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Chemistry and Dynamics of Dissolved Organic Matter in a Temperate Coniferous Forest on Andic Soils: Effects of Litter Quality

Yuriko Yano,[1]* Kate Lajtha,[2] Phillip Sollins,[1] and Bruce A. Caldwell[1]

[1]*Department of Forest Science, Oregon State University, Corvallis, Oregon 97331, USA;* [2]*Department of Botany and Plant Pathology, Oregon State University, Corvallis, Oregon 97331, USA*

Abstract

Dissolved organic matter (DOM) plays an important role in transporting carbon and nitrogen from forest floor to mineral soils in temperate forest ecosystems. Thus, the retention of DOM via sorption or microbial assimilation is one of the critical steps for soil organic matter formation in mineral soils. The chemical properties of DOM are assumed to control these processes, yet we lack fundamental information that links litter quality, DOM chemistry, and DOM retention. Here, we studied whether differences in litter quality affect solution chemistry and whether changes in litter inputs affect DOM quality and removal in the field. The effects of litter quality on solution chemistry were evaluated using chemical fractionation methods for laboratory extracts and for soil water collected from a temperate coniferous forest where litter inputs had been altered. In a laboratory extraction, litter type (needle, wood, root) and the degree of decomposition strongly influenced solution chemistry. Root litter produced more than 10 times more water-extractable dissolved organic N (DON) than any other litter type, suggesting that root litter may be most responsible for DON production in this forest ecosystem. The chemical composition of the O-horizon leachate was similar under all field treatments (doubled needle, doubled wood, and normal litter inputs). O-horizon leachate most resembled laboratory extracts of well-decomposed litter (that is, a high proportion of hydrophobic acids), in spite of the significant amount of litter C added to the forest floor and a tendency toward higher mean DOM under doubled-Litter treatments. A lag in DOM production from added litter or microbial modification might have obscured chemical differences in DOM under the different treatments. Net DOM removal in this forest soil was strong; DOM concentration in the water deep in the mineral soil was always low regardless of concentrations in water that entered the mineral soil and of litter input manipulation. High net removal of DOM from O-horizon leachate, in spite of extremely low initial hydrophilic neutral content (labile DOM), coupled with the lack of influence by season or soil depth, suggests that DOM retention in the soil was mostly by abiotic sorption.

Key words: dissolved organic carbon; DOC; dissolved organic nitrogen; DON; litter input manipulation; soil solution chemistry; sorption.

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Corresponding author; e-mail: yyano@mbl.edu

Introduction

Soil organic matter (SOM) is the largest organic C pool in the terrestrial biosphere and accounts for virtually the entire ecosystem N reserve (Schlesinger 1997), and thus the balance between gains and losses of SOM is an important control on atmospheric CO_2 and N available to plants via mineralization. Because much C and N enter mineral soil as dissolved organic matter (DOM), the retention of DOM can be an important process for the accumulation of organic matter, and thus formation of SOM as well as C and N dynamics.

DOM concentration is generally highest immediately below the O horizon, and most of the DOM is removed as the solution percolates through the mineral soil (McDowell and Likens 1988; Solinger and others 2001). DOM removal in mineral soils is attributed to abiotic sorption and/or biotic uptake (McDowell and Likens 1988; Qualls and Haines 1992; Kalbitz and others 2000), and DOM chemistry strongly affects these processes.

Recent studies have shown strong chemical controls on abiotic DOM sorption. For example, aromatic C is more strongly sorbed to Al- and Fe-hydrous oxides than is alkyl C (Kaiser and others 1997). Several techniques have been proposed to separate DOM into fractions related to processes such as biodegradation and sorption. One commonly used technique separates DOM into hydrophobic and hydrophilic fractions by its affinity to different types of resins (Leenheer 1981; Qualls and Haines 1991). Laboratory studies have documented that hydrophobic DOM has a stronger affinity to mineral soil particles than does hydrophilic DOM (Dai and others 1996; Kaiser and Zech 1998).

DOM removal in mineral soils via biotic uptake can be strongly controlled by the percentage of biodegradable DOC in O-horizon leachate. This percentage varies among temperate forest ecosystems. For Oa-horizon leachate collected from a deciduous forest at Coweeta Hydrologic Laboratory in North Carolina, USA, Qualls and Haines (1992) found that the proportion of rapidly degradable DOC was approximately l5%, using a laboratory batch incubation of soil solution. For Oa-horizon leachate in two northern coniferous and hardwood stands, rapidly degradable DOC, measured by a flow-through bioreactor, was 10%–40% of total DOC (Yano and others 2000), with a higher percentage during the summer. The differences in the chemical properties of DOM across ecosystems and seasons may be due to differences in source litter quality.

DOM chemistry may be determined by litter type. Generally, leaves and fine roots contain more nutrients (for example, N and P) than wood (Aber and Melillo 1991). Recent ^{13}C-NMR analyses have shown that leaves are richer in alkyl C than are wood and fine roots (Zech and others 1997). Correspondingly, the contribution of aromatic C to total OM is often greater in leaves (Kögel–Knabner 1997). Decomposition generally increases proportions of alkyl C and decreases O-alkyl (carbohydrate) C (Kögel–Knabner 1997). Because the decomposition rate of plant litter is closely related to its chemical composition (Aber and Melillo 1991), and microbial decomposition controls DOM production in O horizon (Gödde and others 1996), differences in litter type as well as the degree of decomposition would produce DOM with different chemical characteristics. However, it is still not clear how DOM chemistry and DOM removal in mineral soil are linked with the quality of the DOM source materials.

The primary objectives of the combined field and laboratory studies were to relate initial source chemistry and decomposition stage to (1) DOM chemistry and (2) DOM removal. The ongoing long-term Detritus Input and Removal Treatments (DIRT) study site established in an old-growth stand at the H.J. Andrews Experimental Forest in the Cascade Mountains in western Oregon provided an opportunity to investigate links between litter type and DOM chemistry as well as DOM removal in the field. In the laboratory study, we examined the influence of tissue type and degree of decomposition on the chemistry of water-extractable OM.

