Biogeochemistry **50:** 73–93, 2000.

Throughfall chemistry in a loblolly pine plantation under elevated atmospheric CO_2 concentrations

J. LICHTER[1], M. LAVINE[2,3], K.A. MACE[1], D.D. RICHTER[3] &
W.H. SCHLESINGER[1,3]
[1]*Department of Botany, Duke University, Durham, NC 27708, U.S.A.;* [2]*Institute of Statistics and Decision Science, Duke University, Durham, NC 27708, U.S.A.;* [3]*Nicholas School of the Environment, Duke University, Durham, NC 27708, U.S.A.*

Received 19 July 1999; accepted 30 November 1999

Key words: atmosphere-canopy interaction, atmospheric CO_2, atmospheric deposition, dissolved organic carbon, FACE experiment, loblolly pine (*Pinus taeda* L.), throughfall chemistry

Abstract. Accelerated tree growth under elevated atmospheric CO_2 concentrations may influence nutrient cycling in forests by *(i)* increasing the total leaf area, *(ii)* increasing the supply of soluble carbohydrate in leaf tissue, and *(iii)* increasing nutrient-use efficiency. Here we report the results of intensive sampling and laboratory analyses of NH_4^+, NO_3^-, PO_4^{3-}, H^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, and dissolved organic carbon (DOC) in throughfall precipitation during the first 2.5+ years of the Duke University Free-Air CO_2 Enrichment (FACE) experiment. After two growing seasons, a large increase (i.e., 48%) in throughfall deposition of DOC and significant trends in throughfall volume and in the deposition of NH_4^+, NO_3^-, H^+, and K^+ can be attributed to the elevated CO_2 treatment. The substantial increase in deposition of DOC is most likely associated with increased availability of soluble C in plant foliage, whereas accelerated canopy growth may account for significant trends toward decreasing throughfall volume, decreasing deposition of NH_4^+, NO_3^-, and H^+, and increasing deposition of K^+ under elevated CO_2. Despite considerable year-to-year variability, there were seasonal trends in net deposition of NO_3^-, H^+, cations, and DOC associated with plant growth and leaf senescence. The altered chemical fluxes in throughfall suggest that soil solution chemistry may also be substantially altered with continued increases in atmospheric CO_2 concentrations in the future.

Introduction

Forest canopies capture dusts, aerosols, and gases in dry deposition and dissolved ions in precipitation and cloud droplets. Intercepted chemicals may be absorbed by plant foliage or microbes living on leaf surfaces, or they may be washed off leaves and enter the soil system in throughfall solution. Typically, NH_4^+, HNO_3, and H^+ are absorbed by forest canopies, whereas base cations and organic acids are leached from foliage (e.g., Tukey 1970; Foster 1974; Parker 1983; Cronan & Reiners 1983; Bredemeier 1988; Mahendrappa 1989; Johnson & Lindberg 1992; Lovett & Lindberg 1993; Neary & Gizyn 1994). In industrialized regions and remote from the seashore, most SO_4-S in throughfall solution originates as atmospheric H_2SO_4 from anthropogenic emissions, which is deposited as dry deposition on foliage where H^+ is absorbed and SO_4^{-2} is subsequently washed off (Lindberg & Garten 1988).

Chemical exchange across leaf surfaces occurs by diffusion, uptake, and ion exchange (Schaefer & Reiners 1989). Foliar uptake of H^+ buffers anthropogenic acidity and promotes foliar leaching of cations to maintain charge balance (Hoffman et al. 1980; Lindberg et al. 1986). These chemical exchanges between the atmosphere and the forest canopy can represent important fluxes in many forest ecosystems. For example, foliar uptake of N and S can satisfy a high proportion of plant requirement for growth in some forests (Lindberg et al. 1986; Lovett & Lindberg 1993).

Little is known about the potential effect of elevated atmospheric CO_2 concentrations on the chemical exchanges between the atmosphere and forest canopies, and the resulting chemical flux to soils. Accelerated plant growth under elevated CO_2 may influence throughfall chemistry indirectly by increasing the total leaf area of the canopy and its demand for limiting nutrients. In addition, plant growth under elevated CO_2 concentrations may promote accumulation of sugar and starch in foliage (Körner & Arnone 1992; Körner & Miglietta 1994; Wurth et al. 1998), and the accumulation of labile C compounds may lead to increased leaching of dissolved organic carbon (DOC) compounds in throughfall. If the leaching of organic acids increases, greater leaching of base cations may result as the charge balance of throughfall solution is maintained. Lastly, if trees become more efficient in their use of limiting nutrients under elevated CO_2 (Drake et al. 1997), foliar uptake of limiting nutrients may increase while leaching simultaneously decreases.

