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Composition, Dynamics, and Fate of Leached Dissolved Organic Matter in Terrestrial Ecosystems: Results from a Decomposition Experiment

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Abstract

Fluxes of dissolved organic matter (DOM) are an important vector for the movement of carbon (C) and nutrients both within and between ecosystems. However, although DOM fluxes from throughfall and through litterfall can be large, little is known about the fate of DOM leached from plant canopies, or from the litter layer into the soil horizon. In this study, our objectives were to determine the importance of plant-litter leachate as a vehicle for DOM movement, and to track DOM decomposition [including dissolve organic carbon (DOC) and dissolved organic nitrogen (DON) fractions], as well as DOM chemical and isotopic dynamics, during a long-term laboratory incubation experiment using fresh leaves and litter from several ecosystem types. The water-extractable fraction of organic C was high for all five plant species, as was the biodegradable fraction; in most cases, more than 70% of the initial DOM was decomposed in the first 10 days of the experiment. The chemical composition of the DOM changed as decomposition proceeded, with humic (hydrophobic) fractions becoming relatively more abundant than nonhumic (hydrophilic) fractions over time. However, in spite of proportional changes in humic and nonhumic fractions over time, our data suggest that both fractions are readily decomposed in the absence of physicochemical reactions with soil surfaces. Our data also showed no changes in the $\delta^{13}C$ signature of DOM during decomposition, suggesting that isotopic fractionation during DOM uptake is not a significant process. These results suggest that soil microorganisms preferentially decompose more labile organic molecules in the DOM pool, which also tend to be isotopically heavier than more recalcitrant DOM fractions. We believe that the interaction between DOM decomposition dynamics and soil sorption processes contribute to the $\delta^{13}C$ enrichment of soil organic matter commonly observed with depth in soil profiles.

Key words: dissolved organic matter (DOM); dissolved organic carbon (DOC); decomposition; isotopic fractionation; humic substances; leaf litter; carbon-isotope ratio.

Introduction

Fluxes of dissolved organic matter (DOM) are an important vector for the movement of carbon (C) and nutrients both within and between ecosystems. DOM fluxes from litter and surface organic horizons to lower soil layers also play a role in soil heterotrophic activity (Zsolnay and Steindl 1991; Jandl and Solins 1997). Furthermore, DOM is a source of nutrients to soil organisms through the movement of dissolved organic nitrogen (DON), phosphorus (DOP), and sulfur (DOS) in litterfall

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and throughfall into soils (Qualls and others 1991). Over long-time scales, DOM fluxes through soil are responsible for solid soil organic matter (SOM) formation via sorption of DOM onto mineral surfaces in spodosols (McDowell and Wood 1984; McDowell and Likens 1988). One central issue involved in both the formation of SOM and the fate of DOM is whether DOM is readily decomposable. Although the processes involved in the physical sorption of DOM across soil types and ecosystems are reasonably well known [for example, see Nodvin and others (1986) and McBride (1994), and Kaiser and others (2001a), the biodegradability of DOM has received less attention [but see Qualls and Haines (1992); Yano and others (1998), and McArthur and Richardson (2002)].

DOM fluxes through terrestrial ecosystems are substantial and likely to play important roles in internal ecosystem C retranslocation and in the movement of C from litter to soils (Kalbitz and others 2000; Neff and Asner 2001). Previous work has shown that litter contains a highly soluble fraction that may move into soils with rainfall (Gosz and others 1973 McDowell and Likens 1988; Meyer and others 1998). In addition to C, DOM contains high concentrations of N, P, and other elements, and the movement of DON and DOP into soil represents a large source of available nutrients. The relationship between litter solubility and DOM flux to soils has led two groups to include the solubility of organic matter as a central controlling factor in models of terrestrial element cycling (Currie and Aber 1997; Neff and Asner 2001). The underlying rationale for linking solubility with decomposition is that litter breakdown is controlled by a mixture of physical, chemical, and biological processes. However, there is little information on the direct relationship between chemistry, solubility, and the subsequent biological availability of DOM across ecosystems and vegetation types.

Uncertainty over biological versus chemical and physical controls on DOM decomposition also lies at the heart of an ongoing debate over the mechanisms behind the often noted enrichment of soil carbon $\delta^{13}C$ values with soil depth (Ehleringer and others 2000; Garten and others 2000; Kaiser and others 2001a). Several investigators have suggested that isotopic fractionation during decay, including that of DOM, should leave behind isotopically enriched sources of C as compared to the original SOM pool (Stout and others 1981; Nadelhoffer and Fry 1988), and that variation in $\delta^{13}C$ can therefore provide a potential index of the extent to which a given organic matter pool has been transformed by microbial activity [for example, see Balesdent and Mariotti (1996)]. However, there is substantial isotopic variation among different compound types within plant material [for example, see Wedin and others (1995)], which in turn leads to isotopic variation in DOM prior to any decay. Thus, other studies have suggested that variation in physical stabilization across the range of isotopic values could help produce the observed depth profiles [for example, see Ludwig and others (2000) and Kaiser and others (2001a)]. It is therefore critical to evaluate the potential influence of microbial decomposition on the isotopic composition of DOM from the additional influence of sorption processes.