Methods

Study Sites

Plant litter inputs have been manipulated at the DIRT plots (44°15′N, 122°10′W, 726 m elevation) since 1997. Mean annual temperature at the headquarters site at the Andrews Experimental Forest is 7.9°C and mean annual precipitation is 2370 mm y^{-1}, mostly rain. Over 70% of the precipitation occurs during a ''wet season,'' between November and March on average (Sollins and others 1980). The transitions between a ''wet season'' and ''dry season'' are generally clear, although the timing can vary from year to year by about 2 months. During our study period, we defined the wet seasons to be October 1999–May 2000 and November 2000—May 2001, periods when soil water collection was possible. During the dry season, the soil was so dry that we could not

collect enough water for filtration and analysis. N deposition to this area is approximately 2 kg N $ha^{-1}yr^{-1}$ (Sollins and others 1980), close to levels in other pristine environments where anthropogenic N deposition is minimal (Hedin and others 1995). The DIRT site was established in an undisturbed old-growth Douglas-fir (*Pseudotsuga menziesii*) stand. Other plant species at the site include western hemlock (*Tsuga heterophylla*), vine maple (*Acer circinatum*), western red cedar (*Thuja plicata*), and Oregon grape (*Berberis nervosa*), and the forest floor is covered with mosses. Soils are derived from volcanic parent materials and have been classified as coarse loamy mixed mesic Typic Hapludands. The soils have strong andic properties: high amorphous Al hydroxide and aluminosilicate contents (oxalate-extractable Al = 1.1%) and a pH in 1 N NaF near 11 (Yano 2002). Prior to the establishment of the DIRT plots, the soils had a thin O horizon (~2 cm) that was difficult to separate from the moss and into different subhorizons. The O horizon was lying on a 10–25-cm-thick A horizon with abundant fine roots over a more than 30-cm-thick B horizon with less fine root biomass. A large amount of coarse woody debris lay atop the O horizon.

Field Litter Input Manipulation

In 1997 six litter input treatments, replicated three times, were randomly assigned to the plots. The treatments were: Control, with normal litter inputs; Double Litter, where annual leaf (needle) and fine-litter inputs are doubled annually; Double Wood, where existing woody debris in the forest floor is doubled; No Litter, where aboveground litter is excluded by screening; No Roots, where belowground litter (fine roots) is excluded by trenching; and No Inputs, where above- and belowground litter is excluded by screening and trenching. Plots are typically 10 m × 15 m, although there is a small deviation in size in some plots due to available space or obstacles. In this study, we examined water chemistry under three treatments: Control, Double Needle, and Double Wood.

Because of the great heterogeneity in the amount of fallen logs and mosses accompanying them, and to standardize initial conditions, most logs lying on the ground and the moss layer were removed from plots prior to the start of the treatment. To double needle and fine-litter inputs, the litter on No Litter plots was excluded with 1-mm mesh screens and was transferred to Double Litter plots 4–5 times per year: at the end of the dry season, twice or more during the wet season (November–March), and at the beginning of the dry season. Any large branches and stems that fell on screens were discarded. Between 1997 and 2001, aboveground fine litter addition to Double Litter plots averaged 2020 kg dry weight $ha^{-1}yr^{-1}$. To double the mass of woody debris in the forest floor of Double Wood plots, extremely decomposed woody debris from an adjacent area was added in summer 1997, 1998, and 1999, and the chips of large pieces of intact Douglas-fir in summer 1998, 1999, and 2000. Woody debris addition averaged 14.0 Mg dry weight $ha^{-1}yr^{-1}$ with a ratio of decomposed woody debris to intact woody debris of 1:1.6.

Soil Water Collection and Treatment

Five Prenart Superquartz tension lysimeters were installed in 1997 at a 30-degree angle in each plot according to the method described by Lajtha and others (1999), three each at 30-cm depth and two each at 100-cm depth in the mineral soil. Water percolating through the soil column was collected approximately monthly during two wet seasons, October 1999–May 2000 and November 2000–May 2001, except for a 2–3-month period in winter of the first season when access to the plots was blocked by deep snow.

In summer 2000, one zero-tension lysimeter was installed at the bottom of the O horizon (0 cm), which was free of coarse woody debris, in each treatment plot to collect O-horizon leachate. The lysimeters were designed after the ones used by Currie and others (1996), with a modification in size of the plastic containers (we used 20 cm × 20 cm). An area of about 30 cm × 30 cm of the O horizon was carefully cut out and removed, the lysimeters were installed, then the piece of O horizon was gently put back on the lysimeter. In a previous study adjacent to the DIRT site, this installation method showed little disturbance effect on water chemistry of O-horizon soils. Representative O-horizon leachate for the wet season of 2000–2001 was collected three times: in November, January, and May.

All samples were retrieved within 48 hours after the application of tension (for tension lysimeters) or at the beginning of water collection (for zero-tension lysimeters), to minimize biological and chemical alteration of the solution. All samples were transferred on ice to Oregon State University where volume was measured and samples were filtered through pre-combusted Whatman GF/F glass fiber filters. Samples were composited by plot

and depth (volume weighted) and stored frozen within 24 hours after collection.

Soil Sampling

Plots were divided into 5 m × 5 cm subplots prior to soil sampling. O-horizon material was collected from random points within each subplot in fall 2001. The horizon was cut out with a knife (approximately 10 cm × 10 cm in size), carefully separated from mineral soil, and bulked into a single composite sample per plot. A-horizon soil (0–10 cm) was collected in summer 2001 with an Oakfield corer (inner diameter 2 cm), and bulked into a single composite sample per subplot. Samples were immediately transported to Oregon State University where the soils were air-dried and ground to pass a 0.15-mm screen for analysis of total C and N. Total C and N were determined by Micro-Dumas combustion analysis at the Stable Isotope/Soil Biology Laboratory of the University of Georgia, Georgia, USA.

Collection of Plant Litter

Needles. In August 1999 we collected O-horizon material from three mature Douglas-fir stands in the Andrews Experimental Forest to obtain Douglas-fir needle litter at different Stages of decay. These stands had the advantage of thick (~4 cm) organic horizons that could be separated by sub-horizons of different decay stage, no moss cover or visible roots, unlike the stands in which the DIRT plots were established, and the O horizons contained litter derived mostly from Douglas-fir needles (86% on average by weight). The material was then gently separated into Oi, Oe, and Oa horizons with a knife. The Oi horizon was composed of freshly fallen intact needles with minimal decay, the Oe horizon contained partially decomposed needles, and the Oa horizon was composed of well-decomposed material whose origin was unrecognizable.

Wood. In August 1999, we collected wood from three newly fallen (Class 1) and three well-decomposed (Class 5) Douglas-fir logs from the McDonald–Dunn Research Forest (Corvallis, Or, USA) located about 90 km northwest of the Andrews Experimental Forest. We used the classification method for logs described by Sollins (1982), which is widely used in the U.S. Pacific Northwest. Class 1 logs are intact, with bark and all wood sound and current-year twigs still attached; Class 5 logs are extremely decomposed such that sapwood and bark are absent and wood is mainly fragmented and cannot be lifted intact. Because identification of Class 5 logs to species is difficult, we assumed that the Class 5 logs that we used were Douglas-fir based on the size of the logs and the history of the stand. Class 1 logs were further separated into bark, sapwood, and heartwood.

Fine Roots. Douglas-fir seedlings were grown on a mixture of mineral soil from the study site and commercial silica sand (soil: silica sand = 1:1) for 1–1.5 years. This mixture was used to ease fine-root harvest. Seedlings were then harvested by gently washing in de-ionized (DI) water. Roots were submerged in water no longer than 30 minutes. All roots had morphological features typical of mycorrhizal symbioses. The distribution of root-diameter size was 73%, 20%, and 7% by weight for less than 1.0-mm, 1.0–2.0-mm, and greater than 2.0-mm-diameter classes. All roots harvested were pooled into a single sample because of low total mass.