Our primary objective was to examine the influence of elevated atmospheric CO_2 concentrations on throughfall chemistry. Effects of elevated CO_2 on ecosystem-level processes are difficult and costly to study because atmospheric CO_2 concentrations must be controlled in large replicated experimental plots within an intact forest ecosystem. We studied throughfall chemistry in the Duke Forest Free-Air CO_2 Enrichment (FACE) experiment, which maintains elevated (i.e., $\sim$560 ppm) and ambient (i.e., 360 ppm) CO_2 concentrations in replicated experimental plots within an intact 15-year-old loblolly pine (*Pinus taeda* L.) plantation. The pine canopy is relatively homogeneous, potentially reducing the substantial spatial heterogeneity commonly associated with throughfall chemistry (Kimmins 1973; Kostelnik et al. 1989;

Puckett 1991), and allowing us to discern subtle differences associated with the elevated CO_2 treatment.

Secondary objectives of this study included quantifying total chemical deposition for constructing nutrient budgets and net canopy exchange (i.e., chemical mass in throughfall – chemical mass in incident precipitation) for examining atmosphere-canopy interactions. We also determined the anion deficit and charge density of throughfall DOC. The charge density (i.e., the microequivalents of organic anion per mg of DOC required for charge balance) of organic acids has been used to study the acid-base status of throughfall solutions (Fillion et al. 1998) and the waters of softwater lakes (Hemond 1990; Marmorek et al. 1996).

Methods

Research site and field collections

The Duke University FACE plots were installed in an intact loblolly pine (*Pinus taeda* L.) forest planted in 1983. The canopy is 15 m tall with 98% of the basal area consisting of loblolly pine (DeLucia et al. 1999). Soils are classified as Ultic Alfisols of the Enon Series. Six 30-m diameter experimental plots (i.e., rings) were installed to control CO_2 concentrations throughout the volume of the forest ecosystem. Three rings serve as experimental treatments in which CO_2 concentrations are maintained 200 ppm above ambient levels (i.e., 560 ppm), and three rings serve as experimental controls in which no CO_2 is added (i.e., $\sim$360 ppm). Each ring consists of a large circular plenum that delivers air to an array of 32 vertical pipes positioned around the ring's circumference. The pipes run from the forest floor to the top of the canopy, and they are extended as the canopy grows in height. Each pipe contains adjustable ports at $\geq$50-cm intervals that control atmospheric CO_2 concentrations within the volume of the ring. The CO_2 treatment was initiated on 27 August 1996 after four months of pre-treatment sampling and laboratory analyses. Detailed descriptions of the design of the FACE apparatus are given by Hendrey and Kimball (1994), Lewin et al. (1994), and Hendrey et al. (1999).

Rainfall collectors were installed to sample throughfall and incident precipitation. The throughfall collectors consisted of a 4-L bottle and a 14.6-cm diameter funnel. The stem of the bottle was filled with polyfill to filter coarse particulates. The height of the funnel above the ground was 50 cm. Six collectors were installed in each treatment ring. Two collectors were randomly placed within each of three out of four sectors in each treatment ring. The collectors were exchanged with clean bottles biweekly between May 1996 and January 1999. Samples were returned back to the laboratory, refrigerated, and processing was begun immediately. If less than 100 ml of solute accumulated in a rainfall collector during any two-week time interval, then the two samples collected within each sector were composited, or if necessary, the six samples collected within each ring were composited. A rainfall collector was installed on top of one of the treatment ring towers, and an Aerochem Metrics wetfall/dryfall collector was installed in a nearby open field for sampling incident precipitation.

