

Ecosystem Processes

Dissolved Organic Carbon In Northern Hardwood Stands With Differing Acidic Inputs and Temperature Regimes

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ABSTRACT

We monitored concentrations and fluxes of dissolved organic carbon (DOC) in throughfall and forest floor solutions in two northern hardwood stands located at the northern and southern end of a latitudinal acidic deposition and air temperature gradient in the Great Lakes Region to determine if DOC levels are altered by regional and temporal variation in acidic inputs and temperature. Amounts of precipitation received at the two sites were similar, but precipitation pH and air temperature, respectively, averaged 4.83 and 13.9°C at the northern gradient site and 4.29 and 15.1°C at the southern gradient site. Volume weighted DOC concentrations in throughfall were significantly greater at the northern (20.5 mg L⁻¹) than the southern (15.9 mg L⁻¹) site, but these differences in DOC levels were caused by the differing amounts of throughfall passing through the canopy of the two sites rather than levels of precipitation acidity or air temperature. Temporal variation in the levels of DOC in throughfall was not related to the variation in either precipitation acidity or air temperature. Like throughfall, levels of DOC in forest floor solutions were not found to be altered by acidic inputs. However, DOC in these solutions increased with seasonal increases in soil temperature. A regression equation relating seasonal variation in soil temperature and forest floor concentrations of DOC estimated that an observed 2.1°C difference in soil temperature at the two sites during the growing season could represent as much as 3.7 mg L⁻¹ difference in forest floor solution concentrations of DOC.

THE TRANSPORT of dissolved organic carbon (DOC) in throughfall and forest floor solutions is an important mechanism for the cycling of C, N, and P from the aboveground biomass to the mineral soil in temperate deciduous forest ecosystems. For example, Qualls et al. (1991) estimated annual outputs of dissolved organic C, N, and P from the forest floor to be, respectively, 18, 28, and 14% of the flux of these elements in litter fall from a central hardwoods forest. They calculated that throughfall input of these constituents represented between one-third and one-half of the output fluxes from the forest floor. Not only is DOC important in element cycling, but a large portion of DOC is composed of organic acids ranging from simple to complex humic and fulvic acid, which are important in mediating cation leaching, metal dissolution, mineral weathering, and absorption-desorption of acidic anions (Cronan and Aiken, 1985; Pohlman and McColl, 1988; Vance and David,

1992). Although DOC and related dissolved organic molecules play an important role in a number of ecosystem processes, knowledge concerning the relative importance of the factors affecting the levels of DOC in throughfall and forest floor solutions is limited. Due to this lack of knowledge, it is difficult to evaluate the consequences of differing management or environmental scenarios on forest ecosystem DOC fluxes.

Laboratory studies have indicated that levels of DOC in O horizons or surface soil solutions decrease with increased acidic inputs (Hay et al., 1985; Vance and David, 1989; David et al., 1989). If DOC leaching from forest floor or surface soils is indeed altered by changes in precipitation acidity, then forest stands that experience increased loadings of acidic ions may also show alterations in the transfer of C from aboveground to belowground components. The degree to which results from laboratory tests can be extrapolated to explain alterations in ecosystem processes involving DOC by acidic deposition is not known.

The amount of DOC in soil or forest floor leachates has frequently been related to levels of decomposition, microbial activity, and micro/macro floral activity. Seasonal fluctuations generally show increased levels of DOC with increased temperature and biological activity (Cronan and Aiken, 1985; Dalva and Moore, 1991). If temperature is an important factor controlling the seasonal variation of DOC fluxes from surface soil horizons, it seems likely that DOC fluxes from these soil components would not only vary over temporal scales, but also spatially with differing temperature regimes. However, there have been few comparisons of DOC in soil leachate from similar ecosystems having differing temperature regimes to support this idea.

Most of the research concerning DOC in terrestrial ecosystems has focused on solutions within the soil. Factors such as precipitation pH and temperatures that appear to influence levels of DOC in soil solutions may also determine the levels of DOC in throughfall (Scherbatskoy and Klein, 1983; Dalva and Moore, 1991). Although the DOC in throughfall and soil solutions appear to be intimately linked, it is not known if similar processes are responsible for the production of DOC in these two solutions.

We measured the levels of DOC in throughfall and forest floor leachate during one growing season at two sites at each end of a latitudinal acidic deposition and climate gradient. Our objectives were to determine: (i) if and to what degree levels and fluxes of DOC in

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throughfall and forest floor solutions are related to precipitation acidity at the two sites; (ii) if and to what extent differences in temperature are related to temporal and spatial variation in DOC levels in throughfall and forest floor solutions at these sites; and (iii) if processes that determine the levels of DOC in forest floor solutions and throughfall are linked.

METHODS

Study Sites

Initially four sites were selected along a pollution and air temperature gradient, which traverses the latitudinal range of the northern hardwoods cover type in the Great Lakes Region for inclusion in the study. However, due to canopy defoliation at two sites, only the sites located at the northern (Alberta) and southern (Oceana) ends of the gradient were utilized for this study. The sites were established in northern hardwood stands with similar overstory composition and structure, stand age, soils, and stand history (Burton et al., 1991; MacDonald et al., 1991) but differing in temperature regime and acidic deposition (Table 1). Soils at the sites developed on morainal landforms and are moderately well to well drained. Soils at the Alberta site were classified as a sandy, mixed, frigid Alfic Haplorthod and at the Oceana site as a sandy, mixed, mesic Entic Haplorthod (MacDonald et al., 1991).