In this study, our objectives were to determine the importance of plant-litter leachate as a vehicle for DOM movement into soil and to track DOM decomposition [including both dissolved organic carbon (DOC) and DON fractions], as well as its chemical and isotopic dynamics, during a long-term laboratory incubation experiment in which the influence of soil sorption processes were removed. The rationale for examining both the chemical and isotopic compositions of DOM is that, over the time scales of soil formation, DOM decomposition may contribute to the development of the $\delta^{13}C$ patterns commonly observed in soil profiles.

Methods

Study Sites and Sample Collection

We investigated DOM solubility and the dynamics of DOM decomposition by using both live foliage and senesced litter of species from temperate and tropical ecosystems. Foliar samples from the temperate tree species (*Abies lasiocarpa;* subalpine fir) were collected from a subalpine forest (3400 m) located on Niwot Ridge (40°03'N, 105°36'W), 40 km northwest of Boulder, Colorado, on the eastern slope of the Rocky Mountains. Samples of *A. lasiocarpa* were collected from individuals located along a 50 × 5-m transect by clipping small branches from trees at a height of 1.5 m. Foliage was removed from large stems, and stems and other woody material were discarded prior to extraction. Litter samples of *A. lasiocarpa* were obtained from the forest floor along the same transect. Foliage from two herbaceous alpine species (*Acomastylis rossii,* alpine avens; and *Deschampsia cespitosa,* tufted hairgrass) was also collected on Niwot Ridge, but was collected from a single 20 × 20-m plot located in the alpine tundra. Litter samples were collected following plant senescence from an adjacent 20 × 20-m plot. All samples within a vegetation type were bulked prior to extraction.

Foliar samples from two tropical tree species (*Caryocar costaricense* and *Hieronyma alchorneoides*) were collected from a primary tropical rainforest located in the northwest corner of the Drake River Valley on the Osa Peninsula in southwestern Costa Rica (8°43'N, 83°37'W). Foliage was collected from the canopy (approximately 35 m) of three individuals of each species by climbing trees and excising small branches. Litter of *H. alchorneoides* was sampled from the forest floor below each individual sampled for foliage. Litter of *C. costaricense* was not collected because it is very difficult to identify, whereas litter of *H. alchorneoides* is easily identified on the forest floor. Samples within a single vegetation type were bulked prior to extraction.

Experimental Design

For each vegetation type, six subsamples (of bulked samples) of approximately 50 g (dry-weight equivalent; 70°C) green foliage or senesced litter was cut into small pieces (less than 4 cm^2), placed into 2-L glass beakers, and extracted for 1 h in 1 L of deionized water at 25°C. Following extraction, leachate was prefiltered through a 0.5-mm-mesh sieve and sterile filtered using 0.45 μm MCE (cellulose acetate–cellulose nitrate) filters. Pairs of leachate were pooled, resulting in three leachate samples of approximately 1.8 L each for each vegetation type. Samples were immediately sampled for initial DOC, total nitrogen (TN), inorganic N ($NH_4^+ + NO_3^-$), and δ^{13}C-DOC.

After initial sampling, the three sets of leachate from each vegetation type were transferred to 2.4-L amber bottles equipped with an air-intake port and outlet. Samples were inoculated with 1 mL of a water-diluted (10^{-3}) soil sample from each system (for example, leachate from tropical species was inoculated with tropical soil). The water-diluted soil sample was prepared by transferring 1 g of fresh soil to 9 mL of deionized water, vortex mixing, and transferring 1 mL of the diluted sample to another 9-mL deionized water. Dilution was sequentially repeated until a 10^{-3}-fold dilution had been achieved. DOC added via the inoculum was negligible. Inoculated bioreactors were capped and aerated using pressurized atmospheric air and an airstone to prevent anoxia within the system during the experiment. At regular intervals, reactors were sampled for DOC, TN, and inorganic N. All samples were filtered using Gelman A/E (Gelman "Science, Ann Arbor, MI, USA) glass fiber filters (1.0 μm). Concurrently, total sample volume of each bioreactor was measured, and deoinized water was added as necessary prior to sampling to account for the difference between the total amount of sample removed during previous sampling events and the initial volume of solution in each vessel (that is, water losses from evaporation were replenished).

DOC Fractionation

Fifty-milliliter subsamples of leachate from each reactor (sampled at days 0 and 100) were pooled and fractionated into hydrophobic (humic) and hydrophilic (nonhumic) fractions by using analytical scale column chromatography with XAD-8 Amberlite resin (Sima-Aldrich, Inc, St. Louis, MO, USA) [sensu Thurman (1985)]. What we refer to as the humic fraction is composed of fulvic and humic acids and sorbs to the XAD-8 resin. The humic fraction was determined by back-eluting the XAD-8 resin with 0.1 N sodium hydroxide and measuring the DOC concentration of the eluate after acidification to pH 2.0 with concentrated phosphoric acid. The nonhumic fraction is a heterogeneous class of substances that passes through the XAD-8 resin. The nonhumic fraction is composed predominantly of hydrophilic organic acids and low molecular weight compounds, including carbohydrates, carboxylic acids, and amino acids (Thurman 1985). The nonhumic fraction was calculated by measuring the DOC concentration of the effluent from the XAD-8 resin. The sum of the DOC measured in the humic and nonhumic fractions was typically between 95% and 105% of DOC in the original sample (that is, before fractionation).

