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Chemical and seasonal controls on the dynamics of dissolved organic matter in a coniferous old-growth stand in the Pacific Northwest, USA

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Abstract. Soil organic matter (SOM) is the largest terrestrial C pool, and retention and release of dissolved organic matter (DOM) cause formation and loss of SOM. However, we lack information on how different sources of DOM affect its chemical composition, and how DOM chemical composition affects retention. We studied seasonal controls on DOM production and chemical controls on retention in soils of a temperate coniferous forest. The O horizon was not usually the dominant source for dissolved organic C (DOC) or N (DON) as has been reported for other sites. Rather, net production of both DOC and DON was often greater in the shallow mineral soil (0–10 cm) than in the O horizon. DOM production in the shallow mineral soil may be from root exudation as well as turnover of fine roots and microflora in the rhizosphere. In the field, the two acid fractions (hydrophobic and hydrophilic acids) dominated the soil solution at all depths. A major portion of net production and removal of total DOC within the soil column was explained by increases and decreases in these fractions, although a shift in chemical composition of DOM between the O and mineral soil horizons suggested different origins of DOM in these layers. A larger loss of the free amino fraction to deep soil water at this study site than at other sites suggested lower retention of labile DON. Field DOM removal measurements suggest that field-measured parameters may provide a good estimate for total DOM retained in mineral soil.

Key words: Dissolved organic carbon, Dissolved organic nitrogen, Lysimeter, Soil solution chemistry, Sorption

Introduction

Soil organic matter (SOM) is the largest terrestrial carbon (C) pool, thus understanding processes that form or degrade SOM is critical for understanding the global C cycle. The dynamics of dissolved organic matter (DOM) controls inputs and outputs of C as well as nutrients to the mineral soil in

forest ecosystems. Both dissolved organic C (DOC) and nitrogen (DON) concentrations generally peak at the bottom of the O horizon, then decrease with increasing soil depth, indicating that the O horizon is a major DOM source while the mineral soil is a sink (Qualls et al. 2000; Michalzik et al. 2001). Processes that control DOM production and retention in soils are only partially understood. Recent studies suggest that DOM is produced by decomposition of both new and old OM and by leakage of metabolites from plant and microbial cells (Christ & David 1996; Kalbitz et al. 2000; Qualls 2000). However, we lack understanding of seasonal and source effects on DOM chemical composition, the control of DOM composition on retention, and the control of retention on DOM composition in soils.

Microbial uptake and abiotic sorption to soil minerals are two major processes by which DOM is removed from soil water and incorporated into SOM. McDowell and Likens (1988) reported that the labile C fraction of soil solution (assumed to be mainly carbohydrates) is very small (approximately 3–6% of total DOC), suggesting that abiotic sorption is responsible for most DOM removal from soil solution. In laboratory incubations of soil solution, Qualls and Haines (1992a) found that the labile (rapidly degradable) fraction of DOC in Oa horizon solution was too small (6–19%) to explain the observed 100-fold reduction in DOC between the O and B horizons. Similarly, in a field study, Yano et al. (in press) found nearly complete removal of DOC and DON within the mineral soil in a temperate coniferous forest even though the labile DOC fraction was $<2\%$ of total DOC in O-horizon leachate. These studies suggest the importance of abiotic sorption in SOM formation and a substantial effect of DOM chemical properties on such sorption.

A number of studies have proposed various chemical and physical mechanisms that would cause DOM sorption, such as hydrophobic interactions (e.g. Jardine et al. 1989), ligand exchange (e.g. Greenland 1971; Parfitt et al. 1977; Kaiser & Zech 1997), cation bridging, hydrogen bonding, and Van der Waals forces (Qualls 2000). Therefore, differences in DOM composition should affect the degree of sorption and, consequently, SOM formation. Due to the complex nature of both the sorbate and the sorbent in the natural environment, sorption studies have mostly been limited to laboratory incubation of known DOM compounds and simple minerals (i.e. synthesized clays). Sorption between natural DOM and mineral soils is less frequently studied. More field-relevant studies are needed to understand DOM dynamics in the field.

DOM can be separated by chemical properties based on differences in affinity to various resins (Leenheer 1981; Qualls & Haines 1991). The hydrophilic neutral fraction is rich in polysaccharides (Guggenberger et al. 1994; Dai et al. 1996) and is highly labile, as opposed to the hydrophobic acid (anionic) fraction (Qualls & Haines 1992a; Jandl & Sollins 1997), which is

highly aromatic and rich in carboxylic acids (Guggenberger et al. 1994; Dai et al. 1996). The base (cationic) fractions contain labile N compounds such as free amino acids, peptides and proteins (Qualls & Haines 1991).

In previous work, we found that chemical composition of water-extractable DOM was strongly affected by its source (e.g. needle v.s. root, Yano et al. in press), suggesting a potential shift in DOM composition with the percolation of water through the canopy, O horizon, and the soil column due to difference in DOM sources across these strata. Additionally, differences in sorption affinity among various forms of DOM would also result in a shift in the chemical composition of DOM with soil depth. In this study we examined chemical and seasonal controls on DOM chemistry and dynamics to understand relations between DOM composition and its production/retention in the soil column of an old-growth Douglas-fir rain forest, because little information is available on DOM dynamics in an old-growth coniferous stand. We measured changes in total DOM and its chemical composition with soil depth and season for water collected with lysimeters in a temperate forest ecosystem. We also measured sorption in a laboratory incubation using DOM that had been extracted from various plant source materials and whose chemical composition was known.

Methods

Study site

The study was conducted in temperate coniferous rain forest located at the H.J. Andrews Experimental Forest in the Cascade Mountains of west-central Oregon, USA (44°15′N, 122°10′W, 726 m elevation). Temperature at the nearby headquarters site averages 7.9 °C with mean annual precipitation of 237 cm year^{-1}. Over 70% of the precipitation occurs, mostly as rain, during a wet season between October and March (Sollins et al. 1980), although the timing varies from year to year. During the period of this study (1999–2001), we defined wet seasons to be October–May of 1999–2000 and November–May of 2000–2001. Atmospheric N deposition in this area is $\sim$2 kg N ha^{-1} year^{-1} (Sollins et al. 1980).

In 1998, we established experimental plots in an old-growth Douglas-fir stand. We chose this site because the stand is on relatively level ground with stone-free soil and has good winter access. The stand has features typical of old-growth Douglas-fir, such as coarse woody debris and moss layers on the forest floor. The overstory is dominated by *Pseudotsuga menziesii* followed by *Tsuga heterophylla* and *Thuja plicata*. The understory vegetation is dominated by *T. heterophylla*. Other important understory species include

Table 1. Characteristics of soils at the study site. B-horizon soil was collected in July 2000 and used for the sorption study. A-horizon soil was collected in January 2001. Values in parentheses show 1 SE to indicate analytical precision ($n = 2$ for pH, $n = 3$ for the rest).

Horizon	% of dry soil		C:N	pH		g kg^{-1} dry soil					
	Total C	Total N		in H_2O	in NaF	Fe_d	Fe_o	Fe_p	Al_d	Al_o	Al_p
A (0–10 cm)	10.7 (1.1)	0.3 (0.0)	45.7 (9.8)	5.2*	ND	ND	ND	ND	ND	ND	ND
B (40–50 cm)	1.3 (0.0)	0.1 (0.1)	15.7 (2.1)	5.1 (0.01)	10.7 (0.01)	38.2 (0.3)	11.0 (0.3)	4.8 (0.0)	13.8 (0.1)	11.0 (0.1)	5.2 (0.2)

Fe_d, Al_d: dithionite-citrate extractable Fe and Al.
Fe_o, Al_o: ammonium oxalate extractable Fe and Al.
Fe_p, Al_p: sodium pyrophosphate extractable Fe and Al.
ND: not determined.
* Value obtained by J. Dixon for nearby location (personal communication).