Sample Collection and Analysis

At each site, three 30 m by 30 m plots were established, each with a surrounding 10-m buffer zone. Five throughfall collectors and four zero-tension lysimeters were used for water collections within each plot at each site. As a result of the amount of time and distance between sites, samples were only collected from July after complete leaf expansion until October 1992 before leaf fall. The throughfall collectors were 4-L polyethylene bottles set on the ground and fitted with 16-cm diam. polyethylene funnels. The funnels were covered with a 3-mm mesh polyethylene screen to eliminate large organic debris.

Each zero-tension lysimeter consisted of two 13-cm buckner funnels filled with acid-washed sand placed in the ground and attached by tubing to a 4-L bottle. A 15-cm diam. disk of intact forest floor (O_i , O_e , and O_a horizons) was removed

from each funnel location and each funnel was placed in an excavation so that the top of the funnel was parallel with the mineral soil-forest floor interface. The 4-L bottle was placed in another excavation 1 m from the funnels at a depth that would allow all leachate to drain freely from the funnels. After installation, the 15-cm disks of forest floor were replaced on top of the buckner funnels. Lysimeters were installed at each plot in the fall of 1989 and allowed to equilibrate for 2 yr. Field samples were collected and their volumes recorded weekly during the growing season when adequate water was present.

Incident precipitation was collected weekly at stations within 10 km of each research site. At each station, Aerochem Metrics wet/dry collectors and Belfort recording rain gauges were installed and operated according to NADP protocols. Throughfall and forest floor solutions were collected within 24 h of the precipitation collection. All throughfall and lysimeter samples from a sampling period were individually composited within each plot before any chemical analysis. Due to the high water holding capacity of the forest floor or poor collection efficiency of the lysimeters, fewer forest floor solution than throughfall samples were collected.

The pH and conductivity of the samples were analyzed within 72 h of collection. Samples were then passed through a 0.45- μ m polysulphone filter and stored at 2 to 3°C in dark bottles until further chemical analysis. The DOC concentrations in throughfall and forest floor solution were determined using a Dohrmann 180 total carbon analyzer. All analyses included aqueous quality control samples and a 10% laboratory replication. Analytical accuracy was determined by measuring concentrations of a potassium hydrogen phthalate stock solution diluted to 31.5 mg L⁻¹. Average measured DOC concentration for these samples was 31.1 \pm 0.85 mg L⁻¹ at α = 0.05 while repeated measurement error for the analytical replicates was \pm 12.9% at α = 0.05.

The DOC concentrations in precipitation were not measured because concentrations have been found to average \leq 1.5 mg L⁻¹ in a wide range of temperate forest ecosystems (Hoffman et al., 1980a; McDowell and Likens, 1988; Moore, 1989; Qualls et al., 1991). For this study we assumed that DOC concentrations in precipitation were similar at the two sites and differences in throughfall concentrations at the two sites were related to differences in canopy exchange.

Air and soil temperature were monitored using an automated electronic data collection system. One shielded thermistor temperature probe was located 2 m aboveground and one sealed thermistor probe was buried at a depth of 15 cm in the center of each 30 m by 30 m plot. Temperatures were measured every 30 min and averages recorded every 3 h by this system. Temperatures were averaged later to give an average daily temperature for the entire study period, or for each collection interval for each site.

Statistical Analysis

Weekly measurements were summarized over the study period for each site or, where appropriate, each plot. Throughfall and forest floor fluxes were reported as the average of the totals of the three plots from a site while concentrations were reported as the average of the volume weighted concentrations of the same plots over the entire study period. An ANOVA with plots nested within sites was used to compare total fluxes and volume weighted concentrations of throughfall or forest floor water between sites. Pearson's correlation coefficients (n = 6) were used to determine and quantify any linear relationships among fluxes and concentrations in precipitation, throughfall, and/or forest floor water.

Table 1. Attributes of two study sites at two extremes of a latitudinal acidic deposition gradient in the Great Lakes Region.

Attribute	Alberta	Oceana
Latitude (N)	46°52'	43°40'
Longitude (W)	88°53'	86°09'
Elevation (m)	380	262
Mean annual precipitation (mm)†	870	850
Mean annual temperature (°C)†	4.2	7.6
Air temperature June–October 1992 (°C)	11.8	13.8
Soil temperature (15 cm) June–October 1992 (°C)	10.9	13.0
Forest floor (Mg ha ⁻¹)‡	34.3	36.7
Foliar litter fall (kg ha ⁻¹ yr ⁻¹)§	3242	4053
Basal area (m ² ha ⁻¹)¶		
Total	32.4	32.0
Sugar maple (<i>Acer sacharrum</i> Marsh.)	27.9	23.5
Red maple (<i>Acer rubrum</i> L.)	1.5	4.6
Yellow birch (<i>Betula alleghaniensis</i> Britt.)	2.3	0.0
Black cherry (<i>Prunus serotina</i> Ehrh.)	0.0	2.4
Aboveground biomass (Mg ha ⁻¹)¶	277	259
Overstory age (yr)¶	79	78

† 30-yr mean, National Oceanic and Atmospheric Administration, 1983.

‡ 1988 (MacDonald et al., 1991).

