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Nutrient and mineralogical control on dissolved organic C, N and P fluxes and stoichiometry in Hawaiian soils

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Abstract. We measured DOM fluxes from the O horizon of Hawaiian soils that varied in nutrient availability and mineral content to examine what regulates the flux of dissolved organic carbon (DOC), nitrogen (DON) and phosphorus (DOP) from the surface layer of tropical soils. We examined DOM fluxes in a laboratory study from N, P and N+P fertilized and unfertilized sites on soils that ranged in age from 300 to 4 million years old. The fluxes of DOC and DON were generally related to the % C and % N content of the soils across the sites. In general, CO_2 and DOC fluxes were not correlated suggesting that physical desorption, dissolution and sorption reactions primarily control DOM release from these surface horizons. The one exception to this pattern was at the oldest site where there was a significant relationship between DOC and CO_2 flux. The oldest site also contained the lowest mineral and allophane content of the three sites and the DOC-respiration correlation indicates a relationship between microbial activity and DOC flux at this site. N Fertilization increased DON fluxes by 50% and decreased DOC:DON ratios in the youngest, most N poor site. In the older, more N rich sites, N fertilization neither increased DON fluxes nor decreased DOM C:N ratios. Similarly, short term changes in N availability in laboratory-based soil N and P fertilization experiments did not affect the DOM C:N ratios of leachate. DOM C:N ratios were similar to soil organic matter C:N ratios, and changes in DOM C:N ratios with fertilization appeared to have been mediated through long term effects on SOM C:N ratios rather than through changes in microbial demand for C and N. There was no relationship between DON and inorganic N flux during these incubations suggesting that the organic and inorganic components of N flux from soils are regulated by different factors and that DON fluxes are not coupled to immediate microbial demand for N. In contrast to the behavior of DON, the net flux of dissolved organic phosphorus (DOP) and DOM C:P ratios responded to both long-term P fertilization and natural variation in reactive P availability. There was lower DOP flux and higher DOM C:P ratios from soils characterized by low P availability and high DOP flux and narrow DOM C:P ratios in sites with high P availability. DOP fluxes were also closely correlated with dissolved inorganic P fluxes. P Fertilization increased DOP fluxes by 73% in the youngest site, 31% in the P rich intermediate age site and 444% in the old, P poor site indicating that DOP fluxes closely track P availability in soils.

Introduction

The flux of dissolved organic matter (DOM) through terrestrial ecosystems plays an important role in soil formation and nutrient dynamics (Hedin et al. 1995; Currie et al. 1996; McDowell et al. 1988). The factors that control the sorption of dissolved organic carbon (DOC) in soils are reasonably well characterized (e.g. Moore et al. 1992), but there is surprisingly little information on the mechanisms that regulate the biogeochemistry of DOM. The role of dissolved organic nitrogen (DON) in terrestrial N budgets has been examined in multiple ecosystems (Hedin et al. 1995; Currie et al. 1996; McDowell et al. 1998), but few studies have examined the C, N and P content of DOM simultaneously. In particular, little is known about the relationships between DOM fluxes, stoichiometry and nutrient availability.

From the standpoint of terrestrial ecology, these questions are important because DOC, DON and DOP fluxes play important roles in terrestrial C, N and P budgets. Within-system fluxes of DOC are large and range between 10 and 80 g of C m^{-2} yr^{-1} in throughfall or soil fluxes (McDowell & Likens 1988; Qualls et al. 1991; Moore 1989). DON and DOP play important roles in the maintenance of nutrient capital in terrestrial ecosystems (Hedin et al. 1995; Vitousek et al. 1998), and are important for the formation of soils (Schoenau & Bettany 1987).

Carbon, nitrogen and phosphorus are all present in organic matter, yet most studies focus on a single element at a time, and few have evaluated the relative changes of C, N and P in DOM with solution movement through ecosystems (but see Qualls et al. 1991) or in response to changing nutrient availability (but see Currie et al. 1996). It has been suggested that DON losses may occur despite overall ecosystem demand for N (Sollins & McCorison 1981; Hedin et al. 1995; Lajtha et al. 1995) but little is known about the specific mechanisms that control these fluxes. To clarify these issues, it is important to understand the role that nutrient availability plays in the regulation of DOM flux and C, N and P content.

DOM can be produced and consumed by micro-organisms or plants and can be stabilized or solubilized on and off of soil surfaces (McDowell & Wood 1984; Kielland et al. 1986; Kaiser et al. 1996). This suite of competing reactions greatly complicates interpretation of the regulation of DOM fluxes at the ecosystem scale. In terrestrial systems, the upper, organic-rich, horizons of ecosystems are often an important source of DOM, and the generation of DOM in these soil layers is commonly attributed to microbial processes (McDowell & Likens 1988; Qualls et al. 1991; Currie et al. 1996). This suggestion is supported by studies which show close relationships between DOC and CO_2 fluxes from soils (Seto & Yanagiya 1983; Jandl & Sollins 1997; Brooks et al. 1999) and evidence that DOC fluxes increase with temperature

(Christ & David 1996; Toland & Zak 1994). Studies of sorption reactions generally show significant capacity for DOC sorption and desorption across a range of soil types (Kaiser et al. 1996) and DOC can compete with other anions for binding sites on organic matter (Johnson et al. 1986; Nodvin et al. 1986). These studies raise the possibility that DOC flux is controlled by physical rather than biological factors in soils. Similar controls may apply to DON and DOP as well. In this study, we explore the factors that influence biological vs. physical control of net DOC, DON and DOP flux from the O horizon of soils using a chronosequence of sites in the Hawaiian islands that differ in both mineralogical control over organic matter stabilization and in nutrient availability. We also take advantage of long-term field fertilization experiments to examine the impacts of artificial changes in nutrient availability on the N and P content of DOM.