Analytical Methods

Foliar and litter C and N composition was analyzed using a Carlo Erba EA 1110 elemental analyzer (CE Elantech, Lakewood, NJ, USA) after samples were ground to a fine powder (40 mesh), and for lignin and other plant products by using the method of Van Soest and Wine (1968). Plant leachate DOC and total dissolved nitrogen (TDN) were measured using a Shimadzu TOC 5050A combustion analyzer (Shimadzu, Kyoto, Japan). Inorganic N (NH_4^+/NO_3^-) was determined colorimetrically on an Alpkem autoanalyzer (OI Analytical, College Station, TX, USA). δ^{13}C-DOC was measured on days 1 and 100 of the experiment. At each time point, 250-mL subsamples of leachate from each vessel were filtered to 0.45 μm and transferred to amber vials, acidified to pH 2 by using 0.5 M H_2SO_4 [to liberate any dissolved inorganic carbon (DIC) from samples], and then returned to neutral pH (approximately 7.0) by using fresh, 1 N sodium hydroxide. Frozen samples were placed on a freeze dryer until reduced to a fine powder. δ^{13}C of freeze-dried DOC

Table 1. Intial Foilage and Litter Chemistry

	Component (%)					
Vegetation Type	Soluble Cell Contents	Hec, Bpr, Cel, Lgn, Re	Hec, Bpr	Cel, Lgn, Re	Cel	Lgn, Re
Hieronyma alchorneoides	24.7	75.7	3.8	71.9	22.4	49.5
H. alchorneoides (litter)	31.0	69.4	4.3	65.0	20.1	44.9
Caryocar costaricense	55.1	45.3	8.1	37.2	13.7	23.5
Abies lasiocarpa	53.9	46.5	13.8	32.7	14.6	18.2
A. lasiocarpa (litter)	36.6	63.8	14.3	49.4	20.6	28.9
Acomastylis rossii	65.4	35.0	16.2	18.8	14.5	4.4
A. rossii (litter)	78.0	22.3	7.9	14.4	10.5	3.9
Deschampsia cespitosa	28.4	72.1	35.4	36.7	28.2	8.5
D. cespitosa (litter)	28.4	72.0	34.3	37.7	34.5	3.2

Hec, hemicellulose; Bpr, bound proteins; Cel, cellulose; Lgn, lignin; and Re, recalcitrants.

Table 2. Carbon (C) and Nitrogen (N) Composition of Foliage, Litter, and Leachate Samples

				Solubility		
Vegetation Type	%C	%N	C–N	C (μg/g)	N (μg/g)	DOC–TDN (DOM)
Hieronyma alchorneoides	52.1	2.4	21.7	1612.2 ± 230.4	815.3 ± 79.2	2.0 ± 0.1
H. alchorneoides (litter)	51.3	1.4	36.6	3139.3 ± 617.5	299.4 ± 29.4	10.43 ± 1.1
Caryocar costaricense	51.4	2.0	25.7	8353.9 ± 2867.0	271.6 ± 92.9	35.6 ± 22.4
Abies lasiocarpa	52.4	1.1	47.6	3574.1 ± 452.0	56.4 ± 3.7	63.3 ± 3.9
A. lasiocarpa (litter)	52.7	0.8	65.9	1594.3 ± 255.8	104.3 ± 13.7	15.2 ± 0.5
Acomastylis rossii	46.4	1.8	25.8	29108.6 ± 1299.1	792.0 ± 55.8	36.8 ± 1.4
A. rossii (litter)	48.0	0.8	60.0	29608.9 ± 1966.9	498.9 ± 30.5	59.3 ± 1.9
Deschampsia cespitosa	45.8	1.7	26.9	5137.4 ± 1065.7	551.8 ± 84.2	9.3 ± 1.1
D. cespitosa (litter)	47.8	1.1	43.5	7335.9 ± 487.2	530.0 ± 17.7	13.8 ± 0.5

Values are mean ± 1 standard deviation of triplicate samples. DOC, dissolved organic carbon; DOM, dissolved organic matter; and TDN, total dissolved nitrogen.

was analyzed using a Carlo Erba EA 1110 elemental analyzer coupled to an Isoprime mass spectrometer (Micromass International, Manchester, UK). Isotopic results are expressed in standard notation ($\delta^{13}C$) in parts per thousand (‰) relative to the standard Pee Dee Belemnite, where $\delta^{13}C = [(R_{sample}/R_{standard}) - 1] \times 1000$, and R is the molar ratio $^{13}C/^{12}C$. The average standard deviation based on analysis of replicated samples was ± 0.87.

Results

Litter Chemistry and Solubility

Initial concentrations of the water-extractable total organic C, N, lignin, and C fractions obtained from foliage and litter used in the incubations differed (Tables 1 and 2). C–N ratios were higher in litter than foliage for all species. Although concentrations of lignin and other forest-product C fractions were variable between vegetation state (foliage versus litter), foliage and litter from woody species had higher lignin concentrations than herbaceous species (Table 2). We found only a weak relationship between DOM solubility and lignin–N ratios of the original plant material (data not shown).