§ 1988–1991.

¶ As of fall 1992.

The temporal variation in DOC fluxes and concentrations was also investigated in the study. We felt that quantification of the temporal as well as spatial variation in DOC produced a more powerful evaluation of the objectives than the assessment of spatial variation alone. Each individual weekly measurement of flux, concentration, or amount at each plot was used in this portion of the analysis. Pearson's correlation coefficients were again used to evaluate linear relationships among response variables. The number of observations differed with water type being $n = 57$ for throughfall and $n = 45$ for forest floor water analysis. When precipitation fluxes were considered correlation coefficients were calculated using site averages for each weekly sampling interval ($n = 19$ for throughfall and $n = 15$ for forest floor water). All tests were evaluated at $\alpha = 0.05$.

RESULTS

Throughfall

Although the two sites received similar amounts of precipitation, fluxes of H^+ were 3.2 and volume weighted concentrations 3.5 times greater at the Oceana site than the Alberta site (Table 2). As a result of canopy buffering, volume weighted concentrations of H^+ were lower in throughfall than precipitation (Lovett et al., 1985; Foster and Nicholson, 1988; Shepard et al., 1989) and did not significantly differ between the two sites (Table 2). Like H^+ , concentrations of DOC were significantly greater at the Oceana site (8.08 mg L^{-1}) than the Alberta site (5.88 mg L^{-1}). Although DOC concentrations differed among sites, there was no significant difference in fluxes of DOC at the two sites due to the significantly lower amounts of throughfall collected in the Oceana site compared with the Alberta site. Both leaf area index (LAI) and air temperature were slightly greater at the Oceana site than at the Alberta site, but only air temperature differed significantly between sites (Table 2).

Plot volume weighted concentrations ($n = 6$) of DOC in throughfall were significantly correlated with throughfall amounts ($r = -0.951$, $P = 0.004$), precipitation amounts ($r = -0.833$, $P = 0.040$), precipitation H^+ concentrations ($r = 0.833$, $P = 0.040$), and net throughfall fluxes of H^+ ($r = -0.853$, $P = 0.031$) measured at each of the six plots. However, DOC concentrations were not related to plot measurements of LAI ($r = 0.427$, $P = 0.398$) or air temperature ($r = 0.615$, $P = 0.193$). Total throughfall fluxes of DOC measured in the six plots were not significantly correlated with any measured precipitation, throughfall, or stand variable.

Individual weekly plot concentrations and fluxes of DOC in throughfall ($n = 57$) were more strongly correlated with amounts of precipitation and throughfall collected than the acidity of either solution or the amounts of precipitation H^+ buffered by the canopy. Concentrations of DOC in throughfall were negatively correlated with amounts of throughfall ($r = -0.729$, $P < 0.001$) and precipitation ($r = -0.638$, $P = 0.003$) collected but were not significantly correlated with the amounts or concentrations of H^+ in throughfall or precipitation and only weakly correlated with the net change in H^+ concentrations of throughfall and precipitation ($r = -0.329$, $P = 0.012$). Fluxes of DOC in throughfall

Table 2. Comparison of mean fluxes and volume weighted concentrations for DOC and H^+ , water amounts, leaf area index, air temperature, and net throughfall flux of H^+ at two sites during the 1992 growing season when volumes of throughfall were adequate for DOC analysis. Values within parentheses are standard deviations.

Parameter	Alberta	Oceana	<i>P</i> value†
Precipitation			
Amount (cm)	21.8†	20.2	
pH	4.83	4.29	
H^+ ($\mu\text{g L}^{-1}$)	11.1	39.2	
H^+ (mg m^{-2})	2.4	7.9	
Throughfall			
Amount (cm)	20.5 (0.92)	15.9 (1.48)	0.010
pH	5.25	5.14	
H^+ ($\mu\text{g L}^{-1}$)	7.2 (1.2)	6.1 (0.5)	0.226
DOC (mg L^{-1})	5.88 (0.61)	8.08 (0.11)	0.040
H^+ (mg m^{-2})	1.5 (0.3)	1.0 (0.1)	0.046
DOC (g m^{-1})	1.21 (0.11)	1.27 (0.08)	0.429
Net throughfall H^+ (mg m^{-2})	-0.9	-6.9	<0.001
Number of weeks (<i>n</i>)	(10)	(9)	
Stand			
Leaf area index‡	7.48 (1.02)	8.61 (0.58)	0.172
Air temperature ($^{\circ}\text{C}$)	13.9 (0.33)	15.1 (0.20)	0.008

† Probability level (*P* value) determined by ANOVA using plot averages.

‡ A.J. Burton, 1992, personal communication.

were not significantly correlated with precipitation or throughfall acidity.

The decreased concentrations of DOC with increasing throughfall or precipitation are consistent with the reduction in the available pool of leachable ions in foliage with increased duration, amounts, or frequency of precipitation events (Scherbatskoy and Klein, 1983; Schaefer et al., 1988; Potter, 1991). Given the differences in the amount of throughfall collected at the sites and the limitations this imposed on comparisons of throughfall DOC between sites, we fitted an exponential equation to the weekly throughfall DOC concentrations and amounts measured at each plot to account for the effects of water amounts on DOC concentrations ($12.15e^{-0.21 \text{ cm}}$, $r^2 = 0.644$, $\text{SE} = 0.247 \text{ mg L}^{-1}$). Neither coefficients nor intercepts significantly differed between the two sites. The residuals (observed - predicted) were then compared with precipitation, throughfall, and stand level attributes to determine the factors other than water flux affecting DOC concentrations.