Methods

Site description

The three sites used in this study are part of a more extensive soil chronosequence described by Crews et al. (1995). The sites along the chronosequence have similar average precipitation, mean annual temperature and vegetation cover (Table 1) but differ considerably in substrate age. The youngest site (Thurston) is approximately 300 years old and was formed during eruptions of Kilauea volcano on the island of Hawaii and developed on 0.4 m of tephra overlaying lava (Crews et al. 1995). The intermediate age site (Laupahoehoe) is also located on the island of Hawaii and is developed on 20,000 year old tephra deposits. The oldest site (Kauai) is located on the island of Kauai in Kokee State Park and is approximately 4.1 million years old.

Substantial changes in mineralogy occur on this chronosequence during ecosystem development, and O horizon mineral content decreases from Thurston to Kauai (Torn et al. 1997; Chadwick et al. 1999; Table 1). These sites are of balsaltic origin, and as the soils age, there are marked changes in the crystalline content of the soil minerals. The highest noncrystalline (allophane, imogolite and ferrihydrite) mineral content occurs at the intermediate age site (Table 1). As the soils age, the noncrystalline minerals are transformed into crystalline minerals including halloysite, gibbsite, kaolinite, goethite and haematite, and at the oldest site (Kauai) there is substantially lower noncrystalline mineral content compared to the other two sites (Chadwick et al. 1999; Torn et al. 1997; Table 1).

Table 1. Hawaiian Chronosequence Sites: Site descriptions and years of field fertilization. All sites have similar vegetation cover and are developed from the same parent material. Percent organic C and % total N were determined for this study. Site characteristics from Crews et al. (1995), Torn et al. (1997), Chadwick et al. (1999) and Olander and Vitousek (in press). % Total P from Olander and Vitousek (in press). MAT is mean annual temperature, MAP is mean annual precipitation and PMA is parent material age.

Site characteristics	Elevation (m)	MAT (°C)	MAP (mm)	PMA (10^3 years)	Years of field fertilization	Soil classification
Thurston	1176	16	2500	0.3	12	lithic hydrudand
Laupahoehoe	1170	16	2500	20	4	hydric hydrudand
Kauai	1134	16	2500	4,100	6	plinthic acrudox

Soil characteristics	O horizon depth	Bulk density (g/cm^3)	% Organic C	% Total N	% Total P	% Mineral content of the O horizon	% Noncrystalline mineral content of the O horizon
Thurston	0–10 cm	0.32	25.4	1.17	0.07	48.7	6.7
Laupahoehoe	0–12 cm	0.29	41.7	2.22	0.07	29.5	9.2
Kauai	0–7 cm	0.25	37.5	1.58	0.03	26.5	3.5

These mineralogical transformations are important for this study because mineral surfaces in general, and noncrystalline surfaces in particular, stabilize organic matter as demonstrated on this sequence by Torn et al. (1997). For this study, these changes are useful because, to the extent that physical mechanisms regulate DOM fluxes from soils, we would expect to observe the highest physical control over DOM dynamics in the sites with the greatest mineral content. Where physical (mineralogical) controls are less intense, we would expect greater biological control over DOM stabilization and release.

Each of the sites in this study has vegetation that is dominated by the tree *Metrosideros polymorpha*, but each also differs substantially in nutrient availability and nutrient limitation to primary productivity. Factorial N and P fertilization experiments have been carried out for at least 4 years at each of the sites (Table 1, Vitousek et al. 1993; Vitousek and Farrington 1997; Herbert and Fownes 1995) with all sites fertilized at a similar rate (100 kg N or P per year). Nitrogen has been added as a 50/50 mix of urea and ammonium nitrate and phosphate as triple superphosphate. Aboveground net primary productivity (ANPP) at each of the three sites responds differently to added nutrients. ANPP responds to N alone at Thurston, to P at Kauai and to N and P together, but not either individually, at Laupahoehoe (Vitousek et al. 1993; Herbert and Fownes 1995; Vitousek and Farrington 1997).

Field sampling and incubation design

The experiments presented in this paper involve laboratory experiments on soils taken from the three chronosequence sites including the field fertilization experiments at each site. These soils were then incubated in a laboratory setting and the fluxes of DOM and CO_2 were measured over time. The samples used in this experiment were collected from the O horizons from control, N, P and N+P plots at each site in late June, 1997. The characteristics of the O horizons are presented in Table 1 but briefly, we sampled from the upper 1–10 cm of the soil profile (below the surface litter layer) which was made up of well decomposed amorphous organic matter and abundant roots. Although these soils were from O horizons, there is significant mineral content present in each site (Table 1). For Thurston and Laupahoehoe, there were four replicates in each of the fertilization treatments, and for Kauai, there were three replicates. Immediately after collection, the soils were placed on ice in coolers and were shipped overnight to Stanford University. Upon receipt, we sieved field-moist soils through a 4 mm sieve and hand picked all root fragments from the samples. Samples were refrigerated for 2–6 days before beginning the experiment. To maintain water content in these soils at a common level, we estimated field capacity operationally as the amount of water the soils could hold against gravity and then added water to any samples below field capacity. We maintained the samples at field capacity through the experiment.

