Biogeochemistry (2008) 88:127–138
DOI 10.1007/s10533-008-9200-0

ORIGINAL PAPER

Tropical tree species composition affects the oxidation of dissolved organic matter from litter

William R. Wieder · Cory C. Cleveland · Alan R. Townsend

Received: 2 July 2007 / Accepted: 24 March 2008 / Published online: 22 April 2008

Abstract Plant species effects on soil nutrient availability are relatively well documented, but the effects of species differences in litter chemistry on soil carbon cycling are less well understood, especially in the species-rich tropics. In many wet tropical forest ecosystems, leaching of dissolved organic matter (DOM) from the litter layer accounts for a significant proportion of litter mass loss during decomposition. Here we investigated how tree species differences in soluble dissolved organic C (DOC) and nutrients affected soil CO_2 fluxes in laboratory incubations. We leached DOM from freshly fallen litter of six canopy tree species collected from a tropical rain forest in Costa Rica and measured C-mineralization. We found significant differences in litter solubility and nutrient availability. Following DOM additions to soil, rates of heterotrophic respiration varied by as much as an order of magnitude between species, and overall differences in total soil CO_2 efflux varied by more than four-fold. Variation in the carbon: phosphorus ratio accounted for 51% of the variation in total CO_2 flux between species. These results suggest that tropical tree species composition may influence soil C storage and mineralization via inter-specific variation in plant litter chemistry.

Keywords Carbon · Decomposition · Dissolved organic matter · Species composition · Nutrient limitation · Soil respiration

W. R. Wieder (✉) · A. R. Townsend
Department of Ecology and Evolutionary Biology and INSTAAR, University of Colorado, 450 UCB/1560 30th Street, Boulder, CO 80303, USA
e-mail: will.wieder@colorado.edu

C. C. Cleveland
Department of Ecosystem and Conservation Sciences, University of Montana, Missoula, MT, USA

Introduction

Litter decomposition controls both the quantity and quality of carbon (C) and nutrients that enter soils, and therefore plays a major role in regulating C and nutrient cycling in terrestrial ecosystems. Two distinct processes, direct mineralization to CO_2 in the litter layer and leaching of dissolved organic matter (DOM), contribute to litter mass loss during litter decomposition. While the first pathway may dominate mass loss in many ecosystems, the second pathway—DOM leaching—can be substantial in others (Neff and Asner 2001; Cleveland et al. 2006). In any terrestrial ecosystem, the rates, sizes and timing of DOM fluxes are directly related to the solubility of the organic material being decomposed, and the solubility of plant litter shows considerable variability between species (Currie and Aber 1997; Neff and Asner 2001; Allison and Vitousek 2004; Cleveland et al. 2004a). In addition to litter

solubility, however, high inputs of precipitation can also promote large fluxes of DOM from litter to the soil profile, and DOM leaching may represent a dominant avenue for litter mass loss in mesic ecosystems (Cleveland et al. 2006). For example, in many tropical forests fine litterfall accounts for ~60% of aboveground net primary productivity (Clark et al. 2001) and rainfall is frequent and plentiful. In these sites movement of litter-leached DOM represents important flux of C that fuels significant soil heterotrophic respiration and could account for a large proportion of annual soil CO_2 fluxes (Townsend et al. 1996; Cleveland et al. 2006; Cleveland et al. 2007).

The potential to generate large quantities of DOM clearly exists in tropical rain forests, but the biodegradation of leached DOM is subject to a number of important controls. These include climate, soil type, quality of organic matter, and soil microbial community dynamics (Meentemeyer 1978; Swift et al. 1979; Chapin et al. 2002). Within a site, however, the quality of organic matter is the most important predictor of litter decomposition rates (Melillo et al. 1982). Similarly, while litter solubility and rainfall interact to promote high DOM production in tropical rain forests, the fate of leached DOM in soil also depends on DOM chemistry. For example, heterotrophic organisms may quickly utilize labile, nutrient rich DOM (Zsolnay and Steindl 1991; Qualls and Haines 1991), while more refractory DOM compounds may resist microbial degradation. Specific variations in the carbon chemistry (i.e., quality) and nutrient content of leached DOM are important in regulating its biological decomposition.

Variations in the C chemistry of DOM not only affect its decomposability, but also regulate abiotic interactions in soil. Charged DOM molecules may react to form physico-chemical complexes with soil particles, and this process may effectively remove otherwise biologically available DOM from the soil solution (Qualls and Haines 1992a; McDowell and Likens 1988). This "sorption" of DOM depends not only on soil properties (e.g., soil structure and soil texture; Kaiser and Guggenberger 2000; Kalbitz et al. 2000 and references therein), but also on the chemical composition of DOM. Sorption reactions occur with both labile and refractory DOM. Labile polysaccharides from litter leachate may adsorb to soil particles, although weakly, and ultimately become mineralized by soil microbes (Dahm 1981), while hydrophobic, high molecular weight, or aromatic DOM may adsorb more strongly to soil minerals (Kalbitz et al. 2000). Thus, while long-term DOM sorption and soil organic matter stabilization may result primarily from the accumulation of recalcitrant, lignin-derived DOM onto soil mineral surfaces (Kaiser and Guggenberger 2000), sorption of more labile DOM may also ultimately influence the proportion of DOM that is respired or transported to deep soil via hydrological flowpaths and stabilized (McDowell and Wood 1984, 1988). In any case, while the balance between microbial DOM decomposition versus abiotic DOM retention in soils remains unclear (Kalbitz et al. 2000), DOM chemistry has the potential to affect its ultimate fate in soil.