Taxus brevifolia and *Acer macrophyllum*. The total basal area of this stand is 60.5 m^2 ha^{-1}. Soils at the site, derived from volcanic parent materials, are coarse loamy mixed mesic Typic Hapludands with high amorphous Al hydroxide and aluminosilicate content and a high pH in 1 M NaF (10.7; Table 1). The soils have a thin O horizon (~2 cm) that is difficult to separate from the moss layer, lying on a 10–20 cm thick A horizon with abundant fine roots, over a 30–50 cm thick B horizon with less fine root biomass. Chemical and physical properties of the soils are shown in Table 1.

Collection of water samples

In fall 1998, we set up five blocks in a ~0.2-ha portion of the site. Each block measured approximately 5 m × 5 m, and within each block, one throughfall (TF) collector, one zero-tension lysimeter (at the bottom of the O horizon, or 0 cm), and four ceramic-cup tension lysimeters were installed at 10, 20, 30, and 70 cm depth in the mineral soil. Lysimeters within each block were located at least 2 m apart. To minimize biological degradation and chemical alteration of DOM in the water collected in the TF collectors and zero-tension lysimeters, water samples were retrieved within 24 h after the end of rain events during the dry warm season (April–November). The rest of the year the soil solution was sampled approximately every 3 weeks except for a 2–3 month period when access to the study site was blocked by deep snow. Samples collected before the first wet season (the first 10 months after lysimeter installation) were not included in the analysis to avoid effects of lysimeter installation on DOM chemistry. All samples were transferred on ice to Oregon State University, where volume and pH were determined and samples were filtered through combusted Whatman GF/F glass fiber filers (nominal pore size = 0.7 μm). The means of pH for the two wet seasons were (1 SE in parentheses): TF = 5.1 (0.02), 0 cm = 5.3 (0.30), 10 cm = 7.5 (0.08), 20 cm = 7.7 (0.06), 30 cm = 7.6 (0.30), and 70 cm = 7.5 (0.10). Subsamples were then taken for DOC and DON analysis and stored frozen until analysis. The remainder was also stored frozen, and for samples from the first wet season, the remainder was thawed and combined by depth and by block for each season by volume-weighting to obtain enough sample volume for chemical fractionation (e.g. all samples collected at 0 cm from block 1 during spring of the first wet season were pooled into a single sample).

DOM extracts for laboratory sorption

To test the effect of DOM composition on sorption, we used DOM extracted from several sources: Douglas-fir needles and wood in various stages of decomposition, and newly-harvested roots. Needle litter was collected during

a dry season (August) from three south-facing mature and pure Douglas-fir stands at a site in the Andrews Experimental Forest. These stand conditions were chosen to maximize forest floor thickness and the content of Douglas-fir needle in the forest floor. Unlike typical old-growth stands, including our study site (~2 cm thick, composed of a moss layer with minimal accumulation of needles, unable to separate Oa and Oi layers apart), the O horizons of these mature stands are thick (~4 cm), have no mosses or visible roots, and are composed mostly of Douglas-fir needles. The thicker O horizon of these mature stands compared to old-growth stands is probably due to higher litterfall (i.e. higher canopy cover and stand density) rather than slower decomposition due to less favorable microclimate or lower litter quality. Two subhorizons were separated from the O-horizon soils collected from these mature stands: Oi horizon (freshly fallen needles with minimal decay) and Oa (well-decomposed unidentifiable material). The Oi horizon was composed of 86% needles, 12% twigs, and 2% other. All twigs were removed prior to extraction.

Coarse woody debris were collected for two decay classes (three logs for each decay class), Class 1 and Class 5 (Sollins 1982), from Douglas-fir stands in the McDonald-Dunn Forest near Corvallis, Oregon, about 90 km northwest of our study site. Class 1 is newly-fallen logs whose current-year twigs are still attached and show minimal decomposition of bark and wood. Class 5 is extremely decomposed logs that have no sapwood and bark, and wood is mainly fragmented and cannot be lifted intact. Class 1 logs were further separated into bark, sapwood, and heartwood. Extraction and all chemical analyses for Class 1 wood were done separately on bark, sapwood, and heartwood, then values for whole wood were back-calculated based on % volume of each tissue in Douglas-fir logs of 52 cm (Harmon 1992).

Roots were harvested from Douglas-fir seedlings grown in pots for 1.5 years. The distribution of root-diameter size was: 72.7% <1.0 mm, 20.1% 1.0–2.0 mm, and 6.76% >2.0 mm. All roots harvested were pooled into a single sample due to low total mass. All litter, including roots, was air-dried, ground to pass 30-mesh screen, extracted in DI water at 20 °C for 48–68 h, filtered through Whatman GF/F glass fiber filters, then analyzed to determine initial concentration of DOC and chemically fractionated (see below). Distribution among fractions is shown in Table 2. Details of the collection and extraction of DOM source can be found in a previous paper (Yano et al. in press).

To obtain extracts for initial mass sorption isotherms (see below), O-horizon material was collected from an area adjacent to the study site in January 2001, stored frozen, then extracted in water (solid:water ratio of 1:10) at 22 °C for approximately 48 h with occasional stirring. The suspension was centrifuged (5000 rpm, 5 min), filtered through ashed Whatman GF/F glass-fiber filters then through DI water-rinsed Durapore membrane filters (nominal

Table 2. Chemical fraction composition of litter extracts. The number of replication is three except for fine root extracts, which were pooled prior to fractionation ($n = 1$). Phenol = weak hydrophobic acids, HoA = strong hydrophobic acids, HiA = hydrophilic acids, HoN = hydrophobic neutrals, HiN = hydrophilic neutrals, Base = all bases.

Litter type	Decay stages	%					
		Acid			Neutral		Base
		Weak	Strong				
		Phenol	HoA	HiA	HoN	HiN	
Needle	Oi	9	27	25	4	30	2
	Oa	4	47	35	3	5	5
Wood	Class 1	14	16	17	11	36	1
	Class 5	2	62	18	0	13	6
Fine root	New	16	21	17	3	37	1

pore size = 0.45 μm). Filtrate ('O-solution' hereafter) was analyzed for total DOC, then stored frozen until use.

Laboratory sorption

B-horizon soil (40–50 cm in mineral soil) was collected from an area adjacent to the study site. The soil was sieved (<2 mm) without drying to minimize changes in soil mineralogy, and stored at 3 °C until use. Chemical properties of the B-horizon soil are shown in Table 1 along with some basic information about A-horizon soil above it. Only B-horizon soil was used to test DOM sorption in lab incubation, because net DOM removal in the field was found only in B horizon. To test the effect of DOM composition on sorption, the litter extracts (needle, wood, and root extracts) were thawed, filtered through pre-rinsed 0.45 μm Durapore membrane filters, and diluted to 40 mg L^{-1}. Seventy-five mL of each of these solutions and of DI water as a control were added to 7.5 g of field-moist soil (solid:solution ratio = 1:10, $n = 3$). Prior to incubation, the pH of the suspension was adjusted to 4.1 ± 0.2, the pH of most litter extracts, with 0.01 N HCl. The suspension was shaken gently at 3 °C in the dark for 75 h. A preliminary test showed that this incubation period was necessary for the DOC concentration of the suspension to reach equilibrium, and that C loss from the suspension via respiration was not significant (<4% of the total DOC decrease). The suspension was centrifuged for 40 min at 7000 rpm and filtered through pre-rinsed 0.45 μm Durapore membrane filters to remove particulate organic matter. DOC concentrations were measured before and after incubation and the difference assumed to represent sorption

to the mineral soil. For the chemical fractionation analysis, the three laboratory replicates were combined after DOC measurements of post-incubation samples to ensure enough volume for analysis. Sorption for each fraction was determined as the difference between DOC concentrations before and after the incubation.