Laboratory Extraction of Plant Litter

Subsamples of all litter and coarse woody debris (Oi, Oe, Oa, Classes 1 and 5, and root) were air-dried and ground to pass a 0.6-mm screen. The ground litter was then extracted in DI water with solid-to-water ratios of 1:40, 1:25, and 1:25 for needle, wood, and root litter, respectively. The extraction was conducted in a shaker at 100 rpm at 22°C for 48–68 hours followed by centrifugation at 7000 rpm for 15 minutes. The supernatant of each extract was filtered (Whatman GF/F glass fiber filters) and stored frozen. The frozen samples were used for the determination of initial concentrations of water-extracted DOC (WEDOC) and DON (WEDON) as well as for further chemical analysis. A portion of the ground litter was further ground to pass a 0.15-mm screen for the analysis of total C and N. Total C and N were determined in the same way as described above for the O- and A-horizon soils.

Chemical Analysis

DOC and DON. Soil water samples collected in the field and the water extracts of organic materials were analyzed for DOC by Pt-catalyzed high-temperature combustion (Shimadzu TOC-5000A HTCO C analyzer). Nitrate N was measured using the hydrazine sulfate reduction method and NH_4–N was determined by the Berthelot reaction method with a Scientific Instruments autoanalyzer. Total dissolved N (TDN) was measured using Cabrera and Beare's (1993) persulfate digestion procedure, followed by NO_3^- analysis. Because NO_2^- in soil water

or solutions in an aerobic environment is negligible (Qualls and others 1991; Currie and others 1996), DON was calculated as

$$[\text{DON}] = [\text{TDN}] - [\text{NO}_3^- - \text{N}] - [\text{NH}_4^+ - \text{N}]$$

Because DON was calculated by difference, values were sometimes slightly negative due to the detection limits of the analyzers, in which case a value of 0 mg L^{-1} was assigned.

Chemical Fractionation. Soil water collected from lysimeters and extracts of plant litter were separated into 6 operationally defined fractions by a method modified from Qualls and Haines (1991) and Leenheer (1981). In brief, the method fractionates DOM by its affinity to three different types of resins (Amberlite XAD-8, noninonic; Amberlite AG MP-50, cation exchange; and Duolite A-7, anion exchange). The weak hydrophobic acid fraction (termed Phenolics here) includes small phenolic compounds (for example, tannin and flavonoids). The strong hydrophobic acids (HoA) are mainly microbially altered plant-derived material rich in aromatic C of larger molecular size, and may contain bound amino acids and carbohydrates. The hydrophilic acid fraction (HiA) contains partly microbially synthesized and partly plant-derived material of smaller molecular size with high carboxyl-to-C ratios. Weak acids (Phenolics) are dominated by —OH, whereas strong acids (HoA and HiA) have more —COOH. 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) is highly biodegradable (Qualls and Haines 1992; Jandl and Sollins 1997), contains carbohydrates and polysaccharides, mainly of microbial origin, and may contain simple sugars (for example, hexose, deoxysugars). The hydrophobic and hydrophilic base fractions contain free amino acids, peptides, and proteins. Because the proportions of the hydrophobic base fraction were very small for all soil solutions and litter extracts tested in this study (≤ 2 % of total DOC), both hydrophobic and hydrophilic bases were combined and reported as Bases. Details of the composition of each fraction were summarized by Qualls and Haines (1991) and Guggenberger and others (1994).

DOM Net Removal in the Field

Net removal of DOM in the mineral soil was determined for each sampling event for three soil layers (0–30 cm, 30–100 cm, and 0–100 cm) as the difference in DOM concentration between water that enters and exits each soil layer. Net DOM removal was then regressed against DOM concentration in the water that enters the soil layer to see whether treatment, season, and soil depth affect the pattern of net DOM removal. We assumed that any biotic and/or abiotic effect on DOM removal would appear as differences in the parameters of the regression lines. For example, an increase in DOM removal via biotic uptake during warm seasons would result in a steeper slope of the regression lines. Concentration effect due to water loss via evapotranspiration (ET) during water percolation was corrected for each sampling event prior to the regression analysis. Water loss via ET in the mineral soil between 0 and 100 cm was assumed to be 21% of O-horizon leachate based on a previous study at a nearby site (Sollins and others 1980). We assumed that annual ET at their site is similar to ET during our study period (wet seasons), because more than 70% of precipitation occurs during wet seasons (Sollins and others 1980). We also assumed that 85% of the total water loss occurred from the 0–30-cm mineral soil layer, based on the distribution of fine roots (diameter <1 mm) within the mineral soil of a site adjacent to ours.

Data Analysis

All measurements of DOC and DON for soil water were grouped by plot ($n = 3$) within each year. Repeated-measures analysis of variance (ANOVA) was used to determine any effects of treatment, time, and depth on DOC, DON, and DOC:DON ratio. Chemical fraction composition was determined for the O-horizon leachate and litter extracts. A paired *t*-test was used to detect the effect of litter type or litter-input treatment on the proportions of chemical fractions. A one-way ANOVA was used to test treatment effects on the chemistry of bulk soils, litter, and DOM. Values were natural-log or square-root transformed to ensure appropriate normality prior to the analysis, followed by back-transformation to obtain least square means and 95% confidence limits. SAS Institute (1999, ver. 8, Cary, NC) software was used for all statistical analyses.

Extractions and all chemical analyses for Class 1 wood were done separately on bark, sapwood, and heartwood. Values for whole wood were then back-calculated based on the percentage of tissue volume of whole wood for Douglas-fir with mean log diameter of 52 cm (bark = 12%, sapwood = 30%, and heartwood = 58%) (Harmon 1992).

Table 1. Total C, N, and C:N Ratio of Litter and WEDOM in Litter Extract

	Bulk litter				WEDOM		
Litter type	Decay stage	C (%)	N (%)	C:N	WEDOC (mg/L)	WEDON (mg/L)	WEDOC: WEDON
Needle	Oi	47.3 **a** (42.5, 52.0)	0.71 **ab** (0.50, 0.92)	66.9 **b** (56.8, 78.8)	384.7 **a** (156.9, 943.3)	0.16 (0.03, 0.98)	840 **ab** (148, 4755)
	Oe	39.0 **b** (34.3, 43.7)	0.99**a** (0.78, 1.20)	39.6 **ab** (33.6, 46.6)	146.9 **ab** (59.9, 360)	1.09 (0.21, 2.65)	173 **ab** (41.9, 711)
	Oa	26.8 **c** (22.1, 31.5)	0.90 **a** (0.69, 1.11)	30.6 **ab** (26.0, 36.0)	37.6 **b** (15.3, 92.2)	0.43 (0.01, 1.54)	27.7 **b** (4.9, 157)
Wood	Class1	48.6 **ab** (43.8, 53.3)	0.09 **b** (−0.12, 0.30)	527 **a** (448, 621)	384.6 **a** (156.8, 943.0)	0.30 (0.00, 1.29)	1719 **a** (418, 7078)
	Class 5	53.1 **a** (48.4, 57.8)	0.28 **b** (0.07, 0.49)	189 **b** (160, 222)	42.6 **b** (17.4, 104.4)	0.73 (0.07, 2.07)	65.5 **b** (15.9, 270)
Fine root	Newly harvested	44.2 **a**	0.74 **ab**	59.4 **ab**	843.1 **a**	3.39	249 **ab**

Numbers in parentheses are 95% confidence limits. Bold letters refer to significant differences within each column. All measurements for litter and extracts were based on n = 3 except for the root extract (n = 1). Statistics are shown only for columns where significant differences were found.