DOM processing in soil is linked to its C chemistry, but nutrients delivered with DOM pulses also control its fate. For example, species variations in litter C quality and nutrient availability are important in determining rates of decomposition in agricultural systems (Johnson et al. 2007) and in forest ecosystems (Hobbie et al. 2006). Similarly, Cleveland and Townsend (2006) showed that the mineralization of leached DOM is linked to soil nutrient availability, and that higher soil CO_2 losses occur when additions of DOM are combined with nutrient fertilizations. While landscape-level processes control soil nutrient availability at large scales (Walker and Syers 1976), variations in plant foliar nutrient content could drive variations in soil biogeochemistry and soil microbial processes at small scales (Schimel et al. 1998; Bowman et al. 2004). For example, even within a common soil type, individual tree species in the tropics show tremendous variation in foliar nutrients (Townsend et al. 2007), and species-specific differences in litter solubility (Allison and Vitousek 2004) and chemistry (Burghouts et al. 1998) suggest that tree species may regulate fluxes of both C and nutrients into soils. Species driven differences in DOM solubility, combined with the fact that variations in DOM chemistry can influence DOM processing in soil, suggest that canopy species composition may regulate soil processes, at least at local scales.

Here, our objective was to assess the potential effects of plant species composition on biogeochemical processes in tropical rain forest soil using a series of laboratory incubation experiments. Plant species

diversity and composition play important roles in ecosystem function (Hooper and Vitousek 1997; McGrady-Steed et al. 1997; Chapin et al. 2000; Loreau et al. 2001; Heemsbergen et al. 2004). However, field studies examining species affects on litter decomposition dynamics and soil C sequestration in tropical forests typically use plantation studies or other low diversity systems (Spain and Lefeuvre 1987; Bashkin and Binkley 1998; Vitousek 1998; Goma-Tchimbakala and Bernhard-Reversat 2006; Lemma et al. 2006), and thus provide only limited insight into the potential affects of canopy species composition on soil processes in species-rich forests. Our goal was to explore how species-specific differences in litter chemistry affect DOM quantity and quality—and how such differences regulate rates of C mineralization in soil—in a site where leaching of DOM is a dominant mass loss vector during litter decomposition. Under these conditions high species diversity may combine with significant inter-specific variation in foliar chemistry and solubility to drive considerable spatial variation in soil C and nutrient cycling. We hypothesized that species-specific variations will regulate rates of microbial C mineralization through: (1) nutrient availability in the DOM, and (2) difference in C-quality.

Methods

Site description and field sampling

The research site is a diverse, mature, lowland tropical rainforest located on the Osa Peninsula in the Golfo Dulce Forest Reserve in southwest Costa Rica (8°43′ N, 83°37′ W). Annual temperature at the site is 26.5°C, and rainfall averages >5000 mm year^{-1}. A short dry season occurs between December and April, coinciding with high leaf senescence and maximum annual litterfall (Cleveland et al. 2006). Soils at the site have been classified as ultisols (for more detail see Bern et al. 2005; Cleveland et al. 2006; Cleveland and Townsend 2006).

Recently senesced litter from six canopy tree species [*Brosimum utile* (Moraceae), *Caryocar costaricense* (Caryocaraceae), *Manilikara staminodella* (Sapotaceae), *Qualea paraensis* (Vochysiaceae), *Schizolobium parahyba* (Fabaceae/Caes.), and *Symphonia globulifera* (Clusiaceae)] was collected from under at least four individuals of each species in June 2006 and bulked by species. At the same time, we collected one 5 × 10 cm soil core directly beneath the crowns of eight individual trees of each species (i.e., within a 2 m radius of the tree trunk). Within 72 h of collection, samples were transported in a cooler to the laboratory at the University of Colorado, and field moist soil samples were sieved to 4 mm to remove rocks and organic debris. Approximately 25 g of field moist soil from each species-specific soil sample was bulked to form a single, composite soil sample, and homogenized for immediate use in sorption experiments and DOC decomposition incubations. Sub-samples of all individual soils and composite soil samples were dried at 105°C for 72 h to determine field moist water content. Remaining soils were stored at 5°C until use. Leaf litter was air-dried and total litter P was extracted using sulfuric acid/hydrogen peroxide digest; extracts were analyzed colorimetrically on an Alpkem autoanalyzer (OI Analytical, College Station, TX).