To determine an initial mass sorption isotherm for the mineral soil, a laboratory experiment was conducted for the O-solution in the same manner described above, except that we used four different initial DOC concentrations (0 or DI water, 18, 36, and 72 mg L^{-1}) with three laboratory replications. The sorption isotherm was determined by plotting sorption (difference between DOC concentrations before and after the incubation) versus initial DOC concentration.

Net DOM removal in the field

Net removal of DOM in the field was determined as the difference between the concentrations of DOC in incoming water at 10 cm and outgoing water at 70 cm on a sampling event basis, after correcting for transpiration. (For details of correction for transpiration, see below *Annual fluxes of chemical fractions*.) The depth interval of 10–70 cm was chosen due to net DOM production between 0 and 10 cm. Net removal was then plotted against incoming DOC concentration to compare with DOM removal in the laboratory sorption study.

Chemical analysis

DOC and DON

All samples were analyzed for DOC by high temperature platinum-catalyzed combustion (Shimadzu TOC-5000A HTCO carbon analyzer). DON was determined as the difference between total dissolved N (TDN) and dissolved inorganic N. TDN was measured by persulfate digestion (Cabrera & Beare 1993), followed by NO_3^--N analysis. Nitrate-N was measured with the hydrazine sulfate reduction method and NH_4^+-N was determined by the Berthelot reaction method with a Scientific Instruments Autoanalyzer. DON was calculated as:

$$[\mathrm{DON}] = [\mathrm{TDN}] - [\mathrm{NO_3^-\text{-}N}] - [\mathrm{NH_4^+\text{-}N}] \quad (1)$$

Because DON was calculated by difference, values sometimes fell slightly below 0 mg L^{-1}. Negative DON values were considered to be 0 mg L^{-1}.

Chemical fractionation

For the water collected in the field by lysimeters (all depths except for 30 cm) and by TF collectors (pooled by depth and by block for each season, see above

for details) three blocks were chosen for chemical fractionation. The lysimeter water, TF, and litter extracts were separated into six functional fractions using the method of Qualls and Haines (1991). In brief, the method fractionates DOM into hydrophobics versus hydrophilics, then into acid (anionic), base (cationic), and neutral fractions by its affinity to three different types of resins (non-ionic, cation-exchange, and anion-exchange resins). The hydrophobic acid fraction was further fractionated into weak acid and strong acid fractions. The weak hydrophobic acid fraction (Phenol) includes small phenolic compounds (e.g. tannin and flavonoids). The strong hydrophobic acid fraction (HoA) includes microbially altered plant-derived material of larger molecular size, humic substances and humic-bound amino acids and carbohydrates. The hydrophilic acids (HiA) are partly microbially synthesized and partly plant-derived material that are lower molecular size humic-like substances with high carboxyl-to-C ratios. The hydrophobic neutral fraction (HoN) is less microbially altered plant-derived material and contains waxes, fatty acids, and microbial lipids. The hydrophilic neutral fraction (HiN) contains non-humic-bound carbohydrates, mainly of microbial origin, and may contain simple sugars (e.g. hexose, deoxysugars). The hydrophobic and hydrophilic base fractions contain free amino acids, peptides and proteins. Because the amount of hydrophobic base fraction was very small for all soil solutions and litter extracts tested in this study ($\leq$2% of total DOC), both hydrophobic and hydrophilic bases were combined and reported as a base fraction (Base).

Annual fluxes of chemical fractions

All measurements of DOC and DON for the water samples were grouped into three periods within the wet season: October–November (fall), December–March (winter), and April–May (spring). Annual net fluxes of each chemical fraction were estimated for TF and soil solution from four depths (0, 10, 20, and 70 cm), using the chemical composition of samples collected during the first year. We used annual water fluxes determined for a nearby old-growth watershed for the period of 1973–1975 (WS-10, Sollins et al. 1980), modified for evapotranspiration (ET) estimated from long-term data collected for a control old-growth watershed (WS-2) between 1958 and 1996. In brief, a hydrologic budget of WS-10 was obtained using a hydrologic simulation model (Sollins et al. 1979) that was calibrated against daily data for precipitation and streamwater discharge, and tri-weekly values for TF (cumulative), litter moisture content, and soil moisture content, measured between 1973 and 1975. Because measured annual precipitation for the 1973–1975 study period was 2370 mm, very close to that during our first year (2340 mm), we assumed the proportions of TF and O-horizon leachate of our study site for

the first year were the same as those reported by Sollins et al. (1980) based on their simulation model. Using a relationship between precipitation and ET obtained from the long-term data (J. Jones, unpublished data), we estimated ET during our first year at 986 mm. Thus, during our first year, TF was assumed to be 1975 mm, O-horizon leachate 1955 mm, 100 cm soil solution 1374 mm, and transpiration from rooting zone 600 mm. We assumed that water flux at 70 cm depth in our study site equaled that at 100 cm in the above-cited study. We also assumed that the contribution of different soil layers to total transpiration paralleled the distribution of fine root in the soil column; for example, 45% of total fine root mass is found in the top 10 cm soil layer, thus this layer contributes to 45% of total transpiration. DOC concentrations at different soil depths were then corrected for water loss via transpiration estimated from fine root distribution (0% for the O horizon, 45% for 0–10 cm, 18% for 10–20 cm, and 37% for 20–70 cm soil layers; Yano, unpublished data). Using these transpiration estimates, annual water fluxes for 10, 20, 30, and 70 cm depths were estimated to be 1685, 1579, 1443, and 1354 mm, respectively. We then multiplied these by annual average DOC concentration for each chemical fraction to calculate flux over the three seasons. We did not determine seasonal fluxes for DOC, DON, or chemical fractions because Sollins et al. (1980) reported only annual fluxes.

Data analysis

To examine the effects of soil depth and season on total DOC, DON, and DOC: DON ratio, we used repeated measures analysis with time as the repeated factor. ANOVA was used to detect differences in DOC sorption among different litter extracts. Values were natural-log transformed to obtain appropriate normality prior to the analysis, followed by back-transformation to obtain least square means and 95% confidence limits. To evaluate the relationship between initial DOC chemistry and sorption, correlation analysis was used. The SAS System (SAS Institute Inc. 1999) was used for all statistical analyses.