There were two main components to this experiment, respiration measurements and a leaching experiment, each of which was carried out on separate soil samples. For the respiration component, we added approximately 10 g of soil to plastic cups and then incubated the cups at field capacity inside mason jars at approximately 24 °C for 1 year. For the leaching component, we added approximately 10 g of soil to filtration units fitted with Whatman GF-F glass fiber filters overlaid with glass wool and also incubated at 24 °C. These soils were leached with deionized water at a 5:1 ratio of water to soil at 1, 3, 7, 14 days and then subsequently at 2 week, 1 month or 2 month intervals (with decreasing frequency through the incubation). To examine the fraction of DOM removed during each leaching, we carried out sequential leachings on several samples at various points during the incubation. On average, the first leaching removed 75 $\pm$ 10% of the total water-extractable (defined as sum of DOM removed over sequential leachings) DOM and this rate of removal did not appear to change through the incubation. Higher removal rates would have been possible with a salt based extractant, but would not be comparable to the normal leaching regime. The flux values presented represent the leachable DOC, DON, or DOP for these incubation conditions; they reflect a

combination of laboratory protocols and interacting processes of DOM production, consumption and stabilization.

In addition to incubating soils from the field fertilization experiments, we examined the short-term response of DOM fluxes to N and P additions by adding N and P to composited soils from the control plots at Thurston. In these experiments, we added 0.7 mg N or P g soil^{-1} as NH_4NO_3 or a 1:1 ratio of NaH_2PO_4 and Na_2HPO_4. The short term fertilization experiment was designed to examine the possibility of rapid alterations of DOM C:N or C:P stoichiometry in response to changes in nutrient availability. After fertilizer additions, the soils were incubated in the same manner and time periods as all the other soil samples.

Analytical techniques

We filtered all samples through Whatman GF-F filters immediately following collection and then either froze the samples or refrigerated them for analysis within a day or two of collection. We measured DOC with high temperature oxidation of DOC to CO_2 followed by detection with a infra-red gas analyzer (Shimadzu Instruments, USA). The minimum detection limit for DOC was approximately 1 mg DOC L^{-1}. We determined DON and DOP concentrations by difference between inorganic N and orthophosphate P concentrations before and after persulfate oxidations (Solorzano & Sharp 1980). For each pre-oxidation orthophosphate sample, we subtracted the absorption of color blanks to account for colorimetric interference. We refer to the pre-oxidation, reactive P as orthophosphate and the difference between total dissolved P and orthophosphate as DOP. There are a wide range of phosphate esters in natural solutions and some of the compounds represented in the orthophosphate class may have been organically bound (RFA Methodology, ALPKEM Corporation). The minimum detection limit for DON was 0.050 mg DON L^{-1} and for DOP was 0.070 mg DOP L^{-1}. We intended to follow DON concentrations through the course of the experiments, however the soils began to mineralize considerable amounts of inorganic N beginning by day 117 in all sites. Against these background concentrations ($>$ 20 mg DIN-N L^{-1}), measuring DON concentrations became impossible, particularly in the samples with the highest inorganic N concentrations. For DON, we present results to day 117 in the incubation, and for both DOP and DOC we show results through a full year of sampling. In order to compare the ratio of DOM C:P to the soil C:Po ratio (which we did not measure), we used data from T. Crews (unpublished) for bicarbonate and NaOH extractable soil P fractions from the O horizon of these sites. From this data we calculated a ratio of mineralizable soil C to available soil organic P. The bicarbonate and NaOH extractable soil P fractions represent the labile soil organic P pool on a 1–2 year time scale (Crews

et al. 1995). Mineralizable soil C was determined from cumulative CO_2 flux values.

We measured chloroform-labile C and N on sub-samples of all soils and treatments within 1 week of collection using the chloroform fumigation direct extraction (CFDE) technique (Beck et al. 1997; Brookes et al. 1985). Briefly, this technique involved extraction of nonfumigated soils with 0.5 M K_2SO_4 followed by fumigation of paired sub-samples with ethanol-free chloroform for 72 hours followed by K_2SO_4 extraction. The total C in nonfumigated and fumigated samples was determined by high temperature oxidation of soluble C to CO_2 followed by detection with a infra-red gas analyzer (Shimadzu Instruments, USA). Total N in nonfumigated and fumigated samples was determined with Kjeldahl digests followed by colorimetric determination of NH_4^+. We calculated chloroform labile C and N as the difference between N and C values for nonfumigated and fumigated soils. We present chloroform labile C and N data without conversion in this paper, however, the ratio between chloroform labile C and microbial biomass C is often estimated as 0.45 (Beck et al. 1997) while the ratio of chloroform labile N to microbial biomass N is estimated at 0.54 (Brookes et al. 1985). Soil carbon and nitrogen were determined with a Carlo Erba C:N Analyzer (Carlo Erba Instruments, Saddle Brook, New Jersey) and are presented as %C and %N per unit soil mass.

Statistical analyses

For comparisons of dissolved organic fluxes during the incubation experiment, we performed three-way analysis of variance (ANOVA) with site, N, and P as factors. For evaluation of differences in the total loss of DOC, DON and DOP, we carried out ANOVAs on the net incubation flux of DOC, DON and DOP. We evaluated results as the net flux of DOM from soils in this incubation because there were no indications that treatment effects on DOM varied through the incubations. For all the ANOVA analyses, we examined the data for normality and for heterogeneity of variance prior to analysis. In cases of departures from either condition, we log transformed the data prior to analysis and tested again for normality and heterogeneity of variance. For comparisons of relationships between variables, we performed regressions analyses with ANOVA on the residuals. Unless otherwise noted in the text, degrees of freedom (df), F and p values result from the 3 way ANOVA designs mentioned above. All our analyses were carried out using the Statistica software package (Statsoft Inc.)