DOM extraction and chemical characterization

DOM from each species was extracted by leaching 25 g of air-dried, species-specific litter in 500 ml of de-ionized water for 24 h at 25°C. Following extraction, leachate was prefiltered through a 0.5-mm-mesh sieve and sterile filtered using Gelman A/E glass fiber filters (Cleveland et al. 2004a). DOC and total dissolved nitrogen (TDN) content of the leached DOM were measured using a high temperature combustion total carbon and nitrogen analyzer (Shimadzu TOCvcpn, Kyoto, Japan). We measured the pH of leachate samples and sub-samples of from each species were diluted with de-ionized water (DI) to standard DOC concentrations of 250 mg C l^{-1} (used in soil decomposition incubations) and 100 mg C l^{-1} (used in sorption isotherms); the remainder of the leached DOC was frozen for further analyses and incubations. To assess the P content of leached DOM, 5 ml of undiluted DOM was digested with potassium persulfate and sulfuric acid (Tiessen and Moir 1993), and extracts were analyzed on an Alpkem autoanalyzer. Finally, to measure DOM aromaticity (McKnight et al. 1997), we measured UV absorbance at 280 nm on DOM samples diluted to 2 mg C l^{-1} with an Agilent 8453 UV spectrophotometer (Agilent Technologies, Santa Clara, CA).

Soil sorption isotherms

We conducted 2 h sorption isotherm experiments following the Initial Mass (IM) method using DOM leached from species-specific litter on bulked soil samples as outlined by Nodvin et al. (1986). Briefly, solutions of 0, 10, 25, 50, and 100 mg C l^{-1} were added to two sub-samples of bulked soil in a 10:1 ratio of solution to soils and shaken continuously at 150 rpm at 5°C for 2 h. Samples were centrifuged and filtered through pre-combusted glass fiber filters to obtain a sample solution to be measured for TOC. For each species we plotted the concentration of DOC added g^{-1} (dry weight) of soil against the DOC absorbed. The slope (m) of the linear regression $RE = mX_i - b$ gives the sorption affinity coefficient of the DOM to the soil (Kaiser et al. 2001).

DOM decomposition experiments

We assessed the effects of species-specific differences in DOM chemistry on DOC sorption and decomposition by conducting three separate decomposition incubations. First, we added DOM to soil samples to assess how chemical differences in species-specific DOM affect the overall fate of that DOM in soil (i.e., net DOM losses through both physical sorption and biological decomposition processes). We standardized concentrations of DOC added to each treatment to minimize concentration effects on DOC mineralization (Zsolnay 2003) and to avoid excessive microbial growth (Hongve et al. 2000). In soil treatments, 7 ml of 250 mg C l^{-1} DOM was added to 25 g of field moist soil in 1 l glass vessels jars ($N = 5$ replicates per species). Samples were incubated in the dark at 23°C and DOC decomposition was determined by sampling CO_2 concentrations in the vessel head spaces at regular intervals. The CO_2 concentration was measured with a GC-14A gas chromatograph equipped with a thermal conductivity detector (Shimadzu Corporation, Kyoto, Japan). After each sampling, incubation vessels were purged with room air. Mean background soil respiration was determined from five control samples (25 g soil and 7 ml DI). We concluded sampling after 34 days, when CO_2 fluxes from control samples were greater than 75% of samples receiving DOM.

To assess the effects of variation in DOM on biological decomposition (absent the influence of sorption) we conducted two additional DOM incubations using liquid media. First, to assess the overall effects of DOM variation on decomposition rates, 70 ml of 20 mg C l^{-1} DOM was added to 125 ml flasks and inoculated with 1 ml of a water diluted (10^{-3}) soil sample (Kalbitz et al. 2003; Cleveland et al. 2004a). Flasks were sealed and incubated in the dark at 23°C while continuously shaken on an orbital shaker. DOC mineralization was sampled and calculated as previously described for soil treatments, although terminated 21 days after inoculation. Similarly, to separate the effects of DOM nutrient versus C-chemistry between species, a parallel liquid incubation was conducted in which the C:N:P ratio was adjusted to 100:10:1 (mass basis) in the liquid + nutrient treatments by adding NH_4NO_3 and K_2HPO_4 (Don and Kalbitz 2005).

Data analysis

We calculated total net C mineralization in DOM-amended samples by multiplying average rates of C-efflux at each sampling interval by time and subtracting total C mineralization values from the control samples. The ratio of total net C mineralization to the total C added provided percent C mineralization. Differences between rates and percent C fluxes in the incubations were tested using one-way ANOVA and differences between species were determined using Tukey's B post hoc test (SPSS, Chicago, IL). Relationships between DOM chemical characteristics and respiration were determined with linear regressions. Differences between DOM soil sorption coefficients were determined by analysis of covariance (ANCOVA, Zar 1999). The effects of nutrient additions to liquid incubations were analyzed with ANOVA. All results are reported as significant when $P < 0.05$.

Results

DOM solubility and chemistry

A single leaching event elicited a more than eight-fold difference in soluble DOC fluxes from litter from the six tree species. DOC fluxes ranged from 0.5% of

dry litter mass (*Brosimum*; 5.46 mg C g^{-1}) to 4.4% of dry biomass (*Caryocar*; 44.31 mg C g^{-1}, Table 1). TDN and dissolved organic P (DOP) concentrations in the leachate also varied widely between species; TDN values ranged from 0.10 mg N g^{-1} in *Brosimum* to 1.31 mg N g^{-1} in *Caryocar*, and DOP varied by more than a factor of 30 between species (Table 1). Consequently, nutrient availability in DOM leached from the six species also varied greatly (Table 1). When adjusted for C solubility, litter P was an exceptionally strong predictor for DOP ($P < 0.001$, $R^2 = 0.967$).