Results

DOC and DON

DOC concentrations generally increased from TF to 0 or 10 cm in the soil, then decreased to 70 cm (Fig. 1), indicating net release of DOC from the O horizon and 0–10 cm mineral soil layer and net removal of DOC from solution in the 10–70 cm soil layer. None of the increases in DOC were significant with the exception of the first winter, when the increase between TF and 10 cm soil water was significant. For all seasons, DOC concentrations were lowest at 70 cm, and the ratios of means between the highest (found

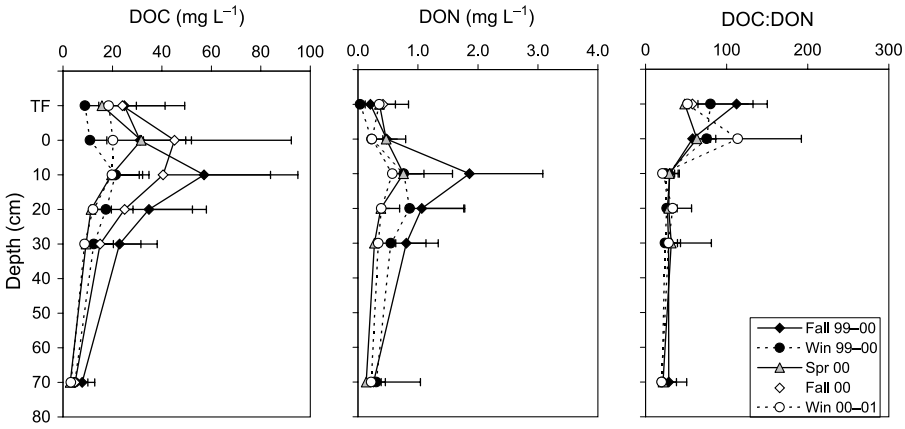

Fig. 1. Depth profiles of DOC, DON, and DOC:DON ratio for samples from 1999–2000 and 2000–2001. The error bars indicate variability of DOC, DON, and DOC:DON of TF and soil water collected from the same depth within the same season. The variability is shown as upper limit of 95% CI ($n = 5$).

at either 0 or 10 cm depth) and the lowest (70 cm) DOC were four-fold to eleven-fold and were statistically significant, indicating strong removal of DOC in the mineral soil. The magnitude of decrease in DOC concentration with soil depth was slightly larger for the fall (decreased by 86–89%) and spring samples (decreased by 91%) than for the winter samples (77–84%), although the magnitude of decrease was not statistically significant for the fall and winter due probably to large variability of DOC values.

The influence of season on DOC concentration differed with soil depth. For O-horizon leachate, DOC concentrations were always greater in the fall than in winter ($P < 0.001$ for the first year and $P = 0.02$ for the second year). At 10, 20, and 30 cm depth in the mineral soil, DOC concentrations in the first fall were consistently greater than in the winter and spring. Generally, the variability of DOC concentration was greater in the shallow soil (0–10 cm) than in deep soil, and greater in fall than in winter or spring (Fig. 1).

DON and DOC patterns generally tracked together. For all seasons, mean DON concentrations increased significantly from TF to 10-cm soil water (two-fold to twenty-one-fold), with the highest mean concentration found at 10 cm in fall (1.8 mg N L^{-1}). However, contrary to DOC, the increase of DON between TF and 0-cm soil water was smaller (17–28% of total increase) than the increase between 0 and 10 cm (72–83% of total increase), indicating that net release of DON from the 0–10 cm mineral soil layer was more important than from the O horizon. After peaking at 10 cm (or 20 cm the first winter), DON concentration decreased to the levels of TF by 70 cm, indicating strong removal of DON between 10 and 70 cm (Fig. 1). Generally, DON concentration varied most across the five replications at 10 cm, where the highest DON was observed, and varied most in the fall for any given depth.

DOC:DON was greatest for TF (48–112) and the O-horizon leachate (58–113). Ratios decreased to 20–34 for the 10 cm soil water and stayed relatively constant below 10 cm (20–28), although a slight decreasing trend was found between 30–70 cm depths (Fig. 1).

Profile of chemical fractions

Increases and decreases in total DOC concentration were generally associated with changes in the two dominant acid fractions, HoA and HiA (Fig. 2). For

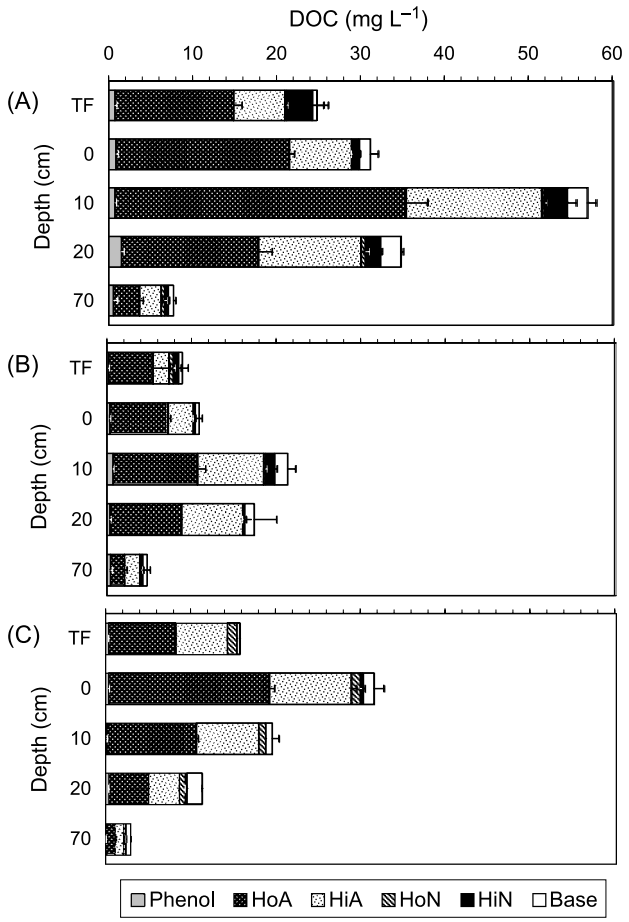

Fig. 2. Depth profiles of total DOC concentration and the distribution of chemical fractions for lysimeter water and TF. The samples were collected in (A) fall 1999, (B) winter 1999–2000, and (C) spring 2000. Water samples from three blocks were pooled by depth, block, and season prior to chemical fractionation ($n = 3$). Error bars indicate 1 SE. TF = throughfall, Phenol = weak hydrophobic acids, HoA = strong hydrophobic acids, HiA = hydrophilic acids, HoN = hydrophobic neutrals, HiN = hydrophilic neutrals, Base = all bases.

all seasons, the increase in total DOC from TF to the O-horizon leachate was associated with an increase in these acid fractions. Increases in the concentrations of HoA and HiA together accounted for 86–95% of the total increase in DOC concentration, indicating that DOC produced within the O horizon and the 0–10 cm mineral soil layer was mostly in the form of acids. Of the total increase in these acid fractions, 45–68% was due to the increase in the HoA fraction. Increases in HiA, HiN and Base fractions were more important between 0- and 10-cm soil water than between TF and O-horizon leachate, while HoA increased constantly from TF to 0-cm soil water to 10-cm soil water (Fig. 2). For example, the increases in HiA fraction between 0- and 10-cm soil water were 4–7 times greater than those between TF and 0-cm soil water.

The decrease of total DOC concentration from 0 or 10 cm to 70 cm paralleled the large decreases in both HoA and HiA fractions as well as small decreases in other fractions, indicating little inter-fraction conversion. The HoA and HiA fractions together accounted for 86–92% of the total DOC decrease, of which 58–70% was due to the decrease in HoA fraction, indicating preferential removal of HoA over HiA in the mineral soil. The concentrations of other fractions (Phenol, Base, HoN, and HiN) changed somewhat with total DOC, but none of the changes affected total DOC concentration as much as did changes in HoA and HiA.