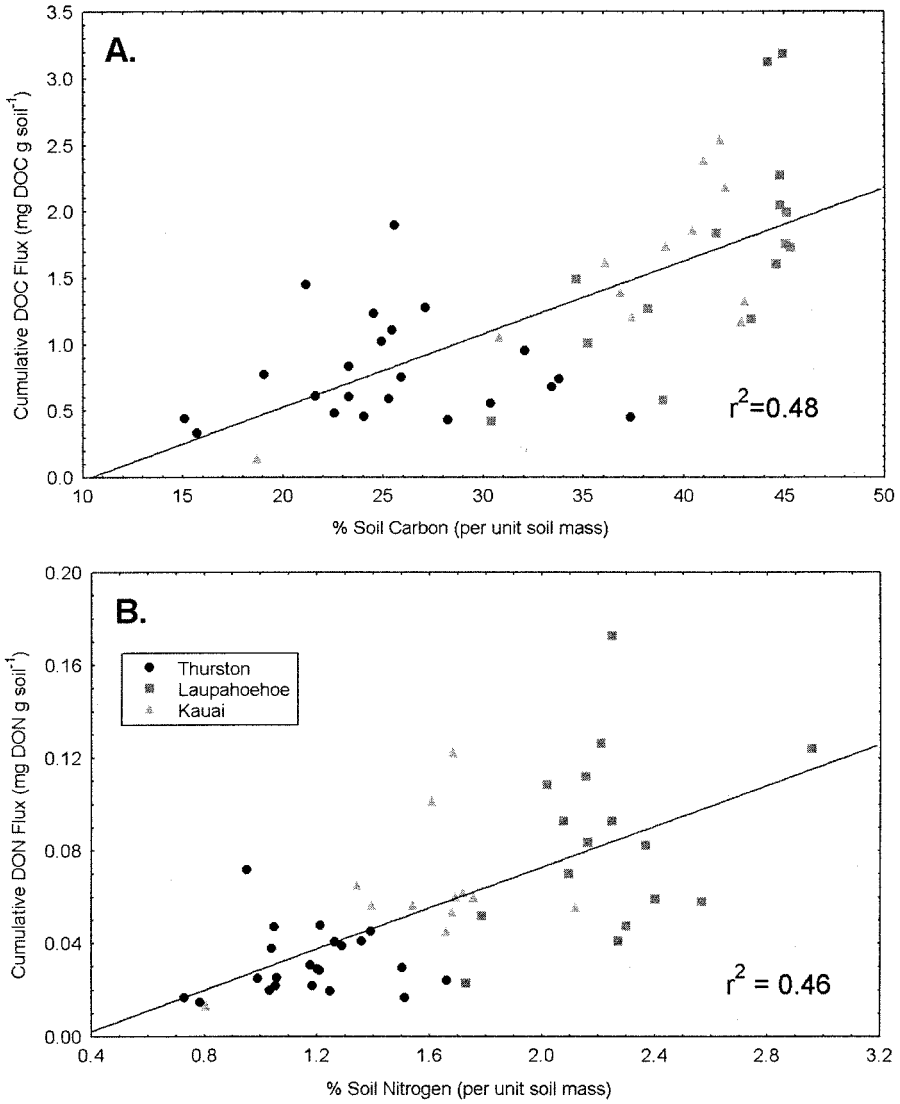

Figure 1. Relationships between cumulative DOC flux (1 year, Figure 1(A)) and cumulative DON flux (117 days, Figure 1(B)) and % soil carbon and % soil nitrogen.

Results

Biological and physical controls on DOC, DON and DOP leaching

DOC, DON and DOP fluxes were highest in the first month of the incubation experiment and then declined with time. CO_2 fluxes followed a similar pattern

with high initial rates of respiration and reduced rates later in the incubation. A steady state of release was not reached during the incubation and the patterns in net DOC, DON, DOP and CO_2 fluxes across sites and treatments were consistent through the incubation and showed no evidence of changing site or treatment effects with time. When all the chronosequence sites are considered together, total DOC and DON fluxes (summed to 365 days and 117 days, respectively) were strongly related to the %C and %N of the soil organic matter. There were strong regressions between DOC flux and % soil C ($r^2 = 0.48$, $F = 9.22$, $p = 0.001$) and DON loss and % soil N ($r^2 = 0.46$, $F = 42.2$, $p = 0.001$) (Figures 1(A) and 1(B)). Total DOC and DON fluxes were not related to rates of soil respiration or the chloroform extractable C pool which are indices of microbial turnover and pool size, respectively (Beck et al. 1997). Relationships between initial DOC and DON fluxes (summed to 7 days) vs microbial biomass C or N also were not significant.

The patterns of linkages between DOC loss, % SOM C and CO_2 flux vary across the three chronosequence sites. At Thurston, net DOC flux was not related to CO_2 flux or to SOM %C content (Figure 2). At Laupahoehoe, there was no relationship between net DOC flux and CO_2 flux but there was a significant regression between net DOC flux and % SOM C (Figure 2). For Kauai, there were positive relationships between net DOC flux and both cumulative CO_2 flux and % SOM C (Figure 2). Comparisons of DON leachate vs. cumulative CO_2 flux and % SOM N for the three sites, considered individually, were not significant. Likewise, DOP flux vs cumulative CO_2 flux at each of the three sites was not significant.

Nutrient and site controls on DOC, DON and DOP fluxes

Net DON and DOP fluxes were different across the chronosequence but DOC fluxes were not (Tables 2 and 3). There was lower DON leaching from Thurston soils vs Laupahoehoe (Tukey test, $p = 0.001$) and Kauai ($p = 0.001$) but not between Laupahoehoe and Kauai (Tukey, $p = 0.227$). Overall losses of DON ranged between a low of 2.32 mg DON g soil N^{-1} at Thurston to 5.61 mg DON g soil N^{-1} in the N fertilized sites at Laupahoehoe. We did not measure organic P content individually for these soils, so we present DOP leaching data per g soil. DOP leaching from Thurston soils averaged 6 mg DOP g $soil^{-1}$ whereas Laupahoehoe DOP losses were approximately 4 fold higher (Tukey $p = 0.003$). DOP fluxes at Kauai were extremely variable and ranged from 4 mg DOP g $soil^{-1}$ in the control plots to 64 mg DOP g $soil^{-1}$ in the NP fertilization plots.