Similarly, measures of C chemistry varied significantly between species. Soil sorption coefficients (m) for DOM leached from different tree species in 2 h sorption isotherms and were significantly different (analysis of covariance $F = 4.65$, $P < 0.002$); ranging from 0.247 (*Schizolobium*) to 0.362 (*Manilkara*) and fit the isotherm model well ($R^2 \geq 0.92$). UV absorbance ($SUVA_{280}$) of DOM leached from different species also varied greatly, with values between 0.56 (*Schizolobium*) and 2.33 (*Caryocar*, see Table 1).

Soil incubation experiment: species-specific effects on DOM decomposition

Rates of CO_2 efflux from soil incubations were significantly different between species at all sampling times through 360 h after DOM additions (one-way ANOVA, $P < 0.02$, Fig. 1). Rates of CO_2 flux were greatest in the first days following DOM additions and decreased by an order of magnitude after 3 days. For example, initial (28 h) CO_2 respiration rates ranged from 55.48 ± 0.65 μgCO_2-C h^{-1} (*Qualea*) to 65.40 ± 1.39 μgCO_2-C h^{-1} (*Schizolobium*). After 360 h soil respiration rates ranged from 26.62 ± 0.86 μg CO_2-C h^{-1} (*Qualea*) to 29.42 ± 0.83 μgCO_2-C h^{-1} (*Schizolobium*). Three weeks after DOM additions, between-species differences in soil respiration rates were no longer significantly different from one another, or background rates of soil respiration (one-way ANOVA, $P = 0.39$).

Species-driven differences in soil respiration rates were also strongly correlated with total C respired over the course of the soil incubation (one-way ANOVA, $P < 0.01$; Fig. 2). Twenty-eight h after the soil incubations began, samples receiving *Schizolobium* DOM had respired nearly half of the DOC added and significantly more CO_2 than any other species (one-way ANOVA, $P < 0.001$; Tukey's B, $\alpha < 0.05$). Similarly, 360 h after inoculation soils receiving *Schizolobium* DOM respired significantly more CO_2 (141.6% ± 27.6 of initial DOC added) than soils receiving DOM leached from either *Qualea* (50.6% ± 18.8) or *Manilkara* litter (63.7% ± 10.1; one-way ANOVA, $P = 0.009$; Tukey's B, $\alpha < 0.05$).

Liquid incubation experiment: carbon and nutrient effects on DOM decomposition

While CO_2 fluxes were considerably lower in liquid and liquid + nutrient treatments, we observed the same relationship between species; generally *Caryocar*, *Manilkara*, and *Qualea* had low rates of respiration while *Symphonia* and *Schizolobium* had significantly higher rates of respiration (Fig. 1; Tukey's B, $\alpha < 0.05$). Trends in total species DOC mineralization observed in soil incubations were consistent in liquid incubations as well. Total CO_2 fluxes were significantly different between all species 28 h following liquid inoculations (one-way

Table 1 Inttial DOM characterization following leaching of 25 g leaves in 500 ml of water

Species	Solubility		Sorption (m)	C:N	C:P	UV absorbance[a]	pH
	C (mg/g)	P (μg/g)					
Qualea	6.44	14.2	0.339	50.61	452.72	0.92	5.07
Manilkara	18.85	69.0	0.362	37.64	273.16	0.78	5.31
Caryocar	44.31	483.0	0.336	33.94	91.75	2.33	4.28
Brosimum	5.46	64.6	0.294	57.12	84.51	1.13	5.31
Symphonia	8.07	42.2	0.289	20.59	191.31	0.97	6.59
Schizolobium	16.80	260.0	0.247	22.97	64.62	0.56	5.95