Generally, the two strong acid fractions (HoA and HiA) dominated all samples collected in the first wet season (Fig. 3). HoA dominated in TF and the O-horizon leachate (53.4–66.5% of total DOC, Fig. 3), but its contribution to total DOC decreased with increasing depth. Percent HiA generally increased with increasing soil depth due to preferential removal of HoA over other fractions and equaled percent HoA at 70 cm. Percent Base generally increased with increasing soil depth and became the third largest fraction in the deep soil water (up to 19.5% of total DOC). Percent Phenol, HiN and HoN were consistently small in TF and the soil profile in all seasons.

Annual fluxes of chemical fractions

Fluxes were calculated at each soil depth to compare the amounts of each fraction (as opposed to percentage composition) taking into account decreases in water flux. The major forms of DOC that moved through the soil column were HoA and HiA (Fig. 4). The largest flux for strong acids (HoA and HiA) was found at 10 cm, right after passing through the layer with the most fine root biomass (31.1 $g\,m^{-2}\,year^{-1}$ for HoA and 17.7 $g\,m^{-2}\,year^{-1}$ for HiA), although the flux of weak acids (Phenol) did not increase at this depth. HiN

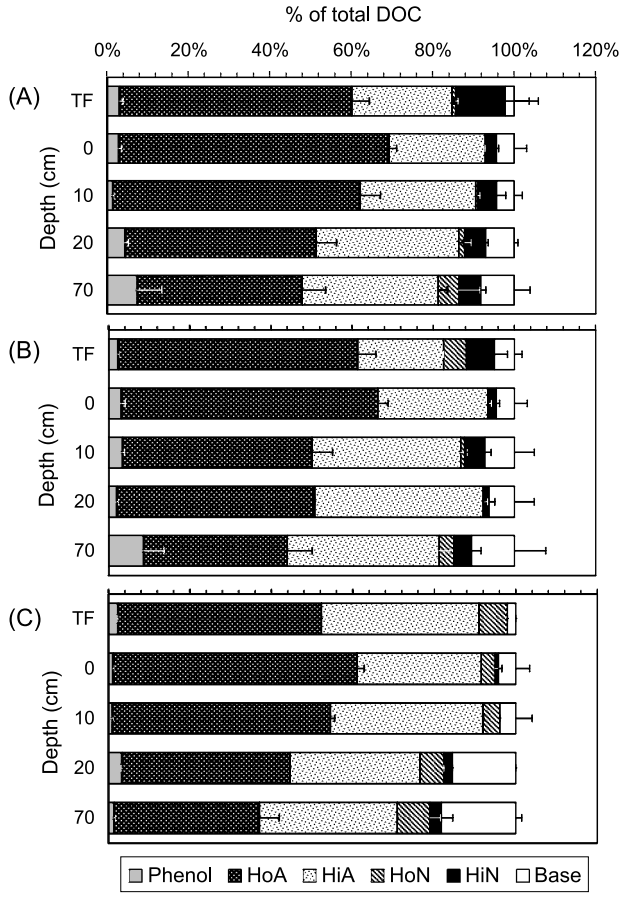

Fig. 3. Depth profiles of chemical fraction composition as percent of total DOC. Samples were collected in (A) fall 1999, (B) winter 1999–2000, and (C) spring 2000. Water samples from three blocks were pooled by depth, block, and season prior to chemical fractionation ($n = 3$). Error bars indicate 1 SE. TF = throughfall, Phenol = weak hydrophobic acids, HoA = strong hydrophobic acids, HiA = hydrophilic acids, HoN = hydrophobic neutrals, HiN = hydrophilic neutrals, Base = all bases.

(the labile C fraction) was removed as it percolated through the O horizon (decreasing from 2.4 to 0.9 g-C m^{-2} $year^{-1}$), but increased by 133% (from 0.9 to 2.1 g-C m^{-2} $year^{-1}$) during transit through the 0–10 cm soil layer. In contrast, base (the labile N fraction) increased by 133% (from 0.9 to 2.1 g-C m^{-2} $year^{-1}$) as water passed through O-horizon, and by 29% (from 2.1 to 2.7 g-C m^{-2} $year^{-1}$) in the 0–10 cm mineral soil.

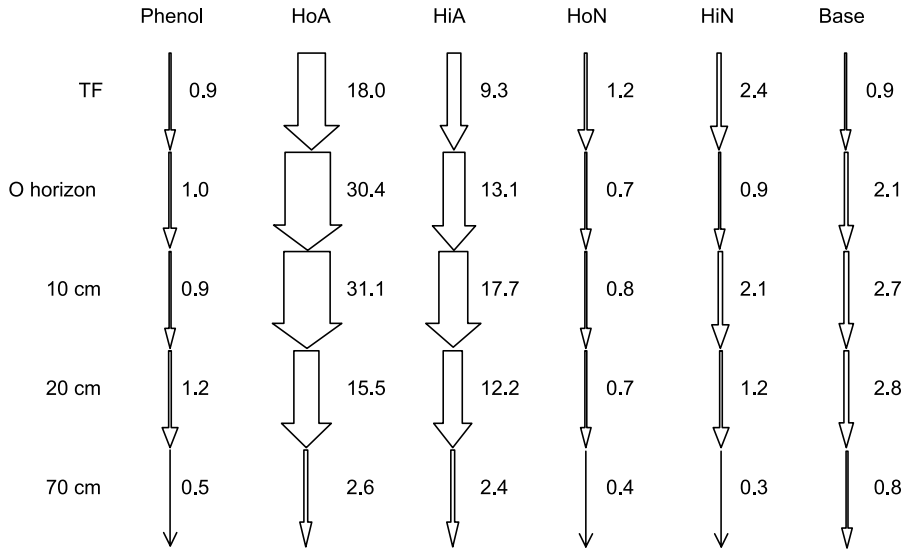

Fig. 4. Annual fluxes of DOC for each chemical fraction. Fluxes were estimated for TF and soil solution at 0, 10, 20, and 70 cm depths for the first year (1999–2000). Values are in $g\,m^{-2}\,year^{-1}$, and the width of arrows corresponds to the magnitude of flux. Water flux in the mineral soil was corrected for loss via transpiration (see text). TF = throughfall, Phenol = weak hydrophobic acids, HoA = strong hydrophobic acids, HiA = hydrophilic acids, HoN = hydrophobic neutrals, HiN = hydrophilic neutrals, Base = all bases.

Relationship between chemical properties and removal of DOM

In the laboratory sorption study of litter extracts, the Phenol and Base fractions showed high affinity to mineral soil (i.e. $\geq$70% of DOC in initial fraction was sorbed), and neutral fractions (HoN and HiN) showed low affinity, except for HoN in Class 1 woody extracts (Table 3). Affinity of strong acids (HoA and HiA) was generally high and affinity increased considerably with increases in stage of decay of DOC sources. For example, when stage of decay for needle litter increased from Oi to Oa, affinity of HoA as percent sorption of initial HoA increased from 47 to 82%, and affinity of HiA increased from 40 to 63%. Similarly, when stage of decay for wood litter increased from Class 1 to Class 5, affinity of HoA increased from 24 to 52% and that of HiA from 25 to 100% (Table 3).

In the field study, all fractions were well removed in the B-horizon soil (10–70 cm) as reflected in the percent total removal of initial DOC (36–58% for the laboratory study v.s. 86% for the field study; Table 3). Strong acid fractions and base showed high affinity to the mineral soil (70–91% removal), as was found in the laboratory study. Removal of HiN was higher (84%), and Phenol lower, in the field study than in the laboratory study.