Laboratory analyses

Laboratory analyses were conducted to determine chemical concentrations of NH_4^+, NO_3^-, PO_4^{3-}, total N, total P, H^+, Si, K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, and DOC. Particulates were removed from the solutions with a 1.0-μm followed by a 0.4-μm polycarbonate Nucleopore filter. NH_4^+, NO_3^-, and PO_4^{3-} concentrations were measured with a Traacs 800 autoanalyzer within two days of sample collection. Ca^{2+} and Mg^{2+} concentrations were measured with atomic spectrophotometry, whereas K^+ and Na^+ concentrations were measured with flame emission on a Perkin Elmer Model 3100 Atomic Absorption Spectrophotometer. Concentration of anions (Cl^-, SO_4^{2-}, PO_4^{3-}, and NO_3^-) were measured with a Dionex 2010*i* ion chromatograph. Total N and total P were measured by first oxidizing organic N and P with a persulfate digestion and then measuring concentrations of total NO_3^- and PO_4^{-3} on the autoanalyzer. Throughfall pH was measured with a Metrohm 691 pH meter, DOC with a Shimadzu Model TOC-5000A total organic carbon analyzer, and conductivity with a YSI Model 32 conductance meter. Alkalinity was measured by titrating with a Brinkman Dosimat to pH <5.0. Chemical concentrations were converted to estimates of deposition per unit area.

Statistical analyses

We considered the mean of the six throughfall collectors located in each treatment ring to be the experimental unit for all statistical analyses. We therefore have a sample size of three (i.e., 3 elevated and 3 ambient treatment rings) for each of 69 two-week time steps. Potential differences in throughfall volume and total deposition of the various constituents were tested statistically with repeated-measures ANOVA. Because the main effect of the treatment is potentially confounded with random site differences not related to the treatment, we considered the treatment × time interaction as the proper test of significance of the treatment. This provides an unambiguous test of the effects of the treatment on the various response variables.

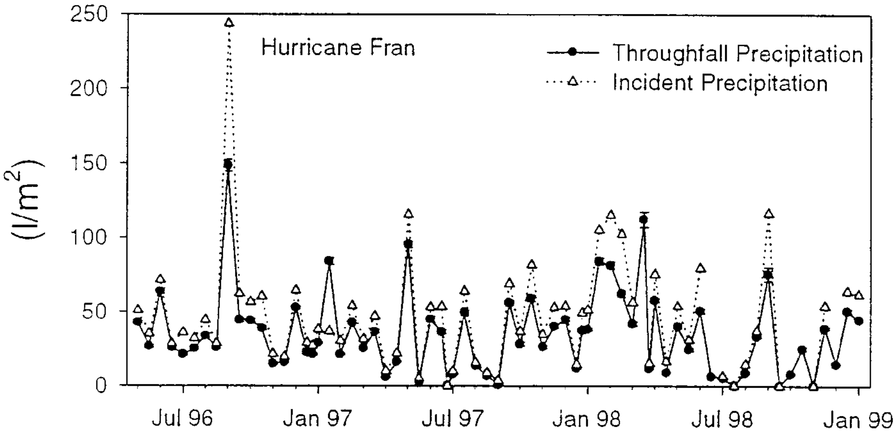

Figure 1. Throughfall and incident precipitation. Throughfall data given as the mean ±1 S.E. of the six experimental rings.

We also modeled trends in throughfall precipitation and chemical deposition as time series. That is, we plotted the difference between elevated and ambient means for throughfall volume and for deposition of each of the measured chemicals against a time axis consisting of 2-week time steps. Differences between elevated and ambient means were adjusted such that zero represented the mean difference for the four-month pre-treatment period (i.e., May through August 1996). Least-squares linear regressions were then used to test whether post-treatment trends were statistically significant. We did not include an intercept term in the linear regression model, and thereby assumed that pre-treatment differences accurately represented random site differences between the elevated and ambient treatment rings.

To examine atmosphere-canopy interactions, we plotted net canopy exchange of each of the measured chemicals against incident precipitation and against time. Relationships among chemicals were examined with Pearson Product-moment correlation, and net canopy exchange of NH_4, strong acid anions, and DOC were tested as predictors of net canopy exchange of base cations with multiple regression.

To determine the charge density of DOC, we regressed the anion deficit (i.e., the difference between the sum of the measured cationic charges and the sum of the measured anionic charges for inorganic constituents expressed in milli-equivalents) against total DOC (in mg). We examined the mean DOC charge density for the entire experiment as well as variability in DOC charge density, and we used repeated-measures ANOVA to test for significant changes associated with the elevated CO_2 treatment.