Results

Chemical Properties of Litter and Litter Extracts

C and N of Litter and Extracts. The bulk litter of various types (needle, wood, and root) and stages of decomposition (from intact to highly decomposed) showed large differences in C and N concentration and in C:N ratio (Table 1). Carbon concentration in the needle litter decreased with the degree of decomposition (that is, C concentration of Oa was approximately 57% that of Oi litter), whereas N concentration increased from Oi to Oa. Regardless of the degree of decomposition, wood litter had approximately 10–40% lower total N than needle or root litter, thus the means of C:N for wood litter were higher (189 and 527) than those of the needle or root litter (30.6–66.9). For both needle and wood litter, means of C:N for well-decomposed litter were less than half that of intact litter.

Fine roots produced more WEDOC and WEDON per gram than did needle or wood litter (more than twice for WEDOC and more than 10 times for WEDON, Table 1). In addition, the mean WEDOC:WEDON of the root extract (249) was 1/3 to 1/7 that of needle (840) and wood litter (1719). Although these differences were not significant, the lack of significance is probably due to the lack of replication for the root extract (n = 1). For decomposition stages within each litter type, WEDOC:WEDON generally followed the pattern of C:N of the bulk litter from which it was extracted (Table 1). For the intact substrates the mean WEDOC:WEDON was higher than C:N of the bulk material (66.9–840 for Oi, 527–1719 for Class 1 woody litter, 59.4 to 249 for intact fine roots). Conversely, for well-decomposed litter, the mean WEDOC:WEDON was lower than C:N of the substrate (30.6–27.7 for Oa, 189–65.5 for Class 5 woody litter). WEDOC as a proportion of litter bulk C was largest for the fine root litter (8% of bulk C), and the proportion decreased with the degree of litter decomposition. On average, the ratio of WEDOC to litter C (Oi, Class 1 wood, and fine root) was 6–8 times greater than for well-decomposed litter (Oa and Class 5 wood) (Table 2). The ratio of WEDON to bulk litter N was largest for the fine root litter, as it was for WEDOC. Contrary to WEDOC, differences in the ratio of WEDON to bulk litter N for the intact versus well-decomposed litter were relatively small, and the degree of decomposition did not show a consistent trend between needle and wood litter (Table 2).

Composition of Chemical Fraction. Differences in litter type produced differences in WEDOM chemistry. HiN was the largest fraction for intact wood and root extracts (36%–37%, Figure 1) while HoA, HiN, and HiA fractions were equally abundant for needle extracts (27%, 30% and 25% of total WEDOC, respectively). The degree of decay appeared to have a stronger influence on the composition of WEDOC than did differences in litter type. For example, proportion of HiN differed more between Oi and Oa (P = 0.001) than between

Table 2. WEDOC and WEDON as Proportions of Bulk Litter C and N for Different Litter Types and Decay Stages

Litter type	Decay stage	WEDOC (%)	WEDON (%)
Needle	Oi	3.7 **a**	0.10
		(2.0, 6.0)	(0.07, 0.77)
	Oe	1.6 **ab**	0.47
		(0.6, 3.2)	(0.01, 1.56)
	Oa	0.6 **b**	0.25
		(0.1, 1.7)	(0.01, 1.13)
Wood	Class 1	3.2 **a**	0.88
		(1.6, 5.3)	(0.14, 2.26)
	Class 5	0.4 **b**	0.63
		(0.0, 1.3)	(0.05, 1.84)
Fine root	Newly harvested	7.6 **a**	1.14

Numbers in parentheses are 95% confidence limits. Bold letters refer to significant differences within each column. All measurements for litter and extracts were based on n = 3, except for the root extract (n = 1).

Table 3. Means of Total C, N, and C:N Ratio for O and A Horizons after Four Years of Litter-Input Manipulation

	O horizon			A horizon		
Treatment	Total (%)	Total N (%)	C:N	Total C (%)	Total N (%)	C:N
Control	38.4 **a**	0.97 **a**	39.4 **a**	6.2	0.20	29.6
	(35.1, 41.8)	(0.80, 1.15)	(32.9, 47.2)	(2.8, 9.6)	(0.15, 0.26)	(21.1, 41.6)
Double Litter	39.8 **ab**	0.92 **a**	43.9 **a**	6.8	0.23	28.4
	(36.5, 43.1)	(0.74, 1.09)	(36.6, 52.5)	(3.4, 10.2)	(0.17, 0.29)	(20.2, 39.8)
Double Wood	44.8 **b**	0.60 **b**	75.9 **b**	7.2	0.22	32.1
	(41.5,48.1)	(0.42, 0.77)	(63.4, 90.9)	(3.9, 10.6)	(0.16, 0.27)	(22,8, 45.0)

Numbers in parentheses are 95% confidence limits. Bold letters refer to significant differences within each column.

Oi and Class 1 extracts ($P = 0.311$). For both well-decomposed needle and wood litter, the proportions of HoA increased and it became the largest fraction of all with increasing degree of decomposition (47% and 61% for Oa and Class 5, respectively). At the same time, the proportions of HiN decreased.

Chemical Properties of Soils and Leachates—Field Collection

C and N Contents of Soils and Leachates. Four years of litter-input manipulation altered the chemistry of O-horizon material. Relative to the other treatments, soil under Double Wood treatment was highest in C and lowest in N. Consequently, the C:N of the O horizon under the Double Wood treatment was about twice that under other treatments (Table 3). Treatments had no significant effect on total C and N of the A-horizon soil.