Table 3. Affinity of chemical fractions to the mineral soil. Percent removal (sorption) of initial DOC is shown for each chemical fraction. For the laboratory study, removal was determined as the difference between values before and after incubation ($n = 1$). Removal for the field study was based on the estimated annual DOC flux at 10 and 70 cm depths (see Fig. 4). Phenol = weak hydrophobic acids, HoA = strong hydrophobic acids, HiA = hydrophilic acids, HoN = hydrophobic neutrals, HiN = hydrophilic neutrals, Base = all bases.

DOC sources	Decay stages	%						
		Acid			Neutral		Base	Total removed*
		Weak	Strong					
		Phenol	HoA	HiA	HoN	HiN	Base	
Laboratory								
Needle	Oi	79	47	40	0	29	100	44 a
	Oa	70	82	63	2	0	100	58 b
Wood	Class 1	83	24	25	85	0	74	36 a
	Class 5	82	52	100	ND	0	78	45 ab
Fine root	New	94	70	10	1	40	82	54 b
Field								
OM above 10 cm		46	91	85	48	84	70	86

ND: Not determined due to no HoN-DOC in the solution.
Negative after removal; 0% removal was assigned.
OM above 10 cm: Any organic matter above 10 cm that can be a source of DOC.
*Letters indicate statistical differences in total DOC removal within the laboratory study.

The chemical composition of DOC that was removed differed with the quality of DOC sources, that is, needle, wood, and root at different decay stages. Greater total net DOC removal observed for the field study than laboratory and for old litter extracts (Oa and Class 5) than new litter (Oi and Class 1) was associated with greater removal of HoA and HiA (Table 3). Unlike fractions derived from other litter materials, root-derived HiN had strong affinity for the mineral soil and 40% of HiN-DOC was sorbed (Table 3).

Sorption patterns in the field and laboratory studies

The correlation between the amount of DOM in incoming water and net removal was strong and positive. If one outlier of DOC was excluded, Pearson's

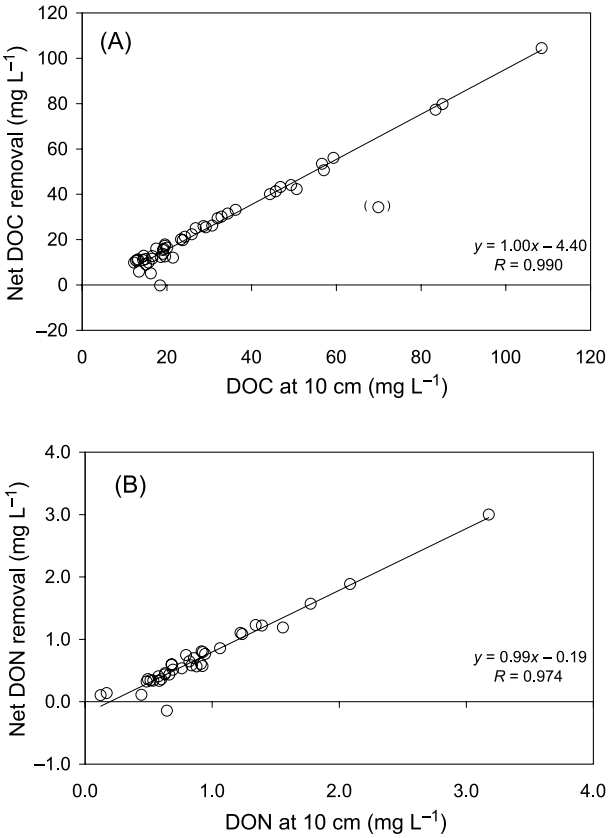

Fig. 5. Relations between DOM concentration in shallow soil water and net removal of DOM in 10–70 cm soil layer. Samples were collected between fall 1999 and spring 2000: (A) DOC, and (B) DON. Note that scale changes between the graphs. Values of deep-soil DOM were corrected for water loss via transpiration, and net removal of DOM was calculated as: shallow soil DOM – deep soil DOM. One outlier DOC value (in parenthesis) was excluded from the analysis. *R* is Pearson's correlation coefficient.

R was 0.99 for DOC and 0.98 for DON (Fig. 5). The slope of the regression lines was close to 1.0 (1.00 for DOC and 0.99 for DON), indicating almost complete net removal of both DOC and DON. In contrast, the laboratory sorption isotherm showed a non-linear relationship between sorption and initial DOC concentration ($R^2 = 0.99$, Fig. 6). The intercepts of regression lines for DOC removal determined in both field and laboratory studies were negative, indicating DOC release from the mineral soil when no DOC was in the solution.

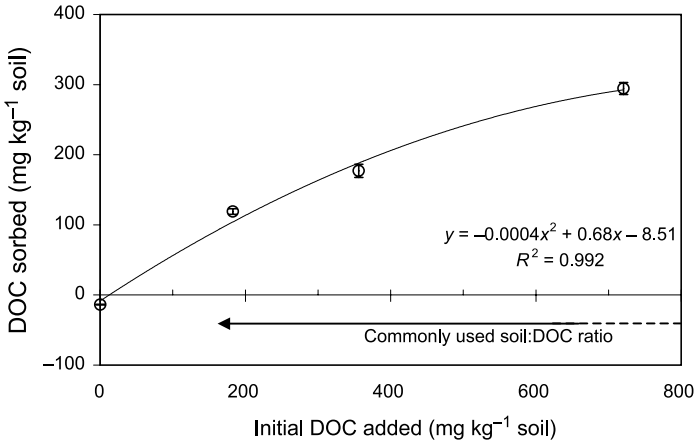

Fig. 6. Initial mass sorption isotherm determined in the laboratory for O-horizon extract ('O-solution'). Soil used was collected from B horizon near the study site. Error bars indicate 1 SE for $n = 3$ to indicate analytical precision. The range of DOC-to-soil ratios commonly used in initial mass sorption isotherm in laboratory studies (1000–6000) is shown as arrows along the *X* axis.

Discussion

DOM sources

DOC concentrations in TF at this study site (9–25 mg L^{-1}) were similar to those observed in other temperate coniferous forests (10–21 mg L^{-1}, Zech et al. 1994; Currie et al. 1996; Solinger et al. 2001). Our DOM profiles with depth suggest that the O horizon at this site is not consistently a large DOM source, whereas in most other temperate forests DOM peaks at the bottom of O horizon (e.g. McDowell & Likens 1988; Qualls & Haines 1991; Zech et al. 1994; Solinger et al. 2001). Rather, the upper mineral soil (0–10 cm) appeared to be a more significant source of DOM than the O horizon, especially for DON. DOM can be concentrated with increasing soil depth due to decreasing water flow by ET. To estimate the magnitude of this possible concentrating effect, we used monthly distribution of ET (McKee et al. 1998) to estimate seasonal ET for our site. We then assumed a worst-case scenario in which all ET was transpiration. Even with this assumption, the concentration effect was very small and could explain only 3–11% of total increase for DOC and 1–3% for DON (the one exception was for DON in spring for which 97% of the increase could be explained by this worst-case concentration effect). We thus concluded that the top 10 cm of mineral soil is an important source for DOC and DON, especially in the fall.

Ammonium and nitrate showed no increase at 10-cm depth (data not shown). Thus, the net production of N in the shallow mineral soil was due only to DON. One explanation for a lack of clear shift in DOM concentration from TF to the O-horizon leachate could be that the O horizon at this site is thin (~2 cm) and thus does not have the potential to add significant DOM to the water percolating downward. The O horizon of this study site is composed of a moss layer with a thin litter layer that lacks a humic layer (Oa horizon), all of which are typical features of old-growth stands in this region. In temperate forests elsewhere, DOM peaks just below the O horizon (e.g. Qualls & Haines. 1991), and the O horizon is thick enough to be further separable into Oi, Oe, and Oa layers. Perhaps greater accumulation of litter and humic substances in the forest floor is necessary for O horizon to be a significant DOM source.