Long-term field fertilization with N did not have a significant effect on DOC, DON or DOP flux. However, there was a significant site x N effect on DON flux, with a 50% increase in DON net flux in N fertilized plots

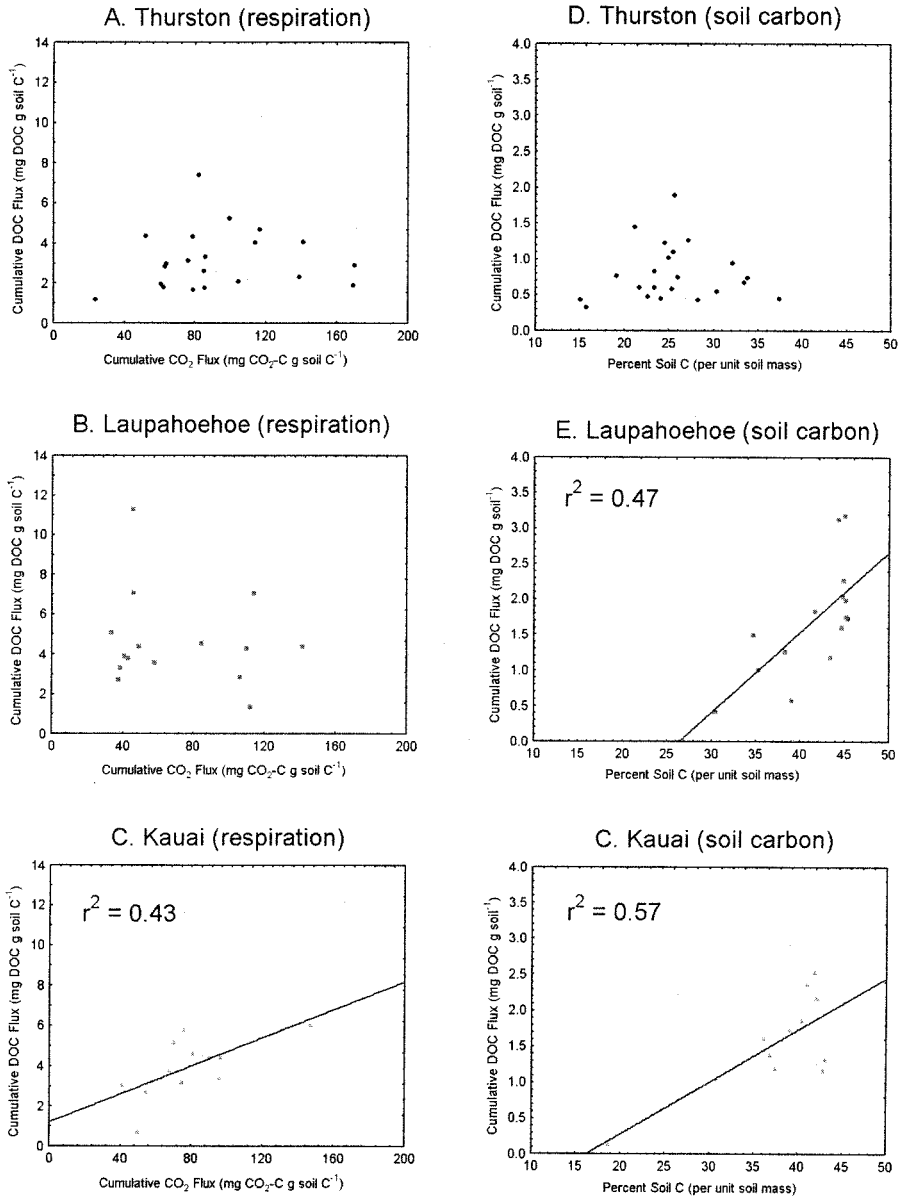

Figure 2. Site specific regressions between the flux of DOC and cumulative CO_2 flux or soil %C content (by mass). Significant regressions are shown with r^2 values in bold.

Table 2. Statistical results for site and fertilizer effects on the cumulative flux of DOC, DON and DOP at 355, 117, and 355 days respectively. The N, P, and site (and interaction term) rows below the long term field fertilization heading refer to field fertilized incubated soils while the N and P columns below the short term lab fertilization heading refer to incubations on laboratory fertilized soils. Significant effects and interaction terms ($p < 0.05$) are shown for the main effects of 3 way analysis of variance with site × nitrogen × phosphorus effects.

Effects	Degrees	DOC flux		DON flux		DOP flux		DOM C:N		DOM C:P	
	freedom	F Value	p-level	F Value	p-level	F Value	p-level	F Value	p-level	F Value	p-level
Long term (field) fertilization											
Site	32	1.67	0.20	**20.7**	**0.01**	**6.29**	**0.01**	**11.23**	**0.01**	**7.44**	**0.01**
N	32	0.09	0.76	3.55	0.07	1.78	0.19	2.29	0.13	0.28	0.59
P	32	**4.05**	**0.05**	**5.76**	**0.02**	**4.92**	**0.03**	0.31	0.58	**11.37**	**0.01**
Site × N	32	2.08	0.14	**3.61**	**0.04**	1.27	0.29	1.54	0.22	1.06	0.36
Site × P	32	0.97	0.38	1.67	0.20	1.93	0.16	3.15	0.06	0.86	0.42
N × P	32	0.03	0.86	0.34	0.56	0.40	0.53	**6.59**	**0.01**	0.02	0.89
Site × N × P	32	2.62	0.08	0.63	0.54	0.07	0.93	0.34	0.71	0.69	0.51
Short term lab fertilization											
N	7	0.18	0.68	0.78	0.40	0.01	0.92	0.32	0.58	1.41	0.27
P	7	0.78	0.40	0.14	0.91	2.89	0.12	**5.04**	**0.05**	3.12	0.12