The residuals from this equation were not significantly correlated with precipitation H^+ concentration, throughfall H^+ concentration, net flux of H^+ , or air temperature but were significantly correlated with the net throughfall fluxes of H^+ expressed as a proportion of precipitation H^+ fluxes ($r = -0.392$, $P = 0.002$). Residuals (observed - predicted concentrations) increased with an increase in the proportion of the H^+ retained by the canopy (Fig. 1). If sites are considered individually, residuals were found to be significantly correlated with net throughfall fluxes of H^+ expressed as a proportion of precipitation fluxes for both the Alberta site ($r = -0.440$, $P = 0.015$) and Oceana site ($r = -0.434$, $P = 0.023$). Comparisons of the throughfall DOC concentration residuals with net flux of H^+ (Fig. 1) indicates that residuals were generally positive during collection periods when more than half of precipitation fluxes of H^+ were buffered by the canopy

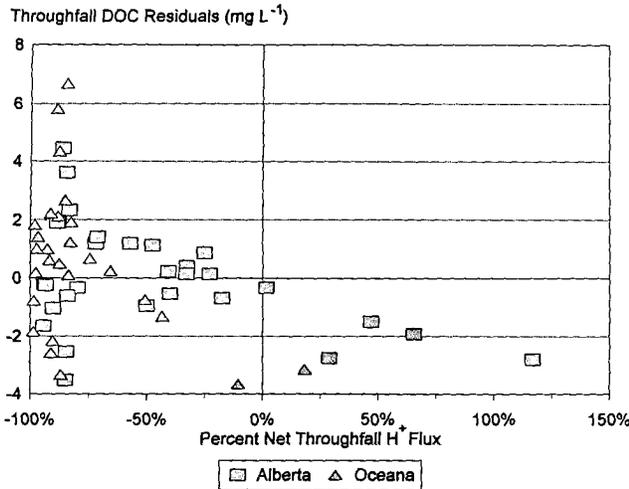


Fig. 1. Predicted throughfall DOC residuals (observed - predicted) calculated from an exponential equation in relation to net flux of H⁺ in throughfall expressed as a proportion of precipitation fluxes of H⁺.

except when amounts of throughfall collected were small (<0.40 cm).

Forest Floor Solutions

Collection efficiency of the lysimeters was low at both sites. Although the quantity of throughfall collected was significantly greater at the Alberta site, amounts of forest floor leachate collected did not significantly differ between the two sites (Table 3). Furthermore, while levels of H⁺ were significantly higher and concentrations of DOC were lower in throughfall at the Alberta site, outputs and concentrations of H⁺ and DOC in forest floor water did not significantly differ between sites (Table 3). Total

Table 3. Comparison of mean fluxes and volume weighted concentrations for DOC and H⁺, water amounts, soil temperature, and net throughfall flux of H⁺ at two sites during the 1992 growing season when volumes of forest floor water were adequate for DOC analysis before leaf senescence. Values within parentheses are standard deviations.

Parameter	Alberta	Oceana	P value†
Throughfall			
Amount (cm)	19.3 (1.19)	15.5 (1.41)	0.020
pH	5.15	5.24	
H ⁺ (µg L ⁻¹)	7.1 (1.1)	5.7 (0.4)	0.112
DOC (mg L ⁻¹)	5.53 (0.63)	7.90 (1.10)	0.032
H ⁺ (mg m ⁻²)	1.4 (0.3)	0.9 (0.1)	0.042
DOC (g m ⁻²)	1.06 (0.11)	1.22 (0.08)	0.118
Forest floor water			
Amount (cm)	4.1 (1.97)	7.6 (2.18)	0.105
pH	5.67	5.95	
H ⁺ (µg L ⁻¹)	2.1 (1.5)	1.1 (0.1)	0.302
DOC (mg L ⁻¹)	26.2 (2.47)	28.0 (1.89)	0.366
H ⁺ (mg m ⁻²)	0.10 (0.09)	0.08 (0.02)	0.737
DOC (g m ⁻²)	1.03 (0.45)	2.13 (0.63)	0.070
Net flux water (cm)	-15.2 (2.88)	-7.9 (1.70)	0.007
Net flux H ⁺ (mg m ⁻²)	-1.3 (0.3)	-0.8 (0.1)	0.074
Net flux DOC (g m ⁻²)	-0.03 (0.55)	0.91 (0.71)	0.140
Number of weeks (n)	(7)	(8)	
Stand			
Air temperature (°C)	13.2 (0.35)	14.8 (0.19)	0.002
Soil temperature (°C)	11.9 (0.16)	14.2 (0.34)	<0.001

† Probability levels (P values) determined by ANOVA using average plot values.

plot fluxes of DOC in forest floor solutions were significantly correlated with average soil temperatures ($r = 0.844$, $P = 0.035$) during the study period. However, neither volume weighted concentrations nor fluxes of DOC measured within the six plots were significantly ($P \leq 0.05$) correlated with any other stand or plot level variable.