DOC and TDN varied widely between species and vegetation state (Table 2). Based on a single extraction, fluxes of DOC ranged from a low of 0.08% of dry biomass (797.17 ± 127.89 μg C g^{-1} *A. lasiocarpa* litter) to a high of 2.11% of dry biomass (21,149.23 ± 1404.98 μg C g^{-1}, *A. rossii* litter). Initial TDN concentrations ranged from 28.28 ± 1.85 μg C g^{-1} from *A. lasiocarpa* litter to 530.04 ± 17.68 μg g^{-1} in *D. cespitosa* litter.

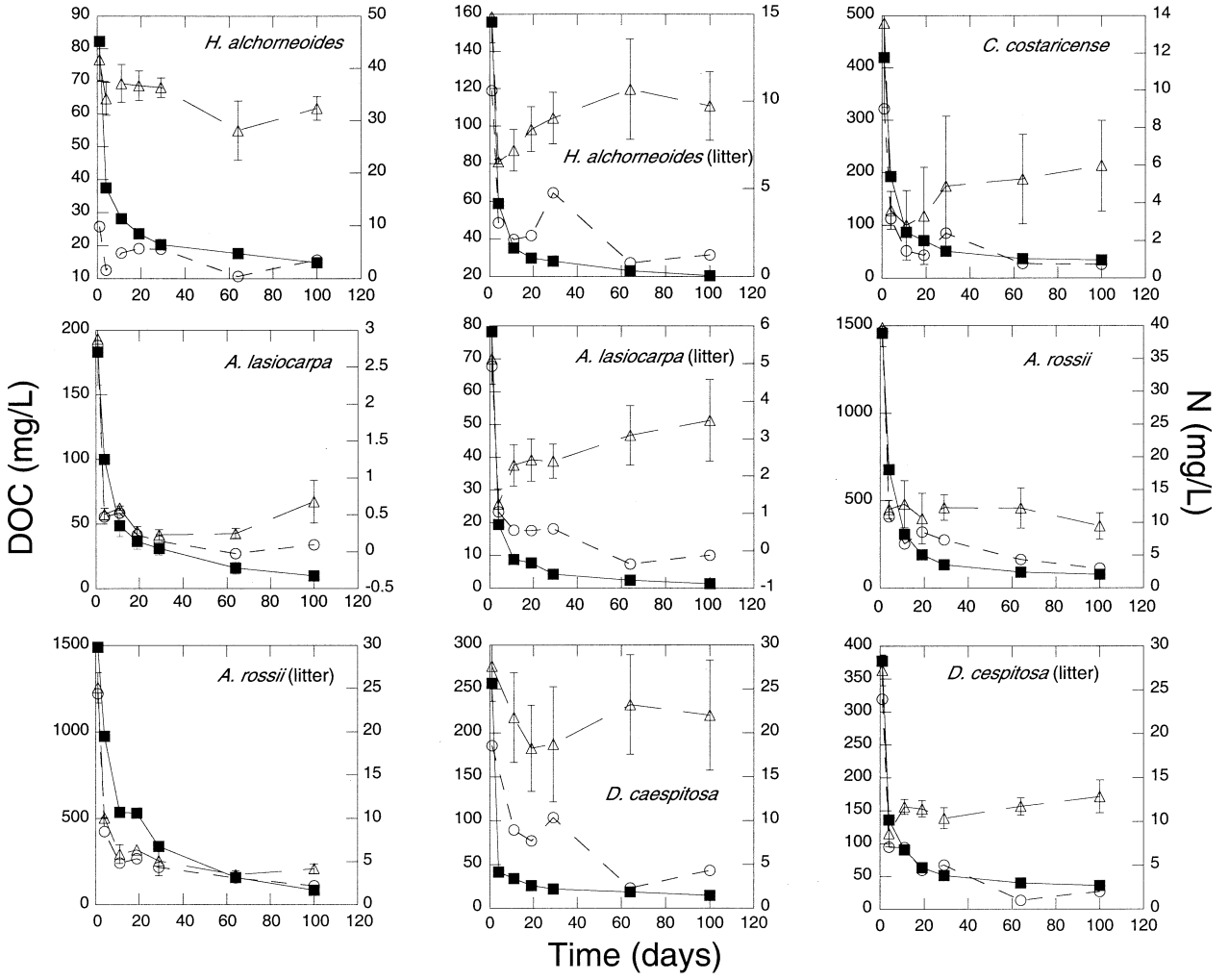

Figure 1. Time course of dissolved organic carbon (DOC, ■), total dissolved nitrogen (TDN, Δ), and total organic nitrogen (○) decomposition in bioreactors with inoculated leachate. Inorganic N values may be calculated as the difference between TDN and organic N. *Symbols* are the mean of triplicate samples, and *error bars* are ± 1 standard deviation.

Biodegradability of Foliage- and Litter-derived DOM

The biodegradable fraction of the DOM was large for all species (Figure 1). In most cases, DOC concentrations were depleted by more than 50% in the first 4 days and by more than 70% in the first 11 days (Figure 1). By the end of the decomposition experiment, less than 10% of the original DOC remained in the extracts from *C. costaricense, A. lasiocarpa* (foliage and litter), *A. rossii* (foliage and litter), and *D. cespitosa* (foliage and litter). Only the leachate from the tropical species, *H. alchorneoides* (foliage), had a final DOC concentration that was more than 10% of the initial DOC concentration.