[a] $SUVA_{280}$

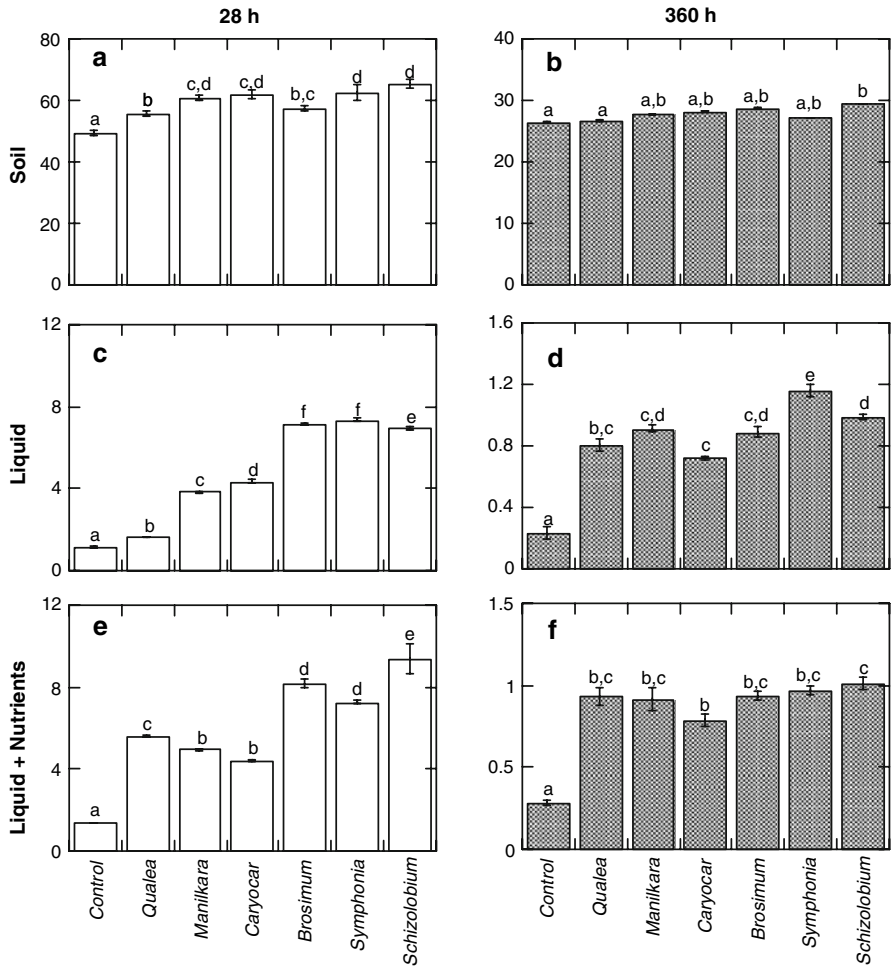

Fig. 1 Mean DOC mineralization rates (μgCO_2-C $h^1 \pm$ SE) for soils (**a**, **b**), liquid DOM (**c**, **d**), and liquid DOM + nutrient incubations (**e**, **f**) after 28 h (open bars) and 360 h (shaded bars). Significant differences between species denoted by lower case letters (Tukey's B, $\alpha < 0.05$)

ANOVA, $P < 0.001$; Tukey's B, $\alpha < 0.05$). Similarly, 360 h after inoculation significantly more *Schizolobium* and *Symphonia* DOC was mineralized than all other species (48.2% ± 1.0, 49.1% ± 0.6 respectively). Total CO_2 fluxes were significantly different between all other species, with only 16.6% ± 0.9 of *Qualea* DOC mineralized (one-way ANOVA, $P < 0.001$; Tukey's B, $\alpha < 0.05$).

Experimentally removing nutrient differences between species significantly altered cross-species patterns of C mineralization. Nutrient additions to liquid incubations caused dramatic increases in to total CO_2 fluxes in some species, notably *Qualea* and *Manilkara*. Total C fluxes after 360 h ranged from 26.9% ± 0.5 (*Caryocar*) to 48% ± 1.7 of initial DOC added (*Schizolobium* and *Manilkara*, one-way ANOVA, $P < 0.001$; Tukey's B, $\alpha < 0.05$). When comparing effects of species and treatments (liquid DOM and DOM + nutrients) after 360 h we observed significant differences in total DOC mineralized based on species, treatment, and an interaction between species and treatments (two-way ANOVA, $P < 0.001$).

Discussion

In this experiment, we investigated how tropical tree species composition could drive spatial variation in soil C dynamics. We focused on two potential mechanisms that could elicit this effect: (1) the quantity of C delivered to soil (driven by differences in plant litter solubility); and (2) the decomposability of soluble C (driven by differences in plant litter chemistry). After a single experimental leaching, we observed a more than eight-fold difference in DOC

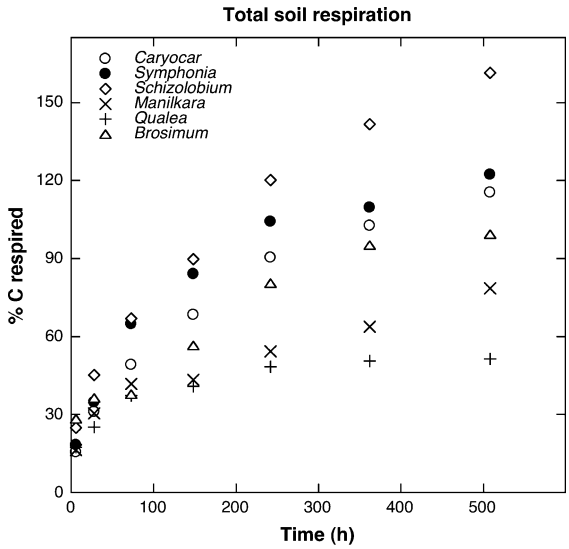

Fig. 2 DOC mineralized for each species throughout the soil incubation experiment. Values represent mean % DOC mineralized

concentrations, and a more than 30-fold difference in DOP concentrations between species (Table 1). In many temperate ecosystems seasonal pulses of DOM are thought to represent a transient phenomena (see Neff and Asner 2001 and references therein). In contrast, at our field site litter decomposition occurs extremely rapidly and litter solubility remains high throughout all stages of litter decomposition (Cleveland et al. 2006), although seasonal differences in DOM leached from the litter layer are not considered here. In the field, peak soil CO_2 fluxes occur at times when DOM pulses are highest (i.e., the wet-to-dry season transition; Cleveland et al. 2006). Between-species differences in the quantity of litter-leached DOM leached indicate that between-species differences in litter solubility alone may exert significant control over the timing and quantity of DOM delivered to the soil profile. Such differences suggest that species composition may strongly regulate rates of soil respiration (and possibly other important soil biogeochemical processes), at least at small scales.