Table 1. Total chemical deposition in throughfall precipitation by year and treatment. Data are given as the mean ± 1 SE of three elevated or ambient treatment rings per month.

Variable	1996			1997			1998					
	Amb.	Elev.	Elev.% of Amb.	Amb.	Elev.	Elev.% of Amb.	Amb.	Elev.	Elev.% of Amb.	Percent Change 1996–98	Mean Annual Ambient	Mean Annual Elevated
TF Volume ($l/m^2/mo$)	80.28 (2.48)	87.46 (1.86)	109	66.71 (1.16)	71.10 (1.31)	107	76.70 (3.23)	78.04 (2.61)	102	–7	894.76 (48.73)	946.40 (56.89)
DOC (kg/ha/mo)	7.95 (0.47)	7.75 (0.34)	97	6.56 (0.38)	7.24 (0.17)	110	8.00 (0.84)	11.56 (1.99)	145	+48	90.04 (5.66)	106.20 (16.36)
NH_4-N	0.10 (0.01)	0.11 (0.01)	110	0.09 (0.01)	0.09 (0.01)	97	0.13 (0.015)	0.12 (0.01)	92	–18	1.27 (0.25)	1.30 (0.13)
NO_3-N	0.23 (0.03)	0.26 (0.02)	113	0.29 (0.03)	0.27 (0.03)	93	0.29 (0.05)	0.24 (0.02)	83	–30	3.24 (0.24)	3.12 (0.12)
H	0.010 (0.002)	0.016 (0.001)	160	0.018 (0.003)	0.021 (0.002)	117	0.016 (0.004)	0.017 (0.001)	106	–54	0.18 (0.03)	0.22 (0.03)
K	1.41 (0.24)	1.25 (0.26)	89	1.02 (0.19)	0.94 (0.18)	92	1.04 (0.19)	0.97 (0.19)	93	+4	13.88 (1.52)	1.05 (1.18)

Table 1. Continued.

Variable	1996			1997			1998					
	Amb.	Elev.	Elev.% of Amb.	Amb.	Elev.	Elev.% of Amb.	Amb.	Elev.	Elev.% of Amb.	Percent Change 1996–98	Mean Annual Ambient	Mean Annual Elevated
Ca	0.69 (0.09)	0.60 (0.11)	87	0.71 (0.07)	0.54 (0.06)	76	0.53 (0.02)	0.45 (0.05)	85	–2	7.72 (0.68)	6.36 (0.91)
Mg	0.33 (0.4)	0.32 (0.03)	97	0.26 (0.01)	0.22 (0.01)	85	0.21 (0.01)	0.18 (0.01)	86	–11	3.24 (0.42)	2.88 (0.04)
Na	0.25 (0.01)	0.25 (0.01)	100	0.18 (0.01)	0.18 (0.01)	100	0.24 (0.01)	0.24 (0.01)	100	0	2.68 (0.26)	2.68 (0.26)
Cl	0.90 (0.03)	0.89 (0.06)	99	0.69 (0.05)	0.61 (0.03)	88	0.82 (0.02)	0.81 (0.05)	99	0	9.64 (0.73)	9.24 (1.00)
PO_4-P	0.03 (0.03)	0.01 (0.01)	33	0.02 (0.01)	0.003 (0.001)	15	0.01 (0.003)	0.002 (0.001)	20	–13	0.24 (0.07)	0.06 (0.002)
SO_4-S	1.92 (0.07)	2.01 (0.09)	105	1.86 (0.12)	1.87 (0.04)	101	1.88 (0.10)	1.91 (0.11)	102	–3	22.64 (0.21)	23.16 (0.50)

Table 2. Results of repeated-measures ANOVA for log-transformed DOC deposition.

Source	df	Mean square	*F*	*P*
Block	2	1.070	4.30	0.189
CO_2 Treatment	1	1.000	4.02	0.183
Error I: Block$*$Treatment	2	0.249		
Time	56	4.683	69.59	<0.001
Time$*$Treatment	56	0.119	1.760	0.002
Error II: Block$*$Treatment$*$Time	224	0.067		

Results

Throughfall precipitation averaged 35.2 l/m^2/2-week interval and ranged up to 148.6 l/m^2 for the two-week interval containing Hurricane Fran (Figure 1). Only four of 69 two-week time intervals lacked sufficient rainfall for chemical analyses.