TDN dynamics in the reactors closely resembled C dynamics early in the experiment (Figure 1). At the beginning of the experiment, TN concentrations declined initially in all of the reactors (due to microbial immobilization of N), but concentrations recovered as the experiment progressed (Figure 1). Furthermore, TDN was dominated by DON (Figure 1) initially, but, as the experiment progressed, organic forms of N became depleted and TN was dominated by inorganic N species (Figure 1).

DOC Chemical Composition

The chemical composition of the DOC (as determined by the XAD-8 fractionation scheme) changed markedly from the beginning to the end of the experiment (Figure 2). Specifically, with the exception of leachate from *H. alchorneoides,* which was composed of approximately 57% nonhumic material at both day 0 and day 100 of the incubation, there was a relative decrease in the proportion

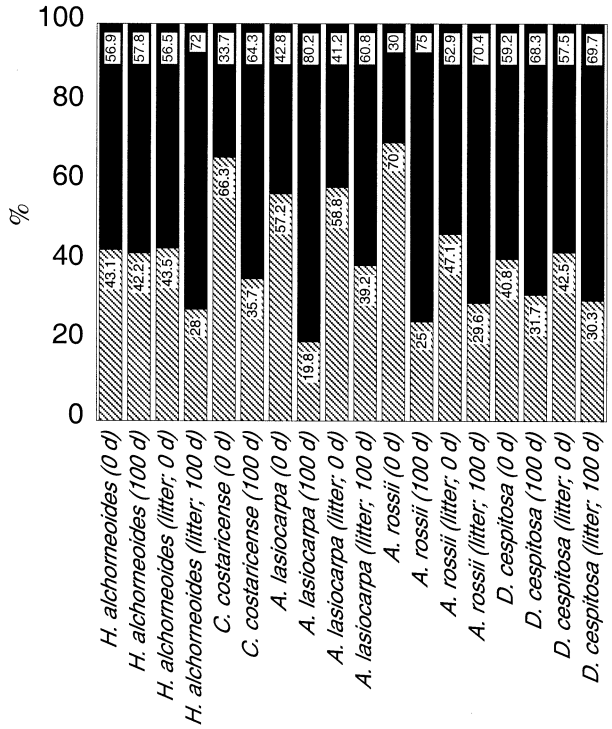

Figure 2. Humic (*solid bars*) and nonhumic (*dashed bars*) fractions of dissolved organic carbon at days 0 and 100 of the incubation experiment.

of nonhumic DOC in all leachates over the course of the experiment (Figure 2). The largest decreases in the nonhumic fraction of DOC following decomposition were in leachate from the foliage of *A. rossii* (−45%), *A. lasiocarpa* (−37%), and *C. costaricense* (−31%), respectively. However, although the proportion of DOC in the humic and nonhumic fractions changed markedly over the course of the experiment, the concentrations of both humic and nonhumic DOC showed strong declines between days 0 and 100, indicating that both fractions were readily consumed in the vessels (Table 3).

DOC Isotopic Composition

The $\delta^{13}C$ of the DOC did not change significantly over the course of the experiment, regardless of species ($P = 0.41$; Student's t test). Initial $\delta^{13}C$-DOC values ranged from −31.3‰ for *H. alchorneoides* litter extract to −25.6‰ in *D. cespitosa* litter extract, and final $\delta^{13}C$-DOC values ranged from −30.6‰ (*H. alchorneoides* litter) to −25.5‰ (*D. cespitosa* litter). However, there were no significant differences between the $\delta^{13}C$ of the initially extracted DOC and the DOC sampled at the end of the experiment from any species. Furthermore, although there were changes in the $\delta^{13}C$ of DOC over the course of the experiment (Figure 3), there was not a consistent directional change in the isotopic composition of the DOC following decomposition.

Discussion

DOM Solubility

Soluble organic material enters the soil as leachate from live and decaying aboveground biomass, and evidence suggests that these fluxes may be large (Czech and Kappen 1997; Kalbitz and others 2000). Estimates of DOM fluxes via litterfall range from 1% to 19% of total litterfall C flux and from 1% to 5% of net primary productivity (Gosz and others 1973; Neff and Asner 2001). Potential litter solubility values (obtained in situ and in laboratory experiments) range from 5% to 25% of litter dry mass and from 5% to 15% of litter C content (McDowell and Likens 1988; Zsolnay and Steindl 1991). In this study, water-soluble DOM was extracted from foliage and litter from temperate and tropical ecosystems. DOC solubility ranged from a low of 0.08% of dry biomass (797.17 ± 127.89 μg C g^{-1}, *A. lasiocarpa* litter) to a high of 2.11% of dry biomass (21,149.23 ± 1404.98 μg C g^{-1}, *A. rossii* litter) from a single extraction. In most cases, foliage produced more DOM than litter of the same species. However, in all cases, litter-extractable DOM was at least 45% of foliage-extractable DOM, and, for two species (*A. lasiocarpa* and *D. cespitosa*), concentrations of DOM extracted from litter were higher than concentrations extracted from foliage of the same species.

The high potentially soluble fraction of senesced litter has been shown in several studies (Yavitt and Fahey 1986; Moller and others 1999). The combination of a highly soluble and biodegradable organic fraction in litter suggests that DOM leaching likely plays an important role in the delivery of labile C and nutrients to surface microbial communities. The losses we observed (that is, up to 2% of litter C mass in a single leaching event) is a significant flux of material out of the litter layer.