Weekly concentrations of DOC in the solutions leaching through the forest floor were not significantly correlated with the amounts of forest floor solution, throughfall, or precipitation collected weekly, and therefore no effort was made to account for variation in concentrations related to weekly leachate amount. The DOC concentrations in forest floor leachate were significantly correlated with concentrations of DOC in throughfall ($r = 0.328$, $P = 0.028$), throughfall pH ($r = 0.309$, $P = 0.039$), average weekly air temperature ($r = 0.464$, $P = 0.001$), and average weekly soil temperature ($r = 0.481$, $P = 0.001$), but not forest floor solution pH ($r = -0.197$, $P = 0.195$). Net fluxes of DOC and net changes of DOC concentrations in forest floor solutions were positively correlated with air and soil temperature ($0.388 \leq r \leq 0.520$, $0.001 \leq P \leq 0.008$) and net changes in DOC were negatively correlated with forest floor solution pH ($r = -0.309$, $P = 0.023$), but neither net change nor flux of DOC in these solutions were significantly correlated with throughfall chemistry. Comparisons of soil temperature with concentrations, net fluxes, and net changes in concentrations of DOC in forest floor leachates generally show a stronger relationship between these variables at the Oceana site compared with the Alberta site (ex. Fig. 2 a-c). Ranges in soil temperature were also greater at the Oceana site (10.4-16.0°C) than at the Alberta site (9.8-13.0°C). When each site was considered individually, soil temperature was significantly correlated with concentrations, net fluxes, and net changes in concentrations of DOC in forest floor leachates at the Oceana site but not the Alberta site.

The lack of any significant correlation of temperature and DOC appears to be caused by the atypical low temperature, high throughfall amounts, and low DOC throughfall concentrations during the earliest July sample collection at Alberta. Except for this collection interval, net fluxes of DOC and net changes in DOC in leachate at the Alberta site like the Oceana site increased with increases in temperature (Fig. 2 a-c). If the Alberta observations from this week are omitted, DOC concentrations in the leachates were weakly correlated ($r = 0.455$, $P = 0.058$) and net changes in DOC concentrations were strongly correlated ($r = 0.570$, $P = 0.014$) with soil temperature at the Alberta site.

To better quantify relationships between DOC concentrations in forest floor solutions and soil temperature, hyperbolic, exponential, and linear regression equations were fitted to forest floor DOC concentration and soil temperature measurements. The linear equation had the best fit with an $r^2 = 0.231$ and a standard error of 6.11 mg L⁻¹. The soil temperature slope coefficient was 1.79, whereas the intercept was 3.43. This equation was used to estimated the potential differences in forest floor solution

DOC concentrations at the two sites related to temperature by solving the equation using the average soil temperatures from June to October 1992 from each site (Table 1). The equation indicated that DOC concentrations in

forest floor water of 26.7 mg L^{-1} at a soil temperature of 10.9°C (Oceana) and 23.0 mg L^{-1} given an average soil temperature of 13.0°C (Alberta).

DISCUSSION

The increases in DOC concentrations in throughfall corresponding to reductions of free H^+ in solutions passing through the canopy at both Oceana and Alberta sites is consistent with increased levels of weak organic acids resulting from strong acid protonation of organic anions directly leached from the apoplasm or exuded as weak bases from foliage (Hoffman et al., 1980b; Richter et al., 1983; Cronan and Reiners, 1983; Lovett et al., 1985). The strong correlation in residual DOC concentrations and reductions of free H^+ in the throughfall also indicates enrichment of DOC with buffering of strong acidity. However, the protonation of organic anions no doubt accounts for a minimal amount of acidic buffering. Assuming that all the DOC in throughfall is associated with protonation of organic anions, the equivalent weight/gram C of organic anions is $12.0 \text{ meq g}^{-1} \text{ C}$ or less, and the pK_a of the organic anions is 4.0; the maximum amount of H^+ buffered by organic anion protonation would be $<25\%$ of the total H^+ neutralized by the canopy.

At these same sites Liechty et al. (1993) has shown that as precipitation acidity increases, a greater proportion of the free H^+ in precipitation is buffered by the canopy. Since canopy buffering increases with decreased precipitation pH and throughfall DOC concentrations are positively correlated with canopy buffering, it would first appear that the higher throughfall DOC concentrations at the Oceana site are related to the higher acidity of the precipitation at this site. However this is unlikely because the DOC concentrations in throughfall are inversely related to solution amounts and residuals associated with predicted throughfall DOC concentrations are poorly correlated with precipitation pH. Protonation of organic anions appears to buffer a small amount of acidity because there is a limited supply of organic ions for protonation, greater pools of exchangeable cations than organic anions, and/or a greater rate of base cation exchange than organic anion protonation. Thus concentrations of DOC in throughfall were not appreciably altered by the precipitation acidity at the Oceana site.