Not only do species vary with respect to DOM quantity, but DOM quality. After adding standardized concentrations of species-specific DOC to soils, we observed ten-fold variations in rates of CO_2 efflux and three-fold differences in total C-mineralization from soils receiving DOM leached from different species (Figs. 1, 2). Notably, *Schizolobium* DOM exhibited a priming effect on soils, respiring more than 160% of C added over the course of the three-week incubation, whereas only 51% of *Qualea* DOM was mineralized over the same time period. These data suggest that chemical variation of DOM leached from different plant species could have important effects on the processing and ultimate fate of that DOM, as well as on more labile soil C pools. Plant litter chemistry could affect soil processing of DOM in two ways: (1) via differences in the proportion of DOM that is susceptible to physical sorption onto soil particles; or (2) via differences in the decomposability of DOM leached from different species.

Physical sorption has important consequences for soil nutrient availability and soil organic C (SOC) dynamics (Neff and Asner 2001; Schwendenmann and Veldkamp 2005; Jimenez and Lal 2006). We observed an inverse relationship between DOM sorption coefficients (m) and total CO_2 fluxes throughout the incubation (28 h $P < 0.001$, $R^2 = 0.51$; 360 h $P = 0.001$; $R^2 = 0.343$). Sorption removes DOM from the soil solution almost immediately (Qualls and Haines 1992b). After 2 h, 25–35% of DOM added to sorption isotherms sorbed to soil particles (Table 1). By comparison, only 16–29% of DOC was mineralized 6 h into the incubation, but 25–45% of DOC was mineralized after 28 h (Fig. 2). Sorption processes may effectively remove DOC from biologically accessible pools and contribute to long-term soil C storage, especially at depth in tropical soils (Schwendenmann and Veldkamp 2005). Our data suggest that species differences may influence soil C dynamics through differential sorption interactions with soil particles.

Models of DOC dynamics in temperate forests indicate that sorption plays an important role in regulating DOC losses from terrestrial systems, but that microbial decomposition of DOC is also important in regulating CO_2 fluxes from surface soils (Neff and Asner 2001). Moreover, biotic processing of leached DOC may be more important in tropical soils, where high annual temperatures allow substantial microbial activity throughout the year, thus promoting lower rates of C sequestration (Lal 2002). Biological decomposition of leached DOC may also depend on the availability of nutrients, especially N and P, to fuel rapid microbial growth (Kalbitz et al. 2000; Marschner and Kalbitz 2003). Widespread

P-limitation is assumed for large areas of lowland tropical forests that grow on highly weathered Oxisols and Ultisols (Walker and Syers 1976; Vitousek 1984; Reich and Oleksyn 2004), and previous in situ measurements of soil respiration showed that both N and P additions drove substantial CO_2 losses from our study site, but that P fertilization had a greater net effect on heterotrophic respiration (Cleveland and Townsend 2006).

In the present study, the nutrient content of leached DOM varied widely between species (Table 1), and rates of soil respiration were strongly related to the nutrient content of the added DOM (Table 2). Specifically, the P concentration of leached DOM was positively related to the total CO_2 respired over the course of the soil incubation in all treatments; soils receiving species specific DOM with lower C:P ratios had higher CO_2 efflux throughout the incubation ($P \leq 0.001$, 28 h $R^2 = 0.41$, 360 h $R^2 = 0.34$, Table 2). In general, CO_2 fluxes from soil samples receiving species DOM with C:P < 250:1 represented nearly 100% of the added DOC, whereas samples receiving DOM with C:P > 250:1 respired less than 65% of initial DOC over the same time period (Fig. 2). Typically, soil microbial communities are thought to be C limited (Lynch 1982), but these data suggest an interesting hypothesis: species delivering DOM with greater P availability lessen a key nutrient constraint (Cleveland et al. 2002; Marschner and Kalbitz 2003), thus promoting rapid mineralization of relatively abundant, labile DOC and SOC.

Our liquid incubations support this hypothesis. Between species differences in DOC mineralization rates were even more pronounced than in the soil incubation, but they generally followed trends seen with soils (Fig. 1c, d). Total C-mineralization in liquid incubations was inversely related with initial C:P and C:N ratios throughout the incubation (Table 2). Within 1 day of inoculation (when labile C is most available and CO_2 fluxes reached their maximum) rates of CO_2 flux in liquid media were strongly constrained by P availability ($P < 0.001$, $R^2 = 0.64$), further suggesting that between-species differences in the nutrient content of leached DOM are critical in regulating rates microbial DOM decomposition. While evidence for P-limitation could be an unintended consequence of the liquid inoculum treatment where microbial growth may be necessary before DOC mineralization (e.g. Marschner and Kalbitz 2003), the consistency of data from liquid and soil incubations, along with other field data (e.g. Cleveland and Townsend 2006) strongly suggest nutrient limitation over DOC mineralization.