DOC concentration under Double Wood tended to be higher than under Control at 0 cm for the second year and at 30 cm for both years. This was true also for Control versus Double Litter, although only for 0-cm soil water in the second year. The lack of significance in these trends may be due to large variability among replicates (Table 4). Any suggestion of a trend disappeared by 100-cm depth. For any combination of two depths, the concentration of DOC decreased significantly with increasing soil depth under all treatments for both years, indicating net DOC removal in the entire soil column (Table 4). The DOC ranges were widest under Double Wood treatment at both 0- and 30-cm depths; 12.2–178.0 mg C/L for 0-cm soil water and 1.3–48.5 mg C/L 30-cm soil water, as opposed to Control and Double Litter where DOC concentrations ranges were 14.6–84.9 mg C/L for 0-cm soil water and 0.9–13.8 mg C/L for 30-cm soil water. The wide ranges under Double Wood were the

Table 4A. Means of DOC, DON and DOC: DON Ratio for Soil Water: 1999–2000

	30-cm depth			100–cm depth		
Treatment	DOC (mg/L)	DON (mg/L)	DOC:DON	DOC (mg/L)	DON (mg/L)	DOC:DON
Control	4.1	0.14 **ab**	58.2	0.9	0.08	28.5
	(1.7, 10.1)	(0.07, 0.30)	(15.9, 213)	(0.6, 1.3)	(0.03, 0.25)	(5.8, 140)
Double Litter	2.9	0.09 **a**	31.1	1.1	0.12	9.5
	(1.2, 7.1)	(0.04, 0.18)	(8.5, 114)	(0.7, 1.6)	(0.04, 0.38)	(1.9, 46.5)
Double Wood	7.5	0.26 **b**	23.6	1.4	0.25	7.8
	(3.1, 18.4)	(0.12, 0.55)	(6.4, 86.2)	(0.9, 2.0)	(0.08, 0.77)	(1.3, 48.9)

result of differences in DOC concentration among lysimeters (that is, locations) rather than among collection events. For example, DOC concentration at 0 cm in one of the replicated plots of Double Wood ranged from 12.2 to 27.3 mg C/L, while DOC of the other plot ranged from 149.5 to 178.0 mg C/L. Removal of leachate DOC during transit through the upper 30 cm averaged about 88% in the second year (note that these DOM values are not corrected for ET). There was no significant difference in DOC between the two years regardless of treatment or depth.

Contrary to DOC, DON concentrations showed some treatment and time effects. DON concentration differed among treatment at 30-cm depth during the first year, although not during the second year. During the first year, the mean DON concentration under Double Wood was higher than under the other two treatments, Double Litter and Control, and the difference was significant only between Double Litter and Double Wood treatments ($P = 0.032$, Table 4). DON concentration in the soil water decreased from the first to second year for both 30- ($P = 0.006$) and 100-cm ($P = 0.010$) depths. The concentration of DON generally decreased with increasing soil depth for both years, but the change was significant only between 0- and 30-cm or between 0- and 100-cm depths of the second year (Table 4). Although the range of DON concentrations observed was wider under Double Wood than under other treatments for both 0- and 30-cm depths, as was true for DOC, both high and low concentrations were randomly distributed across all lysimeter locations. Similar to the pattern observed for DOC, most (~96% of) DON was removed during percolation through the top 30-cm soil layer in the second year (note that these DOM values are not corrected for ET).

DOC:DON ratio of the soil water was not affected by the litter input treatments during either year. Mean DOC:DON of the soil water at 30 cm increased from the first to the second year ($P = 0.049$) due to lower DON values the second year. Generally, DOC:DON ratio decreased with increasing soil depth from 30 to 100 cm (Table 4), but this was significant only in the second year. There was no consistent trend in changes in DON concentrations between 0- and 30-cm depths.

Chemical Fractionations. The chemical composition of the O-horizon leachate collected in the second year was similar among treatments. Major components of the DOC were HoA (60%–69% of total), HiA (25%–46%); and Bases (2%–4%); other fractions accounted for less than 2% (Figure 2). No treatment effect was found for the three major fractions (HoA, HiA, and Bases) ($P > 0.05$). The composition of the O-horizon leachate was close to that of water extracts from well-decomposed litter (Oa and Class 5, Figure 1): high levels of HoA and HiA, lower levels of HiN.

Net Removal and Release of DOM

The concentrations of DOC and DON in water leaving a soil layer (0–30 cm or 30–100 cm) were generally constant regardless of the treatment, season, and the concentrations of water that entered the soil layer (Figure 3). When net DOC removal was calculated on a sampling event basis, with a correction for water loss via ET, the correlations between net DOC removal and DOC concentration of water that enters the soil layer were very high (Pearson's R ranged from 0.990 to 0.999) (Table 5 and Figure 4A and C). The slopes of regression lines for the correlations were close to 1.0, regardless of treatment, season, or depth of soil layers (Table 5, and Figure 5). All intercepts were negative, which indicates net release of DOC from the soil when DOC concentration of the water that enters the soil layer is low. A similar relationship was found for net removal of DON for the same soil layers (Pearson's R ranged from 0.722 to 0.999) with the slope of the

Table 4B. Means of DOC, DON, and DOC:DON Ratio for Soil Water: 2000–2001

Treatment	0-cm depth			30-cm depth			100-cm depth		
	DOC (mg/L)	DON (mg/L)	DOC:DON	DOC (mg/L)	DON (mg/L)	DOC:DON	DOC (mg/L)	DON (mg/L)	DOC:DON
Control	39.8	0.44	102	6.1	0.06	64.6	0.7	0.04	15.8
	(15.1, 104.5)	(0.17, 1.12)	(16.2, 641)	(2.2, 16.9)	(0.03, 0.15)	(25.3, 165)	(0.4, 1.3)	(0,02, 0.08)	(6.9, 36.5)
Double Litter	51.1	0.75	68.6	3.0	0.05	69. 7	0.9	0.02	23.8
	(19.4, 134.3)	(0.30, 1.93)	(10.9, 431)	(1.1, 8.2)	(0.02, 0.13)	(27.3, 178)	(0.5, 1.6)	(0.01, 0.04)	(10.3, 54.8)
Double Wood	46.1	1.29	37.0	12.3	0.07	116	1.2	0.05	24.3
	(17.6, 121.3)	(0.51, 3.31)	(5.9, 233)	(4.5, 33.8)	(0.03, 0.16)	(45.6, 297)	(0.7, 2.1)	(0.02, 0.10)	(10.5, 55.9)

Note that soil water from 0 cm was not collected during the first year. Numbers in parentheses are 95% confidence limits. Bold letters indicate a significant treatment effect within each column. Statistics are shown only for columns where significant differences were found.

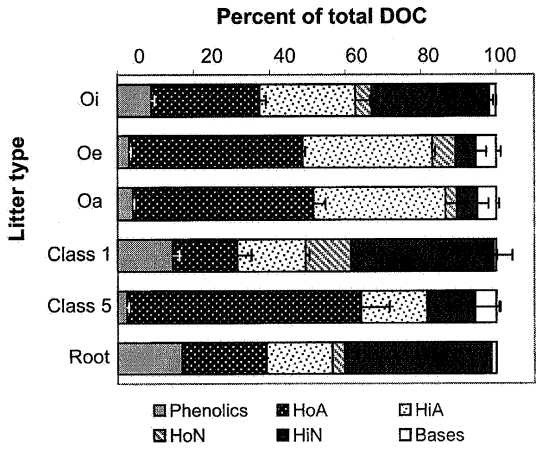

Figure 1. Chemical composition of extracts from litter of different type and decomposition stage. Composition is expressed as percent of total WEDOC.