Traditional conceptual and simulation models of mass loss in litter decomposition have focused on litter-chemistry control over decomposition processes. In a new model that links decomposition to the flux of soluble material out of litter, Currie and Aber (1997) explicitly linked decomposition to the generation of soluble organic material in the litter layer. Other models of decomposition processes also implicitly or explicitly consider solubility as a control over decomposition. In the Century ecosystem model, the flux of material from litter to soil mi-

Table 3. Chemical Composition of Extracted (Initial) and Decomposed (Final) Dissolved Organic Carbon (DOC)

	Initial DOC Composition (mg/L)		Final DOC Composition (mg/L)		DOC consumed (mg/L %)	
Vegetation Type	Humic Acid	Nonhumic	Humic Acid	Nonhumic	Humic Acid	Nonhumic
Hieronyma alchorneoides	46.8 ± 6.7	35.5 ± 5.1	18.7 ± 1.3	13.6 ± 0.9	28.2 (60.1)	21.8 (61.6)
H. alchorneoides (litter)	88.0 ± 17.6	67.8 ± 13.5	14.7 ± 1.8	5.7 ± 0.7	73.3 (83.3)	62.0 (91.6)
Caryocar costaricense	141.4 ± 49.8	278.2 ± 98.0	21.9 ± 3.4	12.2 ± 1.9	119.5 (84.5)	266.1 (95.6)
Abies lasiocarpa	78.3 ± 10.8	104.6 ± 5.1	8.0 ± 2.1	2.0 ± 0.5	70.3 (89.7)	102.7 (98.1)
A. lasiocarpa (litter)	32.3 ± 5.2	46.1 ± 7.4	0.8 ± 0.8	0.5 ± 0.5	31.5 (97.4)	98.9 (99.0)
Acomastylis rossii	437.6 ± 22.3	1021.1 ± 52.0	59.1 ± 5.6	19.7 ± 1.9	378.5 (86.5)	1001.4 (98.1)
A. rossii (litter)	787.7 ± 56.1	701.3 ± 49.9	59.3 ± 0.5	24.9 ± 0.2	728.4 (92.5)	676.4 (96.4)
Deschampsia cespitosa	151.9 ± 29.6	104.7 ± 20.4	9.7 ± 1.1	4.5 ± 0.5	142.2 (92.5)	100.2 (95.7)
D. cespitosa (litter)	217.1 ± 20.3	160.5 ± 15.0	25.1 ± 1.1	10.9 ± 0.5	192.0 (88.4)	149.6 (93.2)

Values are means ± 1 standard deviation of duplicate samples.

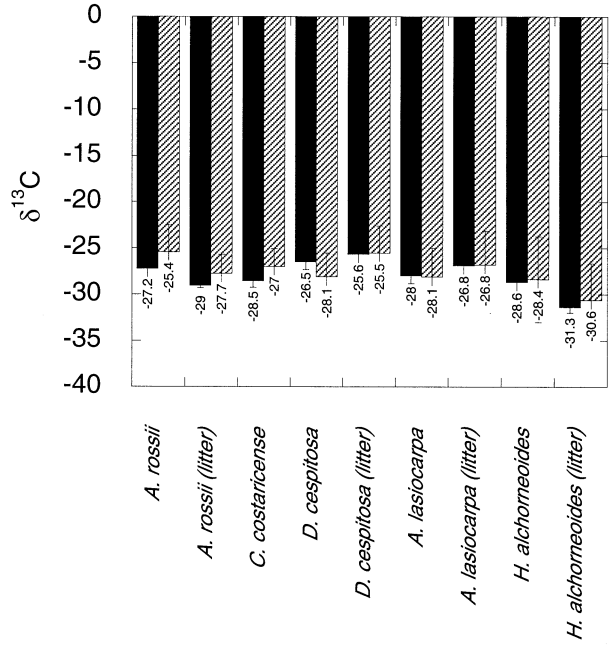

Figure 3. δ^{13}C-DOC at day 0 (*solid bars*) and day 100 (*dashed bars*) of the incubation experiment. Values are the mean of duplicate samples, and *error bars* are ± 1 standard deviation. None of the within-species differences were significant at $\infty = 0.05$.

crobes is controlled by the lignin–N ratio, which is related to the hot-water-soluble fraction of litter (Parton and others 1994). This relationship led Neff and Asner (2001) to explicitly tie the generation of DOC to the lignin–N ratio of vegetation. However, in this study, we found only a weak relationship between lignin–N and solubility. We found that solubility across plant species is much more variable than lignin–N ratios. In other words, although solubility is often low in vegetation with high lignin–N ratios, the supposed general relationship between solubility and lignin–N is overwhelmed by the significant variation in litter solubility across species.

Although our solubility data were not determined using a more common hot-water extraction (Parton and others 1994), we believe that our data more realistically represent the flush of DOM into soil following precipitation events. Accordingly, we suggest that the failure of simple relationships such as lignin–N ratios to predict decomposition rates in a number of systems (Hobbie 2000; Hobbie and Vitousek 2000) could be related to the role of solubility in litter decomposition. Although litter chemistry has been a central focus of litter decomposition studies, litter solubility has not. The large variation and high absolute quantities in the soluble litter fraction across species suggest that more attention should be paid to the role of physical dissolution in controlling litter decomposition rates.