Table 3. Cumulative flux of DOC, DON and at 355, 117, and 355 days respectively during the laboratory incubation. The SE column contains values for plus or minus one standard error. Statistical results for DOM fluxes are given in Table 2.

	mg DOC per gram C	mg DON per gram N	mg DOC per gram soil	mg DON per gram soil	ug DOP per gram soil
	Mean (SE)	Mean (SE)	Mean (SE)	Mean (SE)	Mean (SE)
Thurston					
Control	3.64 (1.56)	2.32 (0.60)	0.94 (0.33)	0.03 (0.01)	4.51 (0.24)
+N	3.96 (0.41)	3.49 (0.39)	1.01 (0.10)	0.04 (0.01)	4.42 (0.43)
+P	2.19 (0.29)	1.90 (0.17)	0.45 (0.05)	0.02 (0.01)	7.87 (2.48)
+N&P	3.12 (0.82)	2.86 (0.90)	0.77 (0.17)	0.04 (0.01)	7.46 (0.84)
Short term +N	3.74 (0.96)	3.15 (0.73)	0.85 (0.30)	0.04 (0.02)	6.67 (1.72)
Short term +P	2.57 (0.54)	2.49 (0.09)	0.82 (0.15)	0.03 (0.01)	4.97 (0.95)
Laupahoehoe					
Control	6.45 (2.12)	4.05 (0.70)	2.06 (0.61)	0.09 (0.02)	20.31 (5.42)
+N	4.81 (0.93)	5.61 (0.85)	2.07 (0.40)	0.13 (0.02)	22.71 (13.98)
+P	2.30 (0.61)	2.31 (0.63)	0.95 (0.27)	0.05 (0.01)	33.02 (28.26)
+N&P	4.28 (0.33)	3.08 (0.62)	1.81 (0.16)	0.07 (0.02)	22.12 (5.80)
Kauai					
Control	3.69 (0.47)	3.60 (0.30)	1.33 (0.21)	0.06 (0.01)	4.15 (2.08)
+N	3.66 (0.62)	3.69 (0.78)	1.39 (0.13)	0.06 (0.01)	14.44 (13.26)
+P	5.20 (0.43)	4.42 (1.16)	2.14 (0.15)	0.07 (0.01)	20.53 (17.92)
+N&P	3.30 (1.89)	3.87 (2.11)	1.33 (0.69)	0.06 (0.03)	63.89 (49.39)

at Thurston, and a 38% increase at Laupahoehoe, but no increase at Kauai. Fertilization with P increased DOP leaching and decreased both DOC and DON fluxes (Tables 2 and 3). At Thurston, P fertilization increased DOP leaching by 73% between no-P and P-addition plots and at Laupahoehoe and Kauai by 31% and 444%, respectively. There were no significant site $\times$ P effects on DOC, DON or DOP leaching. Short term lab fertilization with N or P at Thurston did not affect net DOC, DON or DOP flux rates (Tables 2 and 3).

Ratios of C and N in DOM were weakly related to those in SOM. DOM C:N ratios varied between 14 and 55 but were generally between 20 and 30 while DOM C:P ratios varied widely between 40 and 800 (Table 4). There was a significant relationship between SOM C:N ratio and DOM C:N ratio

Table 4. Ratios of DOM C:N (at 117 days) and DOM C:P (at 355 days) during the laboratory incubation experiment. Values in parentheses are standard errors. Statistical results for DOM C:N and C:P ratios are given in Table 2.

	DOM C:N	DOM C:P
	Mean (SE)	Mean (SE)
Thurston		
Control	44 (4)	1084 (42)
+N	26 (3)	460 (90)
+P	33 (4)	57 (16)
+N&P	29 (3)	108 (40)
Short term +N	32 (3)	305 (51)
Short term +P	27 (3)	193 (31)
Laupahoehoe		
Control	21 (3)	205 (80)
+N	17 (3)	179 (43)
+P	24 (4)	118 (82)
+N&P	26 (3)	109 (51)
Kauai		
Control	35 (5)	592 (112)
+N	29 (2)	398 (172)
+P	27 (3)	317 (123)
+N&P	32 (6)	274 (210)

(regression analysis, F = 7.54, p = 0.008) with a relatively weak r^2 of 0.13 (Figure 3). Average DOM C:N ratios were 32 at Thurston, 20 at Laupahoehoe and 30 at Kauai. There were no significant effects of long-term field N or P fertilization on DOM C:N ratios. Short term, lab based, N fertilization also did not affect DOM C:N ratios at Thurston (Tables 2 and 4).

DOM C:P ratios were strongly affected by both site and long-term field P fertilization. DOM C:P ratios differed significantly across sites (df = 38, F = 7.44, p = 0.001), driven by DOM C:P ratios at the P-poor site, Kauai, which were significantly higher than those at both Thurston and Laupahoehoe (Tukey, p = 0.004). Long term field P fertilization significantly reduced DOM C:P ratios (df = 38, F = 11.37, p = 0.001) with the most dramatic changes at Thurston and Kauai where DOM C:P ratios dropped by 83% and