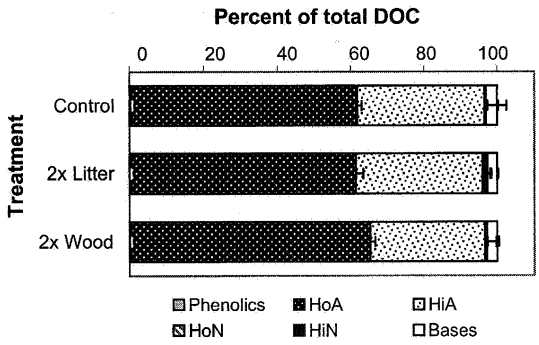

Figure 2. Chemical composition of O-horizon leachate collected at the DIRT site during the wet season of 2000–2001. 2× Litter = Double Litter; 2× Wood = Double Wood.

regression lines being close to 1.0 (Table 5 and Figure 4B and D) and all intercepts negative. The slope became even closer to 1.0 when net DOC and DON removals were determined for the entire soil column (0–100 cm) and regressed against DOC and DON concentrations of the O-horizon leachate (that is, water that entered the mineral soil) (Table 5).

Discussion

Chemical Properties of Litter and DOM Chemistry

Root litter may play the most important role in DOM production, especially in DON production, than any other litter type in this forest ecosystem. Sollins and others (1980) reported organic matter

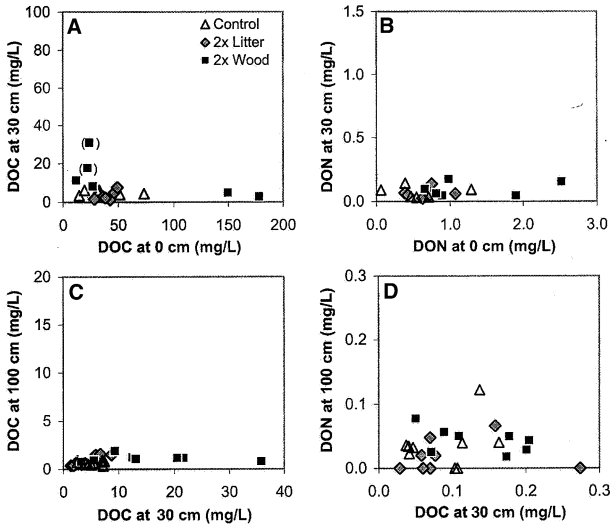

Figure 3. Relationship between DOC and DON concentrations in shallow and deep soil water. (**A**) DOC and (**B**) DON for 0–30-cm soil layer, and (**C**) DOC and (**D**) DON for 30–100-cm soil layer. Note the scale changes between graphs. The net removal of DOM was calculated as: [shallow soil DOM] – [deep soil DOM], and the values of deep-soil DOM were corrected for water loss via evapotranspiration. Concentration factors used were 0.813 for the 0–30-cm soil layer and 0.963 for the 30–100-cm layer. Parentheses indicate data point collected from one of the three replications of Double Wood.

inputs via needle, wood, and fine root litter in a nearby Douglas-fir ecosystem of 2.3, 7.0, and 3.4 Mg $ha^{-1}yr^{-1}$. These estimates, combined with our finding that root litter produced the most WEDOC and WEDON per weight (about 2 times that of needle or wood litter for WEDOC, more than 10 times for WEDON, Table 1), suggest that turnover of fine roots in this forest ecosystem may produce WEDOC that is up to three times that of needle or wood litter and WEDON that is 5–31 times. Additionally, exudates from live roots can potentially be an important DON source, as exudates are rich in N (C:N = 2.5–13) compared to leaf and needle litter (C:N = 40–100; summarized in Grayston and others 1996). We did not determine DON produced as exudates or WEDON from dead and decomposed roots, which would be much lower in N than new roots due to reallocation of nutrients before senescence. Therefore, the contribution of root turnover and exudates to DON in the field cannot be estimated. However, because the O horizon at our study site was very thin (<2 cm) and had few visible roots, the contribution of root exudates as well as turnover to the productions of DOC and DON within the O horizon is assumed to be minor.

Our results suggest that coarse woody debris creates spatial unevenness of DOM production in the O horizon. DOC concentration was highly variable across lysimeters under Double Wood treatment, due perhaps to uneven spatial distribution of the debris. Because wood was added as large wood chips rather than as sawdust, DOC in O-horizon leachate may be affected by ''hot spots'' created by uneven distribution of wood debris. DOC at 30-cm depth was also more variable under Double Wood than other treatments, perhaps due to flow of O-horizon leachate through buried logs, which are quite common at our site, though very unevenly distributed.

Microbial degradation of source material appeared to have a strong control on DOM chemistry. The C:N ratio of litter decreased with degree of decay. This is likely due to loss of C via respiration during decomposition and/or the loss of C via leaching of DOC. The higher WEDOC:WEDON ratio of extracts than in bulk litter indicates that soluble OM in intact litter that is initially in a solid phase but becomes WEDOM upon contact with water has a higher C:N ratio than the rest of OM in the bulk litter. This soluble OM in intact litter may include polysaccharides, simple sugars, phospholipids, and chlorophyll. On contact with water, these compounds leach out of intact litter, resulting in a high WEDOC:WEDON ratio. For well-decomposed litter, however, WEDOC:WEDON ratio were lower than the C:N ratio of source material, indicating that the solid-phase OM that is water-soluble has a lower C:N ratio than the bulk material. As litter ages, microbial degradation and assimilation of insoluble OM of plant origin (for example, lignin, ligno-cellulose), followed by microbial turnover, slowly produces soluble OM of microbial origin. Because the C:N ratio of microbial biomass is around 4–10 (Myrold 1998), soluble OM produced via microbial turnover would have a lower C:N ratio than insoluble OM of plant origin. This idea is supported by the difference in chemical fraction composition between the extracts of intact and well-decomposed litter (Figure 1). The extracts of intact litter had high proportions of HoN and HiN, which contain hydrocarbons and simple sugars and thus have relatively high WEDOC:WEDON ratio. On the other hand, the extracts of well-decomposed litter had high proportions of HoA and HiA, which have relatively lower WEDOC:WEDON ratio. HoA and HiA are produced via microbial degradation of lignin and condensation of lignin-derived compounds (Guggenberger and others 1994). Kaiser and Zech (2000) found a greater proportion of Ho-WEDOC and smaller proportion

Table 5. Correlations Between the Net Removal of DOC and DON and Concentrations in Water Entering the Soil

	Year	Soil layer (cm)	Regression line	Pearson's R	*P*-value
DOC	1999–2000	30–100	$NR_{DOC} = 0.97 \times [DOC_{in}] - 0.96$	0.992	<0.001
	2000–2001	0–30	$NR_{DOC} = 1.04 \times [DOC_{in}] - 8.57$	0.990	<0.001
		30–100	$NR_{DOC} = 0.98 \times [DOC_{in}] - 0.81$	0.999	<0.001
		0–100	$NR_{DOC} = 1.00 \times [DOC_{in}] - 0.77$	0.999	<0.001
DON	1999–2000	30–100	$NR_{DON} = 0.93 \times [DON_{in}] - 0.15$	0.722	<0.001
	2000–2001	0–30	$NR_{DON} = 0.98 \times [DON_{in}] - 0.06$	0.997	<0.001
		30–100	$NR_{DON} = 0.96 \times [DON_{in}] - 0.03$	0.895	<0.001
		0–100	$NR_{DON} = 1.00 \times [DON_{in}] - 0.03$	0.999	<0.001

NR_{DOC} = net removal of DOC, NR_{DON} = net removal of DON, and DOC_{in} and DON_{in} refer to concentrations in water entering the soil layer. All concentrations are in mg/L.