DOC/DON Biodegradability

The distinction between biodegradable and nonbiodegradable DOM is important in understanding DOC biogeochemistry, both conceptually and mechanistically. The results of our decomposition experiment suggest that, in the absence of competing sinks for DOM, DOM from all species and vegetation states is highly biodegradable. A handful of experiments have attempted to partition labile and recalcitrant DOM fractions of plant leachate by examining biological decomposition over a fixed period, and they have typically shown high initial rates of decomposition, followed by a rapid decline

to a lower, constant rate (Zsolnay and Steindl 1991; Bossier and Fontvieille 1993). In throughfall, 18%–50% of the DOM is considered biodegradable, and, in litter leachate, the biodegradable fraction ranges from 6% to 20% (Qualls and Haines 1992; Yano and others 2000). However, many studies of bioavailability have used field collection of DOM to assess the decomposability of DOM (Jandl and Sollins 1997). Comparison of relatively low estimates of DOM bioavailability with the 70%–90% disappearance of DOM in this experiment suggests that field collections may underestimate the initial bioavailability of DOM generated in the litter layer due to rapid decomposition following production.

In this experiment, DOC decomposition followed a negative exponential relationship, but decomposition rates did not decline significantly until the majority of DOC (that is, more than 70%) had been consumed. Our results are in contrast to studies of soil DOM decomposition that show a clear two-pool decomposition pattern with a significant, recalcitrant residual DOM fraction (Zsolnay and Stiendl 1991). One explanation for this discrepancy is the absence in our experiment of physical destabilization/desorption mechanisms in soils, which may serve to generate a flux of more humified/recalcitrant DOC to the soil solution. The high biological availability of DOC generated in litter breakdown may also help explain the strong relationships between water-extractable DOC and microbial activity in soils (Jandl and Sollins 1997). Both in surface soils that receive inputs from litter dissolution and in deeper soils where other processes of DOC generation are involved, it is clear that DOC fluxes should be closely tied to overall rates of heterotrophic activity in soils (Yavitt and Fahey 1986; McDowell and Likens 1988; Qualls and Haines 1992; Brooks and others 1999).

Our results are consistent with conceptual models of DOM decomposition that suggest C decomposition is tightly coupled with N availability. In this experiment, DON decomposition dynamics closely resembled those of DOC. In all of the reactors, TN was initially dominated by DON species, and the decomposition of DOC was clearly fueled by N mineralized from organic forms. In species with initially high DOC–DON ratios, N was efficiently retained in microbial biomass over the course of the experiment, as suggested by consistent decreases in total "free" N (organic and inorganic) in the system throughout decomposition. In DOM with relatively low DOC–DON ratios, TDN in the system decreased initially, but, as DOC concentrations decreased, DON was mineralized to inorganic N species, which dominated TN by the end of the experiment.

It is also noteworthy that the relationship between DOC and DON decomposition may be influenced more by individual species than by the overall N status of a whole system. For example, the alpine species *A. rossii* and *D. cespitosa* are codominant on much of the alpine tundra at Niwot Ridge (considered an N-limited system), yet the decomposition of DOM from each species is strikingly different. Specifically, microbial decomposition of leachate from *A. rossii* (C–N = 60) appears to be tightly constrained by available N, whereas the decomposition of *D. cespitosa* (C–N = 9) leachate rapidly liberates large quantities of inorganic N. Thus, soil microbial communities receiving inputs of DOM via leachate from *A. rossii* may be N limited, whereas microbes receiving inputs from *D. cespitosa* may by C limited, suggesting that individual species exert strong controls on DOM decomposition dynamics (Bowman and others 2003).

DOC Chemical Composition

DOC chemistry may play an important role in determining the balance between decomposition, stabilization, and leaching losses of DOM. In our study, tracking the relative abundance of the humic and nonhumic fractions of DOC during decomposition provided information about how the chemical character of bulk DOC is influenced by heterotrophic activity. Past research has shown that hydrophobic acids are (relatively) biologically recalcitrant and dominate in soil organic horizons, but are effectively removed (via chemical sorption) from solution as water moves vertically through mineral soil horizons. In contrast, hydrophilic acids are considered more biologically available for decomposition, move easily through soil profiles, and are the dominant form of DOM deeper in soil profiles [see references in Easthouse and others (1992)].

In the absence of competing sinks for DOM (for example, chemical sorption in soil), we observed a relative increase in the amount of DOC in the humic fraction over the course of this experiment, suggesting that the nonhumic fractions of the DOC were preferentially decomposed by the microorganisms in the incubation. Moran and Hodson (1990) have previously shown that humic substances support significantly less microbial growth than do nonhumic substances extracted from the same environment. However, Moran and Hodson (1990) also suggested that, although microbial growth was less on humic C sources than on nonhumic C sources, the humic DOC fraction was readily used by natural assemblages of microorganisms as an energy source.

