MacFadyen A (eds) The role of terrestrial and aquatic organisms in decomposition process. Blackwell Scientific, Oxford, pp 341–374

Stedmon CA, Markager S (2005) Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis. Limnol Oceanogr 50(2):686–697

Stedmon CA, Markager S, Bro R (2003) Tracing DOM in aquatic environments using a new approach to fluorescence spectroscopy. Mar Chem 82:239–254

Sun L, Perdue EM, Meyer JL, Weis J (1997) Use of elemental composition to predict bioavailability of DOM in a Georgia River. Limnol Oceanogr 42(4):714–721

Urban NR, Bayley SE, Eisenreich SJ (1989) Export of dissolved organic carbon and acidity from peatlands. Water Resour Res 25(7):1619–1628

USDA (1997) Tongass National Forest Land and Resource Management Plan. R10-MV-338dd. USDA Forest Service, Region 10, Juneau, AK, USA

Ussiri DAN, Johnson CE (2003) Characterization of organic matter in a northern hardwood forest soil by ^{13}C NMR spectroscopy and chemical methods. Geoderma 111:123–149

Valderrama JC (1981) The simultaneous analysis of total nitrogen and total phosphorus in natural waters. Mar Chem 10:109–122

Vitousek PM, Howarth RW (1991) Nutrient limitation on land and in sea—how can it occur? Biogeochemistry 13:87–115

Volk CJ, Volk CB, Kaplan LA (1997) Chemical composition of biodegradable dissolved organic matter in streamwater. Limnol Oceanogr 42(1):9–44

Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujil R (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol 37:4702–4708

Wiegner TN, Seitzinger SP (2004) Seasonal bioavailability of dissolved organic carbon and nitrogen from pristine and polluted freshwater wetlands. Limnol Oceanogr 49(5):1703–1712

Worrall F, Burt T, Jaeban RY, Warburton J, Shedden R (2002) Release of dissolved organic carbon from upland peat. Hydrol Process 16:3487–3504

Wu FC, Tanoue E, Liu CQ (2003) Fluorescence and amino acid characteristics of molecular size fractions of DOM in the waters of Lake Biwa. Biogeochemistry 65:245–257

Xenopoulos MA, Lodge DM, Frentress J, Kreps TA, Bridgham SD, Grossman E, Jackson CJ (2003) Regional comparisons of watershed determinants of dissolved organic carbon in temperate lakes from the Upper Great Lakes region and selected regions globally. Limnol Oceanogr 48(6):2321–2334

Yamashita Y, Tanoue E (2003) Chemical characterization of protein-like fluorophores in DOM in relation to aromatic acids. Mar Chem 82:255–271

Yamashita Y, Tanoue E (2004) Chemical characteristics of amino acid-containing dissolved organic matter in seawater. Org Geochem 35:679–692

Yano Y, McDowell WH, Aber JD (2000) Biodegradable dissolved organic carbon in forest soil solution and effects of chronic nitrogen deposition. Soil Biol Biochem 32:1743–1751

Yano Y, Lajtha K, Sollins P, Caldwell BA (2004) Chemical and seasonal controls on the dynamics of dissolved organic matter in a coniferous old-growth stand in the Pacific Northwest, USA. Biogeochemistry 71:197–223