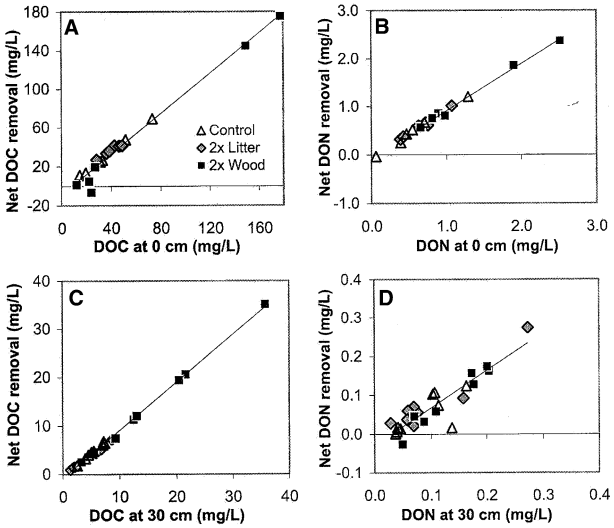

Figure 4. Relationships between DOC and DON concentrations in water entering the mineral soil and the net removal of DOC and DON. Only samples collected during the cold season of the 2000–2001 water year are shown as examples. **A** and **B** correlations for DOC and DON in the 0–30-cm soil layer. **C** and **D** correlations for DOC and DON for the 30–100-cm soil layer. Note that scale changes between graphs. Values were corrected for water loss via evapotranspiration (see text and Figure 3 caption).

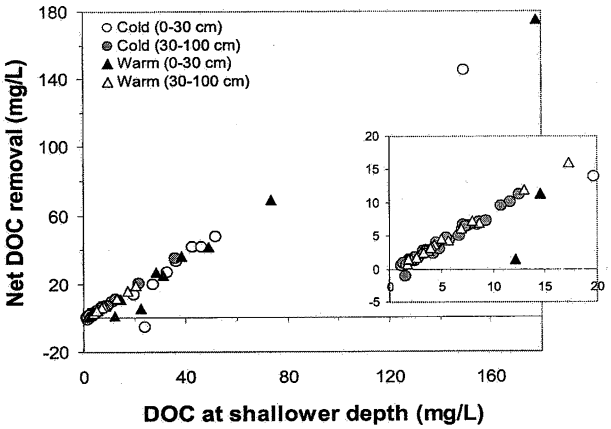

Figure 5. Relationships between DOC concentration in water entering the mineral soil and DOC net removal by season, year, and depth of soil layer. DOC removal refers to the 30–100-cm-depth layer, unless noted in the legend. DOC at shallower depth refers to DOC concentration in water entering the soil layer; 0 cm for the layer 0–30 cm, and 30 cm for the layer 30–100 cm. The circles represent samples collected in the cold season (October–March), and the triangles represent samples collected in the warm season (April and May). A region of low DOC concentration is magnified and shown in a smaller graph inside the larger graph.

of Hi-WEDOC in Oa-horizon extract than in Oi extract. Their findings are consistent with our results where the proportion of Ho-WEDOC increased due to an increase in HoA (from 40% to 54 % for needle, from 40% to 64 % for wood extracts) and the proportion of Hi-WEDOC decreased due to a decrease in HiN with increasing decomposition of DOM sources (Figure 1).

Decomposed litter in the O horizon, rather than newly added litter, appeared to be responsible for most DOM production in the field. Despite the magnitude of total C added via litter additions, the treatment did not significantly increase DOC concentration of the O-horizon leachate or alter the chemical composition of the DOC. Total C added as litter or wood debris during the study period (4 years) was 16% and 110% of existing forest floor C (25.6 Mg ha^{-1} not counting woody debris, Grier and Logan 1977), for Double Litter and Double Wood treatments, respectively. The lack of effect could be due to a lag time before intact needles release DOC. Based on differences between various litter-input treatments at the DIRT study in Mas-

sachusetts, Aitkenhead–Peterson and others (2003) concluded that the Oa-horizon material contributed 88% of DOC in the O-horizon leachate, whereas leaf litter added over the course of the experiment contributed only 7%. Fröberg and others (2003) found that ^{14}C content of lysimeter water below the Oe horizon closely resembled the ^{14}C signature of WEDOC from Oe (partially decomposed), but not WEDOC from Oi (intact litter), and similarly concluded that DOC from the Oi horizon is not a major source of DOM leached from the Oe horizon in the Swedish forest.

The results of DOM chemistry in this study also support the idea that decomposed litter in the O-horizon is more responsible for DOM production than newly added litter. Although litter type affected the chemistry of DOM in laboratory extractions, DOM chemistry of the O-horizon leachate was similar among treatments. Additionally, we found that more DOM was extractable in the laboratory from intact litter than from well-decomposed litter (Table 1) but that the composition of O-horizon leachate most closely resembled that of well-decomposed litter. The simplest explanation for these results is that the amount of DOM released from the litter and wood additions was small relative to the amounts released by the pre-existing well-decomposed litter (Oa and Class 5 wood), obscuring the signal from added litter. Multiplying average values from the laboratory extracts by amounts of needles (Oi) and wood (Class 1 and Class 5) added, then dividing by annual water flow from the Oa (estimated by Sollins and others 1980), gives DOC values of 1.6 mg/L for needle litter added, 4.2 mg/L for Class 1 wood, and 0.3 mg/L for Class5 wood. These values are well below the mean values obtained for Control plots (~40 mg/L) with field lysimeters, thus supporting the idea that pre-existing well-decomposed litter contributes more to DOM production than does intact litter.

Alternatively, microbial activity in the O horizons under different treatments could have yielded similar decomposition products resulting in similar DOM chemistry despite the significant differences in composition of the source materials (wood, needles). The O-horizon leachate of this study site was rich in HoA and HiA but poor in HiN, similar to laboratory extracts from well-decomposed DOM sources (Oa and Class 5 wood). If both HoA and HiA are plant-derived compounds that have been highly modified by microbes as suggested by Guggenberger and others (1994), numerous DOM compounds released from intact litter might have been modified to HoA or HiA prior to leaching, resulting in no measurable effect of the litter type on DOM composition.