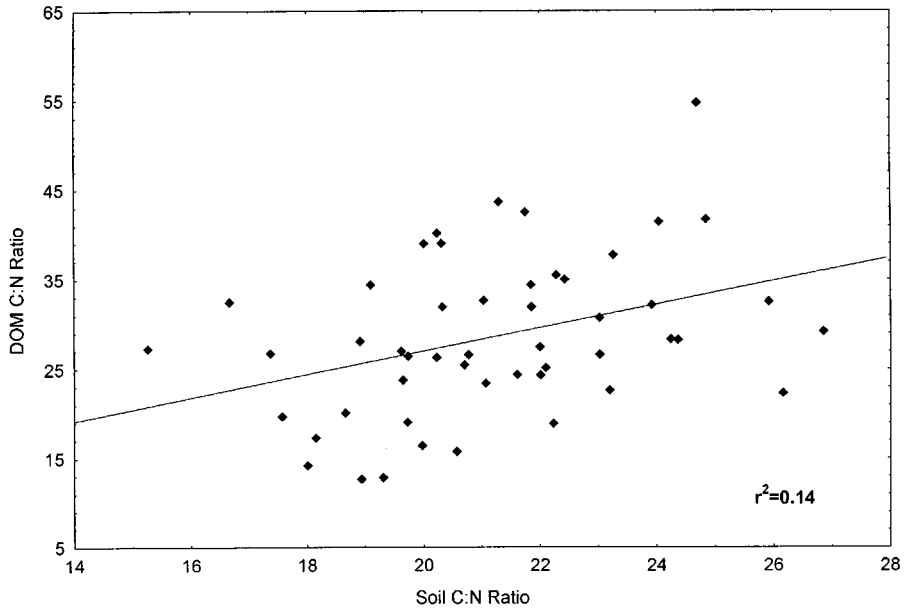

Figure 3. Relationship between soil organic matter C:N ratios and DOM C:N ratios.

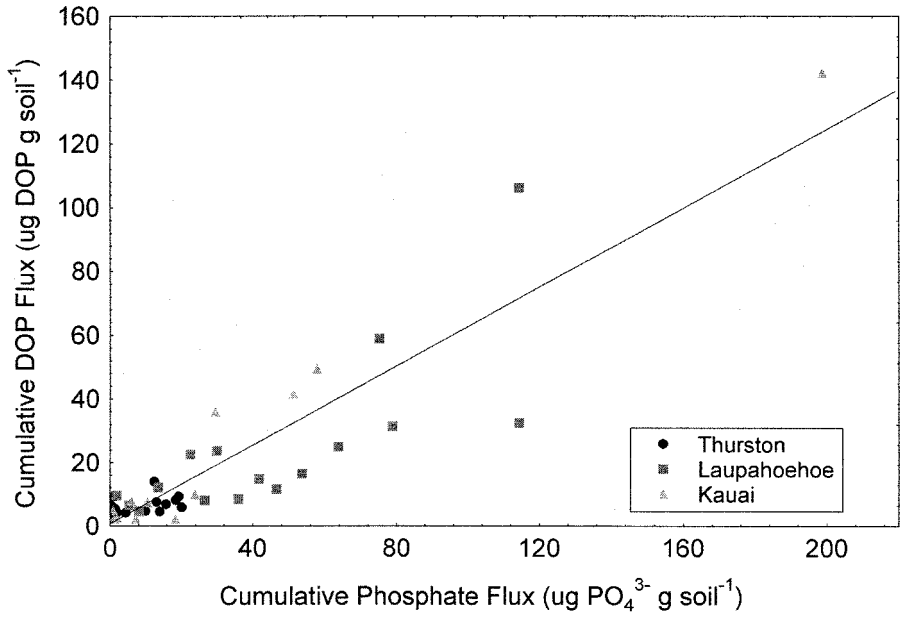

Figure 4. Relationship between cumulative DOP vs PO_4^{-3} Flux.

46%, respectively (Table 4). There were no significant effects of short-term N or P fertilization on DOC:DOP ratios. For the Thurston and Kauai, the DOM C:P ratios were six fold and two fold higher then mineralizable C: available P ratios, respectively. Laupahoehoe DOM C:P ratios were similar to the mineralizable C: available P ratio.

The flux of dissolved organic N and P from these soils was a substantial portion of the total dissolved N and P flux (data not shown) up to the day 117 sampling for N and to 1 year for P. The contribution of DON to total N flux ranged between 75 and 95% until the soils starting mineralizing substantial inorganic N around day 117. The contribution of DOP to total dissolved P ranged between 30 and 70%. There were no significant relationships between NH_4^+, NO_3^- or total inorganic N fluxes and organic N fluxes but there was a strong relationship between PO_4^{3-} loss and DOP loss (Figure 4, $F = 145.3$, $p = 0.001$).

Discussion

Biological and physical controls on DOC, DON and DOP leaching

The results of these experiments suggest that DOC and DON fluxes from the O horizon of these soils are not directly coupled to decomposition processes. The strong relationship between DOC and DON flux and soil C and N content indicates that DOC and DON fluxes from these soils are more closely linked to the overall pool of organic matter than to the rate of microbial turnover. This result contrasts a number of other studies which have shown links between DOC concentrations and CO_2fluxes from soils (Burford & Bremner 1975; Jandl & Sollins 1997; Brooks et al. 1999; Moore & Dalva, submitted). For field studies, the relationships between the litter layer, DOC and CO_2 fluxes are probably related to the inputs of DOC from litter layer (Jandl & Sollins 1997). The higher bioavailability of litter DOM relative to soil DOM may be one of the reasons why strong DOC-CO_2 flux relationships appear in these studies (Qualls & Haines 1992). In lab experiments of forest litter layers or highly organic soils, there are fewer physical controls over DOC release (i.e. no sorption reactions) and so if there are underlying links between CO_2 and DOC production then they should be observed in these studies (Moore and Dalva, submitted) however this is not always the case (Gödde et al. 1996). In soil horizons with substantial mineral content, sorption reactions are likely to play a role in net DOM fluxes and this pattern is clearly shown across the age gradient of sites in this study. Of the three Hawaiian soils, the highest overall mineral content in the three sites is at Thurston and the lack of a relationship between DOC flux and either SOM C or respiration

rate at this particular site may reflect strong mineral control over DOC release. There are numerous studies that show links between DOC sorption capacity and mineral content (Moore et al. 1992; Nelson et al. 1993; Kaiser et al. 1996; Kaiser & Zech 1998). At Thurston the lower % organic matter content relative to the other two sites, reflects the large fraction of mineral surfaces that have not yet become coated with organic materials. This combined with a relatively high noncrystalline mineral content may lead to sorption controls over the net DOC release from the O-horizon of the Thurston soils.