Our results corroborate the findings of Moran

and Hodson (1990) in that we observed shifts in the relative abundance of humic versus nonhumic substances over the course of the experiment, with nonhumic DOC fraction being utilized to a greater extent than the humic DOC fraction. However, our results also provide support for the idea that the humic DOC fraction represents an important, potentially biodegradable C source to microorganisms. In some cases, more than 90% of the humic fraction was biologically consumed in the reactors. However, although our data suggest that a large proportion of humic substances are potential C sources for microorganisms, previous work has shown that the hydrophobic nature of humic substances leads to greater sorption in soil horizons, relative to nonhumic (hydrophilic) substances (Qualls and Haines 1991). The lack of soil sorption mechanisms in our incubation vessels likely increased the ability of the microbial community to access the humic DOC fraction, and, with the absence of soil sorption as a competing sink for DOM, humic fractions became labile substrates for biological decomposition. Neff and Asner (2001) suggested that the competition between physical and biological removal mechanisms for DOC in surface soils is a central feature of the balance between C stabilization and decomposition and an important control on SOM C concentrations. Our results further suggest that, in surface mineral soils, DOC sorption may remove otherwise biodegradable organic matter from solution. This highlights the importance of competition between physical and biological processes in determining the fate of plant C in soils.

DOC Isotopic Composition

A commonly observed phenomenon in soil is a $\delta^{13}C$ enrichment of the bulk soil organic matter with depth (Garten and others 2000; Powers and Schlesinger 2002). Whether isotopic enrichment can provide information on the processes involved in SOM decomposition has not been fully explained. Part of the enrichment with depth is likely related to historical changes in the $\delta^{13}C$ content of the atmosphere [for example, see Fung (1991)], but the atmospheric changes are not nearly sufficient to explain the amount of isotopic change seen in many soil profiles. Thus, if SOM $\delta^{13}C$ enrichment is related to the degree of decomposition as suggested by several authors (ÅAgren and others 1996; Gleixner and others 1999), then these isotopic data could provide useful insight into the relative rates of decomposition across ecosystems. Mechanistic fractionation during decomposition has been observed in several studies. For example, Henn and Chapela (2000) showed that, when grown on $\delta^{13}C$-labeled sucrose, fractionation occurs during sugar uptake by basidiomycete fungi, resulting in fungal $\delta^{13}C$ enrichment. Högberg and colleagues (1999) also demonstrated that mycorrhizal fungi receiving C from host species are enriched in $\delta^{13}C$ relative to their host.

Although selective preservation of fungal derived biomass (which may be $\delta^{13}C$ enriched) may help explain some of the enrichment effect observed with depth in soil profiles (Garten and others 2000), our data suggest that isotopic fractionation during biological decomposition of C compounds is not a significant process. However, there are several important differences between experiments that demonstrate fractionation during decomposition and our results, which do not. First, decomposition in our reactor vessels is likely dominated by bacteria rather than fungi. Second, in contrast to fungal breakdown on solid C substrates where a substantial residual remains, the highly labile DOC in this experiment is nearly fully decomposed, thus reducing the likelihood of kinetic fractionation (Schimel 1993).

Research demonstrating microbial fractionation is typically conducted using pure cultures grown on relatively pure C sources (Henn and Chapela 2000). However, we suggest that, when the C source is a mixture of C compounds (that is, a suite of humic and nonhumic DOM), microorganisms do not preferentially utilize isotopically lighter C compounds as has been suggested elsewhere [for example, see Powers and Schlesinger (2002)]. Furthermore, although our $\delta^{13}C$ data merely suggest this outcome, our DOC chemical fractionation data may explain why preferential decomposition of $\delta^{13}C$-depleted DOM does not occur. Specifically, our data and the data of others suggest that although both humic and nonhumic C fractions are *technically* available for microbial decomposition, the nonhumic (hydrophilic) fraction is mobile and supports high microbial growth, whereas the humic fraction is prone to sorption in the upper soil profile (Kaiser and others 2001a). Furthermore, the relatively labile, hydrophilic fraction tends to be enriched in $\delta^{13}C$ relative to the hydrophobic, humic fraction (Hood 2001; Kaiser and others 2001a). Thus, we believe that although isotopic fractionation via microbial decomposition may be observed using relatively pure C sources, soil C consists of a heterogeneous suite of organic substrates in which the chemical character of the organic C is much more important than its isotopic composition for determining microbial utilization and C uptake.

Our data support the suggestion of Kaiser and

others (2001a) that variable mobility and sorption of DOC with variable isotopic values plays a major role in producing isotopic enrichment with soil depth. In other words, the greater mobility of the isotopically enriched nonhumic DOC, as opposed the greater sorption of the more ^{13}C-depleted humic fraction, should favor the movement and subsequent fixation of more enriched C compounds at depth. $\delta^{13}C$ enrichment with soil depth is often greatest in high-clay soils, as well as in humid tropical systems, and we suggest that these general trends are consistent with the hypothesis that differential sorption of DOC drives much of the observed patterns. Soils with higher clay contents have a higher sorption potential for DOC as compared to coarser textured soils (Neff and Asner 2001); thus, high-clay soils should magnify a sorption-driven change in $\delta^{13}C$ with depth. Similarly, many tropical soils have extremely high clay contents. These clay-rich soils, coupled with high productivity and high soil water fluxes due to abundant rainfall, should combine to produce exceptionally large changes in $\delta^{13}C$ with depth, and indeed the largest isotopic changes are seen in tropical soil profiles (Garten and others 2000). Finally, where isotopic fractionation during decomposition does occur, the high rates of decay seen in tropical systems will only further magnify the pattern set up by differential sorption of DOC.

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