There was no indication that the variation in the canopy exchange of organic C was related to temperature. Frequently the seasonal variation in throughfall concentrations of DOC have been attributed to changes in air temperature (Dalva and Moore, 1991; Guggenberger and Zech, 1994). Guggenberger and Zech (1994) suggest that the primary source of carbohydrates in throughfall collected from coniferous stands is from microbial activity. Our study does not support the idea that C in the throughfall of these deciduous stands is principally derived from microbial activity, because neither DOC levels nor the residuals from the exponential equation were significantly correlated with air temperature. Within the range of temperatures observed during the study, foliar leaching of DOC was found to be a relatively passive

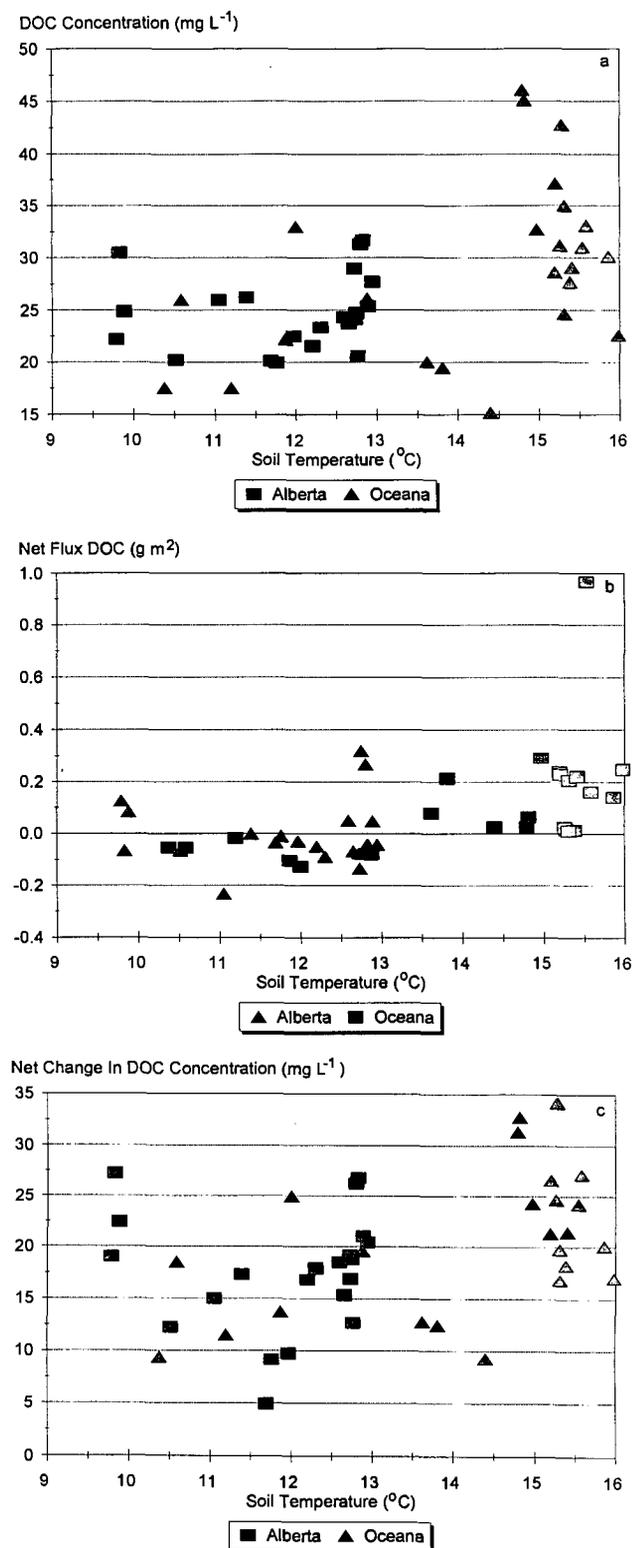


Fig. 2. Relationship of soil temperature at a depth of 15 cm to (a) DOC concentrations in forest floor water, (b) net forest floor water fluxes of DOC, and (c) net changes of DOC concentrations in forest floor water (forest floor water DOC - throughfall DOC).

process that is primarily determined by the amounts of water processed through the canopy.

Differences in the forest floor solution amounts and DOC concentration at the two sites does not appear to be a result of any inherent differences in the amounts of forest floor at the two sites. MacDonald et al. (1991) reported no significant differences in the total amounts of the O_i, O_e, and O_a horizons at these same two sites (Table 1). The differences in the proportion of throughfall passing through the forest floor and collected by the lysimeters at the sites reflect variation in precipitation intensity, differences in temporal distribution of precipitation events, the spatial variation in microrelief or forest floor amounts at the two sites, and/or differences in collector efficiency.

Neither plot average nor individual weekly DOC fluxes or concentrations in forest floor leachate were found to be related to throughfall acidity. A number of laboratory studies have demonstrated decreased levels of DOC in O horizon leachates with increased acidic inputs (Stroo and Alexander, 1986; Vance and David, 1989; David et al., 1989; Duffy and Schreiber, 1990); however, results from this study were similar to results by Cronan (1985), which indicated that DOC concentrations and fluxes were unaffected by throughfall acidity. Although differences in DOC concentrations between forest floor solutions and throughfall were significantly correlated with forest floor solution pH, solution pH was never found to be significantly correlated with throughfall pH. Given the lack of any strong correlation of forest floor solution and throughfall pH, there was no indication that DOC concentrations were altered by acidic inputs at these sites.

Differences between the results from this field study and laboratory studies can be explained by the relatively small differences in throughfall pH at the sites and high pH of the throughfall received at the sites compared with the acidic treatments employed in the laboratory studies. Average volume weighted throughfall pH was 5.15 at the Alberta site and 5.24 at the Oceana site during the weeks of lysimeter collection (Table 3), while the range of throughfall pH for the 47 samples was from 4.5 and 6.2. Studies by Vance and David (1989) only found substantial decreases in O horizon DOC leachates with additions of simulated throughfall having a pH of 4 and below and only small decreases when pH was lowered from 5 to 4. Duffy and Schreiber (1990) and Stroo and Alexander (1986) both reported significant decreases in DOC levels when simulated rain pH was reduced from 5.25 to 4.15 and 5.6 to 3.5, respectively.