Table 2 Linear regression table of total %DOC mineralized after 28 h and 360 h incubation versus initial C:N, C:P, and UV absorbance values for all treatments

	C:N		C:P		UV absorbance	
	R^2	F	R^2	F	R^2	F
Soil						
28	0.10	3.23*	0.41	19.42***	0.06	1.89^{NS}
360	0.17	5.62*	0.34	14.26***	0.00	0.00^{NS}
Liquid DOM						
28	0.04	1.28^{NS}	0.58	38.49***	0.02	0.70^{NS}
360	0.29	11.20**	0.53	31.18***	0.09	2.68^{NS}
Liquid DOM + nutrients[a]						
28	0.13	4.30*	0.24	8.775**	0.32	13.34***
360	0.04	1.23^{NS}	0.002	0.05^{NS}	0.70	68.75***

[a] Based on C:N and C:P ratios that reflect medium matrix following fertilizer additions

* $P < 0.05$

** $P < 0.01$

*** $P < 0.001$

To assess the overall importance of nutrients on DOC mineralization, we calculated a nutrient response ratio by dividing total DOC mineralized after 360 h for each species in the DOM + nutrient addition treatment by the total CO_2 flux in the liquid DOM treatment. We observed a significant relationship between nutrient response ratios and species' initial C:P ratios, best explained by a quadratic relationship ($P < 0.03$, $R^2 = 0.91$; Fig. 3). We did not observe a relationship between response ratios and initial C:N ratios ($P > 0.14$). Nutrient additions released P limitation in species with initial DOM-C:P ratios greater than 250:1 (Fig. 3). Cleveland et al. (2004b) reported microbial C:P > 200:1 during the rainy season at our site. Results from this study suggest that microbes rapidly mineralized labile DOC leached from species delivering relatively P-rich DOM, whereas P limitation constrained mineralization of labile DOC in samples receiving P-poor DOM. Elsewhere, exotic plant species have been shown to drive changes in ecosystem processes like litter decomposition and nutrient cycling by altering

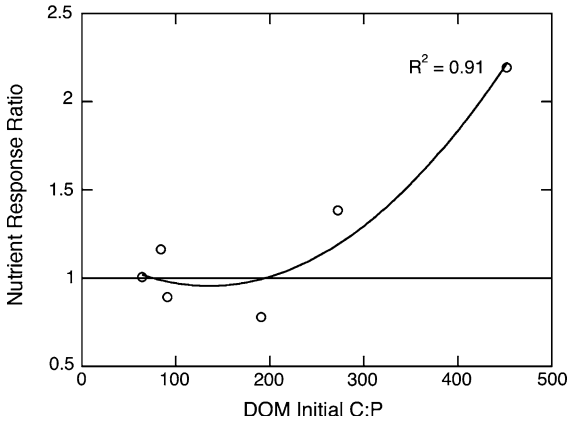

Fig. 3 Nutrient response ratios (calculated by dividing total DOC mineralization after 360 h from liquid DOM + nutrient incubations by total DOC mineralization from liquid DOM incubations for each species) vs. initial DOM C:P ratio ($n = 5$ for each species in each treatment). When fertilization has no affect on total DOC mineralization the response ratio = 1. The relationship between nutrient response ratios and initial C:P is best explained by a quadratic formula ($P = 0.003$). Microbial C:P > 200:1 during the rainy season at our site (Cleveland et al. 2004b)

N and P availability in litter fall (e.g. Ehrenfeld et al. 2001; Rothstein et al. 2004; Hughes and Denslow 2005). Within many natural communities across the tropics, foliar N:P ratios in canopy trees exhibit substantial variation, even between species growing on the same soils (Townsend et al. 2007). Our results suggest that wide inter-specific variation in litter nutrient availability, especially P, controls DOC mineralization, and that soil CO_2 fluxes may be strongly influenced by above ground tree species composition.

Finally, while species-specific differences in DOM nutrient content clearly regulate DOM decomposition rates, variations in DOC chemistry between species also appear important. UV absorbance predicts the aromaticity of DOC and is a simple tool useful in predicting DOC biodegradability (McKnight et al. 1997; Kalbitz et al. 2003; Don and Kalbitz 2005). For example, DOM rich in phenolics leached from freshly fallen litter will have high UV absorbance and inhibit microbial enzyme activity and metabolism (Hättenschwiler and Vitousek 2000). We did not observe a significant relationship between UV absorbance and CO_2 efflux in either soil or liquid incubations (Table 2); although at the end of the liquid incubation rates of CO_2 flux were negatively correlated with this measure of C-chemistry (360 h $P = 0.001$, $R^2 = 0.32$). This suggests that more DOC was mineralized from species with less aromatic DOM, but that sorption and nutrient availability likely exert stronger control over heterotrophic respiration. Subsequent liquid + nutrient incubations removed effects of both sorption and nutrient limitation. Species' variation in UV absorbance explained a significant amount of total CO_2 flux ($P < 0.001$, $R^2 > 0.70$ after 360 h incubation). Other studies report similar findings, with lower biodegradability of more aromatic DOC (e.g. Kalbitz et al. 2003; Marschner and Kalbitz 2003; Don and Kalbitz 2005). Chemical differences in DOM leached from different species likely influence microbial C availability through physical sorption and biological accessibility.