A-horizon SOM, unlike O-horizon material, was little affected by the four years of litter manipulation, due probably to large background OM content of A horizon. Most likely, the C and N in DOM and plant tissues admixed into the mineral soil over four years were insignificant relative to amounts in pre-existing SOM. Using a DOC concentration of O-horizon leachate of 45.7 mgC/L (the average for all treatments from Table 5) and a water flux from O horizon to mineral soil of 1980 mm y^{-1} (Sollins and others 1980), then DOC entering the A horizon would be less than 1.0 MgC ha^{-1} yr^{-1}, very small relative to the total A-horizon SOM (about 70 Mg ha^{-1}).

Net Removal and Release of DOM in the Field

The soil of this study site showed strong DOM removal, and net release of DOC and DON from the soil column was small. The negative intercepts indicate net release of DOC and DON from the soil layers at low DOC and DON concentrations in the water that entered the soil (Table 5). For the soil column (0–100-cm depth), the amounts of net DOC and DON released (intercepts of the regression lines in Table 5) as percentages of the average DOC and DON concentrations in water entering the mineral soil (O-horizon leachate DOC and DON averaged over all treatments) were 2% and 4% for DOC and DON, respectively. Therefore, net retention averaged 98% for DOC and 96% for DON for this stand.

The regressions provide useful information on DOM loss from the soil. From the regression lines, the DOC and DON concentrations of O-horizon leachate at which no net removal or loss of DOM was observed for the soil column (0–100 cm) were 0.77 mg C/L for DOC and 0.33 mg N/L for DON. In other words, when DOC and DON concentrations in O-horizon leachate drop below these levels, the soil would start losing C and N. Additionally, the constant net losses of DOM from the soil extrapolated from the regression lines matched DOM loss observed in the field. The mean DOC concentration for a small creek adjacent to this study site averaged over our study period was 1.2 mg C/L (ranged = 0.3–2.7 mg C/L), when the first rain event of the wet season was excluded to eliminate any runoff effect. Similarly, stream DOC and Kjeldahl-N concentrations at nearby Watershed 10 averaged 1.3–2.8 mg C/L and 0.05–0.07 mg N/L for DOC and DON, respectively (Sollins and McCorison 1981).

These concentrations of DOC and DON in streamflow are close to the intercepts of the regression lines for DOC and DON (0.77–1.56 mg C/L for DOC, 0.03–0.15 mg N/L for DON). Because our model uses deep-soil lysimeter water instead of stream water and does not include any DOM discharged via surface runoff or lateral flow in the shallow soil during storm events, this regression approach may be a useful way to predict DOM concentrations in stream baseflow from forested watersheds.

Although both biotic uptake and abiotic sorption could explain the strong 1:1 relationship found between net DOM retention and DOM concentration in water that entered each soil layer, the strong retention appeared to be due mostly to abiotic sorption. We found that HiN was less than 2% of total DOC in O-horizon leachate. Because HiN is the most biodegradable DOM fraction and several studies have suggested that the proportion of HiN determines the biodegradability of total DOM (Qualls and Haines 1992; Jandl and Sollins 1997), microbial degradation of leachate DOM in the mineral soil may be of minor importance. A lack of difference in slope between seasons and between depths of soil layers also supports only a minor contribution of biotic uptake, because higher biological activity in warmer seasons or at shallower soil depth would make the slope steeper (but see discussion below for depth difference). Strong DOM removal (that is, slope of $\sim$1.0) combined with our assumption of minimal biotic immobilization suggests that the mineral soil of the study site (Andisol) has a large potential to abiotically retain DOM. This idea is supported by findings by Nambu and Yonebayashi (2000), who reported strong DOC retention in Andisols in Japan.

The slopes of the regression differed little between the two soil layers (0–30 and 30–100 cm) in contrast to some recent findings that DOM sorption increases with decreasing soil organic matter content. For example, in a laboratory sorption study, Kaiser and others (1996) found weaker DOM sorption by A-horizon material than by B-horizon material in European forest soils. Kaiser and Zech (1998) found that coating B-horizon soil with organic matter reduced DOC sorption. Similarly, Zysset and Berggren (2001) found in their laboratory study stronger sorption of DOM to the Bs1 and Bs2 horizon of a Podzol than to the Bh horizon. These authors hypothesized that reduced sorption was caused by the saturation of sorption sites on minerals with organic matter. Possibly the lack of change in DOM removal with increasing SOM content in our field study [%C of A horizon, 0–10 cm, of this study site = 6%–7% (Table 3); %C of B horizon, 40–50 cm, adjacent to our study site = 1%–2%] reflects greater sorption capacity in our soils than in the soils used in the above studies. Soils at this study site are Andisols, which are known to strongly sorb DOC (Nambu and Yonebayashi 2000), and are young and rich in amorphous Al-hydroxides and aluminosilicates, which strongly sorb DOM (Kaiser and Zech 1998).

DOM sorption to biofilms may also play a role in DOM removal in the shallower soil layer (0–30 cm). Biofilms (microbial extracellular biopolymers) develop on mineral particles where microbial activity and OM loading are high. Iron hydrous oxides in biofilms may effectively sorb DOM (Lünsdorf and others 2000), and thus potentially serve as a strong sorbent for DOM (Guggenberger and Kaiser 2003). Mineral surfaces in the shallower soil layer may have less sorption capacity than surfaces in deeper soil layers, but this may be offset by higher sorption capacity of biofilms in the shallower layer. The lack of differences in removal patterns between the shallower and deeper soil layers in the field could be also because DOM was exposed to more mineral surface with available sorption sites as water percolated through the soil columns than in the laboratory incubation studies mentioned above.

The slopes and intercepts of the regression lines relating net DOM sorption to DOM concentration in water entering the mineral soil indicate nearly complete net removal and constant net release of DOM, regardless of soil depth. Possibly, DOM in the O-horizon leachate is immediately and almost completely sorbed on the bare surface of mineral soil particles or on biofilms with biotic uptake playing only a minor role. This sorbed DOM would be retained until microbial metabolism and degradation slowly convert it into CO_2 or other forms that can be released into soil water. This idea is consistent with a study by Kaiser and others (2001) who hypothesized that an increase in $\delta^{13}C$ values of bulk DOC with increasing depth is due to two separate processes: preferential sorption of ^{13}C-depleted Ho-DOC and release of ^{13}C-enriched Hi-DOC from SOM. Their hypothesis is consistent with results of Schiff and others (1997) and Dai and others (1996). Schiff and others used ^{14}C dating and showed that DOC in groundwater was older than DOC derived from the forest floor. They attributed this to extensive reworking of DOC in the soil column before elution to groundwater. Dai and others, using ^{13}C-NMR, found a shift in composition from DOM in forest floor leachate to SOM

in the Bhs horizon and concluded that DOC sorbed on the Bhs horizon underwent further decomposition. Slow but constant decomposition of SOM would constantly refill a water-extractable SOM pool, which is subject to leaching (Kalbitz and others 2000; Christ and David 1996), and consequently cause ^{13}C-enrichment and ^{14}C-depletion of DOM in deep mineral soils.

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