Although our study period was relatively limited, the precipitation and throughfall acidity measured during this time period were similar to those measured during the 1988 and 1989 growing seasons (Liechty et al., 1993). Average volume weighted and minimum recorded precipitation pH during the 1988 and 1989 growing season was 5.1 and 4.1 at the Alberta site and 4.5 and 3.7 at the Oceana site. Average volume weighted and minimum recorded throughfall pH during the two growing seasons (Liechty et al., 1993) was 5.5 and 4.6 at the Alberta site and 5.4 and 4.3 at the Oceana site. These

longer-term data demonstrate that the buffering action of the canopy during the growing season maintains the throughfall pH above the acidic treatment levels utilized in the laboratory studies. Therefore, there does not appear to be any significant decrease in forest floor leachate concentrations of DOC in these stands during the growing season due to increased precipitation acidity along the gradient.

It is possible that reductions in DOC leaching from the forest floor could occur during periods when foliage is absent and canopy buffering of acidity is limited. The minimum nongrowing season throughfall pH measured at the two sites from 1987 to 1989 (Liechty et al., 1993) was lower (3.8) than the minimum pH observed during the 1992 study period. However, occurrences of throughfall with a pH <4.5 is relatively uncommon and DOC concentrations in northern hardwood forest floor solutions are reduced by as much as 20 to 30% during the dormant season (Cronan and Aiken, 1985). Given this decrease in DOC concentrations during the dormant season and the high acidity levels required to significantly reduce leaching of this C (ex. Vance and David 1989), we do not expect significant reductions in leaching of DOC from the forest floor given the higher acidity of throughfall during the dormant season.

Temporal variation in DOC levels were more strongly correlated with soil temperature than solution acidity. Temporal DOC levels were strongly coupled to increases in soil temperature during the growing season at the Oceana site and to a lesser degree at the Alberta site (ex. Fig. 2 a-c). The differences in relationships between soil temperature and DOC concentrations at the two sites appear to be related to the differences in the range of temperatures experienced at the sites rather than any inherent differences between the two sites. Increased leaching of DOC from organic horizons with increased temperatures is an effect that has also been observed in laboratory studies (Cronan, 1980; James and Riha, 1987; Duffy and Schreiber, 1990). Cronan (1980) and Duffy and Schreiber (1990) have also compared the effects of acidic loadings and temperature on the levels of DOC in organic horizon solutions and also concluded that temperature altered DOC levels to a much greater degree than did acidic inputs.

Although DOC concentrations of forest floor solutions at the two sites did not significantly differ, comparison of the estimated DOC forest floor water concentrations using the derived temperature equation suggest that the differences in fluxes of DOC from the forest floor could be substantial. Given a similar amount of water passing through the forest floor, the higher soil temperatures at the Oceana site could cause as much as 16% increase in fluxes of DOC. Increased leaching of DOC at the Oceana site would reflect an increase in microbial activity as a result of the higher temperatures at this site. The higher microbial activity at the Oceana site is also evident when comparing the turnover rates (forest floor standing stock/litterfall flux). Turnover rates calculated from Table 1 were 10.6 yr at the Alberta site and 9.1 yr at the Oceana site.

Dissimilar processes appear to be controlling the levels

of DOC in throughfall and forest floor water in these northern hardwood stands. Levels of DOC in throughfall reflect relatively passive exchange processes in the canopy since DOC concentrations decreased with amounts of water passing through the canopy. The DOC in forest floor water is strongly related to temperature reflecting the effects of microbial activity as the primary source of this C. These results suggest that besides the direct input of throughfall DOC to the forest floor, processes controlling DOC fluxes in throughfall and the forest floor are poorly linked.

CONCLUSIONS

Concentrations and fluxes of DOC in northern hardwood throughfall and forest floor water were not significantly altered by the levels of acidic deposition experienced at the northern and southern limits of this cover type. Levels of DOC in forest floor water was unaffected by acidic loadings because the forest canopy buffered precipitation before it reached the forest floor while canopy exchange processes associated with DOC leaching appear to be unrelated to precipitation acidity. Neither spatial or temporal changes of temperature between or within the sites were found to alter DOC levels in throughfall, but seasonal increases in temperatures during the growing season and warmer temperatures at the more southern site increased the levels of DOC in forest floor leachate. It was estimated that the differences in soil temperatures between the northern and southern gradient sites could be responsible for as much as a 16% increase in DOC concentrations in forest floor solutions at the southern compared to northern site.