Conceptual model

Based on these data, we propose a conceptual model that depicts potential species effects on the fate of litter-leached DOM (Fig. 4). Variations in species litter chemistry and solubility directly influence the quantity and quality of DOM delivered to the soil profile. DOC leached into the soil can be physically sorbed to soil particles, microbially mineralized into CO_2, or remain unaltered in the soil; our conceptual model only considers physical and biotic processes that transform DOC. The C chemistry of DOM leached from different species' litter exerts strong influence over both physical sorption through chemical interactions with clay particles, and microbial decomposition by chemically determining the biodegradability of DOM. Nutrients available in DOM, especially P, help determine the rate and extent of labile C mineralization. Thus, nutrient availability and UV absorbance of DOM may determine whether labile DOC undergoes rapid decomposition, is stabilized in soils, or is leached from terrestrial systems.

Species driven differences in DOM processing could strongly affect overall soil C dynamics. In species-rich tropical forests, variations in the sorption or biodegradability of leached DOM may drive small-scale variability in net soil C storage, net C losses from terrestrial to aquatic ecosystems, or both. For example, litterfall is an important source of both C and P inputs to soil in lowland tropical systems (Burghouts et al. 1998; Campo et al. 2001), and P additions drive substantial C losses from tropical soils

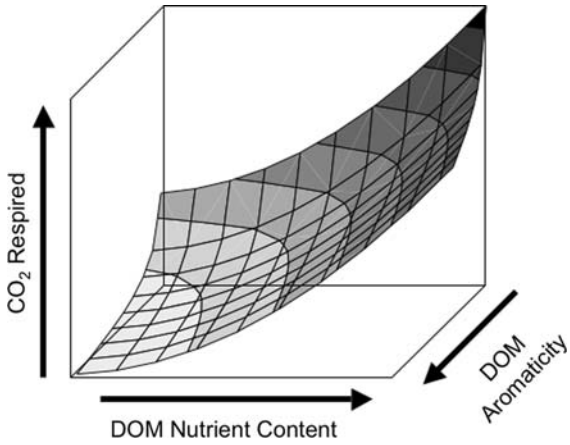

Fig. 4 Conceptual model showing the combined effects of DOM nutrient content and aromaticity on CO_2 flux from soils. In this study we demonstrate that inter-specific variation in litter chemistry influences DOM quantity and chemistry; this variability determines the fate of DOC via physical sorption and microbial decomposition

(Cleveland and Townsend 2006). Our data suggest that inter-specific variation in litter chemistry and litterfall, demonstrated here and elsewhere (Goma-Tchimbakala and Bernhard-Reversat 2006; Hobbie et al. 2006; Townsend et al. 2007), may lead to highly heterogeneous soil C and nutrient distribution at small spatial scales (Burghouts et al. 1998; John et al. 2007). However, data from Powers et al. (2004) contradict this hypothesis, indicating that further research is needed to determine the influence of above ground species composition on soil processes and C-dynamics, especially under field conditions.

These results highlight the potential importance of species composition in regulating terrestrial C-cycling in tropical forests (Bunker et al. 2005). Selective logging operations in the Brazilian Amazon meet or exceed rates of deforestation (Asner et al. 2005a, 2006), resulting in a net loss of goods and services provided by the ecosystem, including C-sequestration (Foley et al. 2007). Results from this study indicate that shifts in above ground species composition may also drive changes in below ground C cycling. For example, removing species that deliver more recalcitrant, nutrient-poor forms of DOM to the soil profile may decrease overall soil C-storage. Such species-level effects may be especially pronounced at larger scales in the context of plantation forestry; here, overall carbon storage in tropical plantations may depend not only on aboveground dynamics, but also on the foliar DOM properties of the species being grown. Finally, we note that while extrapolating species-level effects to larger scales in highly diverse tropical ecosystems can seem daunting, relationships between foliar chemical properties and effects such as those reported here provide some hope. For example, the strong relationship between bulk foliar P and DOP availability suggests that knowledge of foliar chemistry, which is increasingly possible at high resolution over larger areas via new remote sensing methods (Asner et al. 2005b), may allow predictions of species-level influences on soil biogeochemistry even at regional scales.

Acknowledgments We thank H. and M. Michaud of the Drake Bay Wilderness Camp for providing field access and logistical support in Costa Rica, and Francisco Campos and the Organización para Estudios Tropicales (OET) and the Ministerio de Ambiente y Energia (MINAE) in Costa Rica for assisting with research permits and logistics. We are grateful to Daniel Liptzin and Matthew Miller for valuable discussions and insight during the experimental design and data analysis. We appreciate comments on the manuscript made by Nataly Ascarrunz and two anonymous reviewers. This work was supported by National Science Foundation (NSF) Grant DEB-0515744 (to A.R.T. and C.·C.C).

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