The large amounts of DOM produced in the 0–10 cm mineral soil could reflect effects of rhizodeposition (e.g. root exudates, sloughed-off root cells), because C lost in rhizodeposition can be as much as 60–73% of total C assimilated for coniferous trees (summarized by Grayston et al. 1996). Turnover of microbial biomass in the rhizosphere as well as microbial breakdown of dead roots and SOM may also contribute to DOM production in this soil layer. This idea is supported by greater organic matter mass in the 0–10 cm mineral soil than O horizon. At our study site, 45% of the fine root mass present between 0 and 70 cm occurred within the top 10 cm (Yano, unpublished data), and C in fine roots in the top 10 cm (estimated to be 16.6 kg-C m^{-2}) is more than six times greater than C in the forest floor (2.6 kg-C m^{-2}, calculated from Grier & Logan 1977).

High net DOM production in the shallow mineral soil (0–10 cm) in the fall may be due to an increase in fine root growth (Santantonio & Hermann 1985) caused by an increase in water availability at the start of the wet season and an increase in rhizodeposition and microbial activity in the rhizosphere. Alternately, the higher fall concentrations may represent flushing of soluble OM produced by one or more processes mentioned above and accumulated during the summer dry season. Simple dilution of soluble SOM by increased water flux could also result in the lower DOM concentration in the winter.

The DOC:DON ratio decreased from O-horizon leachate to 10 cm soil water while both DOC and DON concentrations increased. The most probable explanation is release of relatively low C:N compounds such as root exudates and/or lysates of microbial cells. This idea is supported by the fact that the increase in total DOC between 0 and 10 cm in the mineral soil was associated with large increases in HiA and small increases in base, both of which have lower DOC:DON ratios than bulk DOC (DOC:DON is generally 10–52 for HiA and 3–10 for base, Qualls & Haines 1991). The C:N of root

exudates ranges from 2.5 to 13 (summarized by Grayston et al. 1996) and that of microbial lysates probably 4–10, because the C:N of microbial biomass is 4–10 (Myrold 1998). A portion of SOM in the A horizon (C:N = 46) may be broken down by extracellular enzymes and dissolve into soil water, mixed with N-rich DOM of root exudates and microbial lysates, resulting in the increase in both DOC and DON while lowering DOC:DON ratio from 0- (58–113) to 10-cm soil water (20–34). A decrease in DOC:DON could also result from strong microbial uptake of labile, C-rich DOM (e.g. carbohydrates). However, the labile-C fraction (HiN) of our O-horizon leachate is too small (<3%) to explain a large decrease in DOC:DON ratio.

A major portion of the net DOC increase from TF to the O horizon was due to an increase in HoA-DOC (>70% of the total DOC increase), consistent with the findings of Guggenberger et al. (1994) who hypothesized that most DOC produced in the O horizon was microbially modified plant-derived material rather than solubilized plant material. Increases in the concentration of HiA from 0 to 10 cm soil water (only in the fall and winter) were much larger than those between TF and 0 cm soil water. This would indicate that the process of DOC production in the mineral soil (0–10 cm) is different from that in the O horizon, that is, top 10 cm of the mineral soil produced significant amounts of HiA in addition to HoA. Guggenberger et al. (1994) found that HiA-DOC appeared to be partly microbially synthesized and partly plant-derived material that has experienced a higher degree of oxidative biodegradation than HoA-DOC (i.e. HiA molecules are smaller and have more side-chains oxidized). Possibly, strong microbial activity in the rhizosphere degraded plant-derived organic matter and SOM to HiA, bypassing HoA.

DOM removal in the field

The decrease of DOM with increasing soil depth between 10- and 70-cm depths indicates net DOM removal in the mineral soil. Because HiN is the most labile fraction (Qualls & Haines 1992a; Jandl & Sollins 1997), and because the content of HiN at 10 cm was too small (≤5% of total DOC, estimated) to account for total net DOM removal in the B-horizon soil (90% of total DOC at 30 cm depth), the removal is likely due mostly to abiotic sorption.

The decrease of DOM concentration with increasing soil depth below 10 cm with minimal change in DOC:DON suggests that the DOM removal processes, probably mostly abiotic, did not favor either C- or N-rich compounds. A similar conclusion was drawn by Kaiser and Zech (2000) from a laboratory sorption study for an Oa horizon water extract from a Norway spruce (*Picea abies*) stand. They compared sorption of C and N within and

between Ho-DOM (all hydrophobic fractions combined) and Hi-DOM (all hydrophilic fractions combined) fractions and found greater sorption for Ho-DOM than Hi-DOM, but no preferential sorption of N-containing compounds within each fraction. They concluded that DOM sorption is affected by the presence of acidic functional groups and not by N content and that DOC:DON ratio of bulk soil changed with sorption due to uneven distribution of N across the chemical fractions. We found little decrease in DOC:DON with soil depth, despite enrichment of HiA and base fractions (N-rich fractions). This suggests that the distribution of C and N in the chemical fractions for our soil solutions might be different from those reported elsewhere.

Based on the balance between annual inputs (TF) and outputs (70-cm depth), we found net retention for all fractions except Base. The same amount of Base (labile-N fraction) that entered the system left the system, although turnover of compounds in this fraction may have been fast (i.e. equal consumption and production within the soil column). The net removal of HiN (labile-C fraction) in the O horizon may be due to microbial uptake, since no mineral surfaces are available for sorption.

Chemical controls on DOM removal

The high percent removal of initial HoA found in the field study is consistent with findings by Dai et al. (1996) that HoA was the fraction most strongly removed in the mineral soil. Although Ho-DOC is known to be more strongly sorbed than Hi-DOC, we did not find any trend of preferential sorption for the HoN fraction itself, with the exception of Class 1 wood extracts (Table 3). Combined with the fact that HiA was the second most strongly sorbed fraction in the field, our results suggest that DOC sorption may be caused by ligand exchange between the hydroxyls of clays and acidic functional groups of DOC, as suggested by Kaiser and Zech (1998), rather than hydrophobic interaction between DOC and clays (attraction between hydrophobic portions of clay and DOC) as proposed by Jardine et al. (1989). The fact that the preferentially sorbed DOC fractions (HoA and HiA) are rich in carboxyls, and that our soil has high content of amorphous Fe and Al oxides (i.e. high Fe_o and Al_o, shown in Table 1) and aluminosilicates (pH in NaF = 10.7), indirectly supports the idea of ligand exchange as the predominant sorption mechanism. Amorphous Fe and Al oxides (Kaiser & Zech 1998) as well as aluminosilicates (Parfitt 1990) are known to be strong sorbents for DOC via ligand exchange.

Our results also suggest that DOC sorption does not result solely from ligand exchange between carboxylic functional groups and hydroxyl groups on clays. Because HiA-DOC has more carboxylic functional groups per C than HoA-DOC (e.g. Qualls & Haines 1991; Vance & David 1991), HiA should

be more strongly sorbed than HoA-DOC, were ligand exchange the dominant sorption mechanism. However, Phenol showed high affinity to mineral soil in the laboratory study as well, in spite of their low content of carboxylic functional groups relative to the two acid fractions (HoA and HiA). Perhaps, a combination of ligand exchange and hydrophobic interaction is involved. The latter mechanism would bring DOM molecules closer to mineral surfaces thus facilitating ligand exchange. This mechanism may be less effective for small molecular-weight organic acids, such as HiA, which may not have significant hydrophobic functional groups relative to their carboxyl functional groups, but may apply better to larger molecular-weight HoA, which is less degraded and has ample hydrophobic functional groups.