As the Hawaiian soils age, the regulation of DOC release changes. At Laupahoehoe, the relationship between DOC release and % soil C content is consistent with many studies of DOC sorption/desorption reactions that have noted the presence of a reactive soluble fraction of C in soils and relationships between this fraction and the organic carbon content of soils (Moore et al. 1992; Vance et al. 1992; Kaiser et al. 1996; Zsolnay & Steindl 1992). The high noncrystalline mineral content of Laupahoehoe leads to the stabilization of large amounts of carbon but also creates a SOM pool which may desorb/dissolve as water flushes through these organic rich surface horizons (Torn et al. 1997). This process is likely responsible for the DOC flux,% soil carbon relationships observed at the Laupahoehoe site.

At the oldest site on Kauai, where noncrystalline mineral content is lower and overall mineral content has declined relative to organic content in the O horizon, there are linkages between CO_2 flux, SOM C content and DOC flux. This result is more consistent with the variety of studies described above which link DOC fluxes to both SOM content and microbial activity. The most obvious explanation for the relationships between DOC flux and both SOM content and respiration fluxes are that both physical dissolution and microbial turnover contribute to the DOC flux from these soils. It is also possible that biological activity helps maintain a soluble carbon pool in these soils. The unique pattern for Kauai, relative to the other sites, is the appearance of a link between respiration and DOC flux. In this transition from young to old soils in the Hawaiian islands, there appears to be a corresponding transition from physical to biological control over DOC release. We suggest, based on this study and others (Torn et al. 1997; Chadwick et al. 1999), that this transition is mediated primarily through the reductions in soil mineral and allophane content that occurs as the volcanic substrates of the Hawaiian Islands age.

Nutrient and site controls on DOC, DON and DOP fluxes

The mechanisms that regulate N and P mineralization in soils differ from one another in fundamental ways which can impact the N and P content of both SOM and DOM. N mineralization generally occurs in conjunction with biological C mineralization, whereas P can be mineralized by both biological

and enzymatic (biochemical) means (McGill & Cole 1981). The difference in these enzymatic decomposition pathways may lead to a close relationship between microbial demand for P and P mineralization rates although there is also evidence that coupled P and C mineralization is important (Gressel et al. 1986). These relationships are also likely affected by alteration in geochemical stabilization rates as soils age and PO_4^{3-} sorption/precipitation reactions become stronger (McGill & Cole 1981).

In these Hawaiian soils, the activity of phosphatase enzymes varies across sites and treatments, reflecting the overall availability of P (Olander & Vitousek, in press). Phosphatase activity is high at all three of these sites, and fertilization with P decreases phosphatase activity in the O horizons. The patterns for net DOP fluxes vary with fertilization and parallel changes in phosphatase activity. Of the three sites in this experiment, Kauai is the most P-poor with substantial amounts of occluded, biologically unavailable P (Crews et al. 1995; Herbert & Fownes 1995). At Kauai, DOM C:P ratios were the highest of the three sites, and long-term field-fertilization with P caused a nearly 5 fold increase in DOP fluxes. DOP fluxes were relatively low at Thurston, the other site with low P availability. In contrast, at Laupahoehoe, which is characterized by high P availability, DOP fluxes were 4-fold higher than that the other two sites and DOM C:P ratios were more narrow (Crews et al. 1995). Comparisons of DOM C:P ratios and the ratio of mineralizable C to extractable P across sites indicates that the P content of DOM (and of OM in general) varies widely. At the most P-poor sites, DOM is either produced with low P content or P is selectively removed from DOM after its production. Selective removal of P from DOM under low P availability conditions is consistent with both the mechanics of phosphatase enzyme activity in soils and with the dynamics of enzyme activity across these sites (Olander & Vitousek, in press; McGill & Cole 1981).

In contrast to DOP leaching, DOC and DON fluxes in this experiment were relatively insensitive to changes in nutrient availability resulting from site differences, field fertilization or short-term lab fertilization. The only DON flux response to fertilization was at Thurston which is the most N limited of the three sites. The increase in DON fluxes in response to long-term field N fertilization at Thurston is similar to results presented by Currie et al. (1996), in which DON fluxes from surface soils in plots at Harvard Forest increased by about 2 fold in response to long-term N fertilization. For this study, the correspondence between SOM C:N ratios and DOM C:N ratios, and lack of a relationship between inorganic and organic N fluxes suggest that DON fluxes are related to the N content of the site via the SOM N pool. This information, combined with the lack of a relationship between inorganic N fluxes and DON fluxes suggest that DON fluxes are not closely regulated

by microbial demand for N in soil but are rather linked to overall abundance of C and N in SOM.

Implications for DOM loss patterns

DON makes up a substantial fraction of dissolved N lost from ecosystems with low N availability, and this form of N loss may contribute to the persistence of N limitation in these ecosystems (Sollins & McCorrison 1981; Hedin et al. 1995; Vitousek et al. 1998). The results of this study suggest that for DON (and for DOC), overall losses are closely linked to the standing pool of SOM with apparent links between microbial activity and DOC/DON flux only when the capacity of soil minerals to stabilize soluble carbon is low. Changes in N availability may influence DON fluxes but through the SOM N pool rather than through short term microbial dynamics. In contrast, for DOP, P availability and DOP flux are closely linked, and consistent with theoretical predictions of controls over P mineralization in soils (McGill & Cole 1981).

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