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REFERENCES

- Burton, A.J., C.W. Ramm, D.D. Reed, and K.S. Pregitzer. 1991. Use of multivariate methods in forest research site selection. *Can. J. For. Res.* 21:1573-1580.
- Cronan, C.S. 1980. Controls on leaching from coniferous forest floor microcosms. *Plant Soil* 56:301-322.
- Cronan, C.S. 1985. Comparative effects of precipitation acidity on three forest soils: Carbon cycling responses. *Plant Soil* 88:101-112.
- Cronan, C.S., and G.R. Aiken. 1985. Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. *Geochim. Cosmochim. Acta* 49:1697-1705.
- Cronan, C.S., and W.A. Reiners. 1983. Canopy processing of acidic precipitation by coniferous and hardwood forests in New England. *Oecologia* 59:216-223.
- Dalva, M., and T.R. Moore. 1991. Sources and sinks of dissolved organic carbon in a forested swamp catchment. *Biogeochem.* 15: 1-19.
- David, M.B., G.F. Vance, J.M. Rissing, and F.J. Stevenson. 1989. Organic carbon fractions in extracts of O and B horizons from a New England spodosol: Effects of acid treatment. *J. Environ. Qual.* 18:212-217.
- Duffy, P.D., and J.D. Schreiber. 1990. Nutrient leaching of a Loblolly pine forest floor by simulated rainfall: II. Environmental factors. *For. Sci.* 36:777-789.
- Foster, N.W., and J.A. Nicholson. 1988. Acid deposition and nutrient leaching from deciduous vegetation and podzolic soils at the Turkey Lakes Watershed. *Can. J. Fish. Aquat. Sci.* 45:96-100.
- Guggenberger, G., and W. Zech. 1994. Composition and dynamics of dissolved carbohydrates and lignin-degradation products in two coniferous forests, N.E. Bavaria, Germany. *Soil Biol. Biochem.* 26:19-27.
- Hay, G.W., J.H. James, and G.W. Vanloon. 1985. Solubilization effects of simulated acid rain on the organic matter of forest soil; preliminary results. *Soil Sci.* 139:422-430.
- Hoffman, W.A., Jr., S.E. Lindberg, and R.R. Turner. 1980a. Some observations of organic constituents in rain above and below a forest canopy. *Environ. Sci. Technol.* 14:999-1002.
- Hoffman, W.A., Jr., S.E. Lindberg, and R.R. Turner. 1980b. Precipitation acidity: The role of the forest canopy in acid exchange. *J. Environ. Qual.* 9:95-100.
- James, B.R., and S.J. Riha. 1987. Forest soil organic horizon acidification: Effects of temperature, time, and solution/soil ratio. *Soil Sci. Soc. Am. J.* 51:458-462.
- Liechty, H.O., G.D. Mroz, and D.D. Reed. 1993. Cation and anion fluxes in northern hardwood throughfall along an acidic deposition gradient. *Can. J. For. Res.* 23:457-467.
- Lovett, G.M., S.E. Lindberg, D.D. Richter, and D.W. Johnson. 1985. The effects of acidic deposition on cation leaching from three deciduous forest canopies. *Can. J. For. Res.* 15:1055-1060.
- MacDonald, N.W., A.J. Burton, M.F. Jurgensen, J.W. McLaughlin, and G.D. Mroz. 1991. Variation in forest soil properties along a Great Lakes air pollution gradient. *Soil Sci. Soc. Am. J.* 55:1709-1715.
- McDowell, W.H., and G.E. Likens. 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook valley. *Ecol. Monogr.* 58:177-195.
- Moore, T.R. 1989. Dynamics of dissolved organic carbon in forested and disturbed catchments, Westland, New Zealand: I. Maimai. *Wat. Resour. Res.* 25:1321-1310.
- National Oceanic and Atmospheric Administration. 1983. Climate normals of the U.S. (Base: 1951-1980). National Climatic Center, Environ. Data and Inf. Service, Gale Research Co., Detroit, MI.
- Pohlman, A.A., and J.G. McColl. 1988. Soluble organics from forest litter and their role in metal dissolution. *Soil Sci. Soc. Am. J.* 52: 265-271.
- Potter, C.S. 1991. Nutrient leaching from *Acer rubrum* leaves by experimental acid rainfall. *Can. J. For. Res.* 21:222-229.
- Qualls, R.G., B.L. Haines, and W.T. Swank. 1991. Fluxes of dissolved organic nutrients and humic substances in a deciduous forest. *Ecology* 72:254-266.
- Richter, D.D., D.W. Johnson, and D.E. Todd. 1983. Atmospheric sulfur deposition, neutralization, and ion leaching in two deciduous forest ecosystems. *J. Environ. Qual.* 12:263-270.
- Schaefer, D.A., W.A. Reiners, and R.K. Olson. 1988. Factors controlling the chemical alteration of throughfall in a subalpine balsam fir canopy. *Environ. Exp. Biol.* 28:175-189.
- Scherbatskoy, T., and R.M. Klein. 1983. Response of spruce and birch foliage to leaching by acidic mists. *J. Environ. Qual.* 12: 189-195.
- Shepard, J.P., M.J. Mitchell, T.J. Scott, Y.M. Zhang, and D.J. Raynal. 1989. Measurements of wet and dry deposition in a northern hardwood forest. *Water Air Soil Pollut.* 43:223-238.
- Stroo, H.F., and M. Alexander. 1986. Role of soil organic matter in the effect of acid rain on nitrogen mineralization. *Soil. Sci. Soc. Am. J.* 50:1218-1223.
- Vance, G.F., and M.B. David. 1989. Effect of acid treatment on dissolved organic carbon retention by a spodic horizon. *Soil Sci. Soc. Am. J.* 53:1242-1247.
- Vance, G.F., and M.B. David. 1992. Dissolved organic carbon and sulfate sorption by spodosol mineral horizons. *Soil Sci.* 154:136-144.