The reasons for the increase in sorption with degree of decomposition of DOC are not clear. Perhaps strong acid fractions extracted from well-decomposed litter are further modified relative to those from new litter (e.g. further oxidation of side chains) such that the affinity of those fractions to mineral surfaces increases.

In addition to the two sorption mechanisms mentioned above, coprecipitation of DOC molecules or DOC molecules and clay particles via cation bridging might also be significant for the removal of acid fractions. Because of the volcanic origin of our soils and fast weathering rates of the parent materials, as shown in relatively high mineral soil solution pH ($\sim$7.6) for this study site and for a nearby site and high Ca^{2+} and Na^{+} output in stream water (Sollins et al. 1980), mineral soil may have abundant surface-complexed divalent bases that either retain organic acids by cation bridging or are released into solution and coprecipitate with DOC molecules. Field and laboratory studies gave different percent sorption values for Phenol, Base and HiA, perhaps because the field and laboratory solutions contained different DOC compounds, even though the fraction composition percentages were similar. Soil water collected in lysimeters contains DOC derived from belowground DOC sources, such as root exudates and the turnover of microbial biomass, that would not have been included in the litter extracts.

Depth profiles of chemical fraction composition

HoA and HiA dominated in both TF and litter/soil solutions in this study, with a shift in dominance by HoA in the O-horizon leachate to HiA in the deeper mineral soil. The dominance of HiA in deep mineral soil has been reported for other ecosystems with different climate and soil; for example, a hardwood forest on an Ultisol (Qualls & Haines 1991), coniferous forests on Inceptisols and Spodosols (Guggenberger et al. 1994), a hardwood forest on a Spodosol (Vance & David 1991; David & Vance 1995), a coniferous forest on

a Spodosol (Dai et al. 1996), and volcanic ash overlain by a thin soil (<20 cm thick, Antweiler & Drever 1983).

Percent Base differed strikingly between our study and others. Percent Base is generally ≤7% of total DOC, most commonly ∼4% (Qualls & Haines 1991; Vance & David 1991; Guggenberger et al. 1994; Dai et al. 1996), with the exception of a study of a volcanic-ash soil (3–12%; Antweiler & Drever 1983). Unlike these studies we found that Base composed up to 19% of total DOC and was the third largest fraction in the deep soil water. Lower percent Base from the non-volcanic forest soils is not likely due to the degradation of Base before the water in the lysimeters was processed, because a similar range of sample collection intervals and transport time (from <24 h to a few weeks) was employed in all studies mentioned above.

Although proportions of Base in deep soil water were high at our site, DOC concentrations (3–8 mg L^{-1}) were within the range reported for various forest and soil types (0.8–12 mg L^{-1} in the B-C horizons, reviewed by Herbert & Bertsch 1995; 0.6–5 mg L^{-1} in C horizons reviewed by Michalzik et al. 2001). This suggests that more Base compounds were lost to the deep soil in our soil than in other, mainly non-volcanic, soils. Perhaps more loss of Base in volcanic soils is due to lower retention rather than higher production (as plant exudates and microbial byproducts). The Base fraction may be more mobile at our site than at other, mainly non-volcanic, sites, due to relatively high concentration of base cations in mineral soil solution that are provided via fast weathering. These base cations then compete with the Base fractions for cation-exchange sites. Young volcanic-ash derived soils are rich in amorphous clays (i.e. high sodium-oxalate extractable Al, Table 1; pH in 1 M NaF of 10.7 at our site; data not shown), and volcanic ash releases bases faster than most non-volcanic igneous parent materials. Because the Base DOC fraction is by definition cationic, we would expect competition for cation-exchange sites between Base and cations, resulting in lower retention of Base in the deeper mineral soil. In addition, because the high weathering rates consume H^+ (e.g. pH of mineral soil water ∼7.6, current study; 4.5–6.5 (Antweiler & Drever 1983), the Base fraction may be deprotonated (isoelectric points of amino acids are generally <6.0, McMurry 1990) and thus show less affinity to cation exchange sites in the mineral soil.

Laboratory sorption isotherm versus field removal

Slopes and intercepts of the regression lines between incoming DOM and net removal within the 10–70 cm soil layer described well the pattern of DOM dynamics observed at our study site: a slope of close to 1.0 with small negative intercepts indicating almost complete removal of DOM in the mineral soil and relatively constant loss of DOM deeper into the soil. Thus, parameters

from regression lines for field DOM removal may be a useful way to estimate net sorption of DOM in the mineral soil, if the magnitude of biotic removal can be assessed.

The laboratory sorption isotherm was, on the other hand, more difficult to relate to DOM removal in the field. The sorption isotherm showed a curvilinear relationship between sorption and initial DOC, and sorption was $\leq$56% of initial DOC (peak at 15 mg L^{-1} initial DOC, Fig. 6). This percent sorption is within the range determined for B-horizon soils in laboratory studies of a wide range of soil types (range from 30 to 80% equivalent to regression slopes between 0.3 and 0.8; summarized by Neff & Asner 2001). The greater sorption (removal) of DOM in our field than laboratory study could be due to: (1) microbial uptake in addition to abiotic sorption in the field, and (2) much larger soil:DOC ratio in the field relative to the laboratory study. The first possibility is not likely, given the consistently low levels of labile DOC (HiN) throughout the soil profile ($\leq$5%, Fig. 3). The second possibility would well explain the discrepancy between laboratory and field studies, as shown by a simple calculation. The mass of soil in the 10–70 cm soil column is $\sim$600 kg m^{-2}, using a mineral-soil bulk density of 1.0 g cm^{-3} (J. Dixon, personal communication). For a typical rainfall event during the wet season at our site (9 mm rainfall), and assuming that the canopy is already wet ET thus negligible, water passing 10-cm depth would be 9 L m^{-2}. Using our annual average DOC concentration at 10 cm depth of 32 mg L, the DOC that was potentially exposed to the mineral soil was $\sim$288 mg m^{-2}. The soil-to-DOC ratio in this case is $\sim 2.1 \times 10^6$, and even if we assume only 1% of soil actually had contact with the DOC, the ratio is still $\sim$21,000, one order of magnitude greater than the ratio commonly used in laboratory sorption studies (ranges from 40 to $\sim$6000; e.g. Nodvin et al. 1986; Dalva & Moore 1991; Qualls & Haines 1992b; Dai et al. 1996; Kaiser et al. 1996; this study).

Additionally, other conditions under which sorption isotherms were measured, such as soil drying, differed among the studies, which makes comparison among various studies and interpretation of results difficult. For example, many studies used air-dried and sieved soil (Nodvin et al. 1986; Dalva & Moore 1991; Kaiser et al. 1996), some freeze-dried soil (Dai et al. 1996), yet others field-moist (Qualls & Haines 1992b; this study). Parameters of sorption isotherms (slope and intercept) determined in laboratory studies are often compared or used to estimate the amount of DOM sorbed and the size of the reactive soil C pool, in order to model soil C dynamics (Nodvin et al. 1986; Neff & Asner 2001). However, these parameters can change easily with experimental conditions. Such differences need to be considered before parameters from laboratory sorption isotherms are compared and used to calculate field DOM dynamics.

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