Elevated CO_2 treatment effects

Between 1996 and 1998 total deposition of DOC increased by 48 percent under elevated CO_2 relative to ambient CO_2 controls (Table 1). This result was statistically significant (Table 2). Most of this change occurred during 1998, which suggests a time lag in the response to the elevated CO_2 treatment (Figure 2). In addition, consistent trends in throughfall volume and deposition of NH_4^+, NO_3^-, H^+, and K^+ were evident. Between 1996 and 1998, throughfall volume decreased by 7 percent and throughfall deposition of NH_4^+, NO_3^-, and H^+ decreased by 18, 30 and 54 percent, respectively, under elevated relative to ambient CO_2. During the same interval total deposition of K^+ increased 4 percent under elevated CO_2 (Table 1). Ca^{2+}, Mg^{2+}, Na^+, Cl^-, PO_4^{3-}, and SO_4^{2-} varied little or inconsistently. The order of chemical deposition by mass (kg/ha) was: DOC $>$ S $>$ K $>$ Cl $>$ Ca $>$ N $>$ Mg $>$ Na $>$ H $>$ P.

Time series analyses showed that several trends were statistically significant (Table 3; Figure 3). The slope parameters for throughfall volume and deposition of NH_4^+, NO_3^-, H^+, K^+ and DOC were each significant and showed gradual trends toward decreasing throughfall volume, decreasing deposition of NH_4^+, NO_3^-, and H^+, and increasing deposition of K^+ and DOC with continued exposure to elevated CO_2. The slope parameters for Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-} were not statistically significant, whereas the slope parameter for

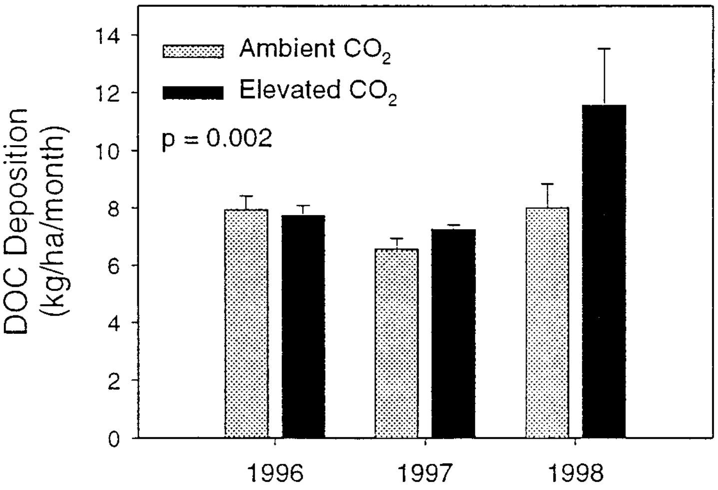

Figure 2. Throughfall deposition of DOC by year and treatment. Data given as the monthly mean ±1 S.E.

Table 3. Regression statistics for time series analyses (Figure 3)

Variable	Coefficient	SE	*t*	*P*	R^2
TF Volume	–0.049	0.009	–5.603	<0.0001	0.360
NH_4-N	–0.034	0.007	–4.784	<0.0001	0.290
NO_3-N	–0.097	0.010	–9.313	<0.0001	0.608
H	–0.006	0.001	–5.694	<0.0001	0.367
K	0.208	0.050	4.157	0.0001	0.236
Na	–0.013	0.006	–2.073	0.043	0.071
Ca	0.001	0.038	0.030	0.976	0.001
Mg	–0.017	0.015	–1.118	0.268	0.022
Cl	–0.030	0.032	–0.940	0.351	0.016
SO_4	–0.077	0.078	–0.986	0.328	0.017
DOC	4.208	1.465	2.87	0.006	0.128

Na^+ was marginally significant (Table 3). Although the experiment lacked sufficient statistical power to distinguish treatment differences in throughfall volume and deposition of NH_4^+, NO_3^-, H^+, and K^+ with the repeated measures ANOVA, the time series analysis shows consistent trends in throughfall volume and deposition of these chemicals that may have important consequences for throughfall chemical flux during the next several years of the FACE experiment.

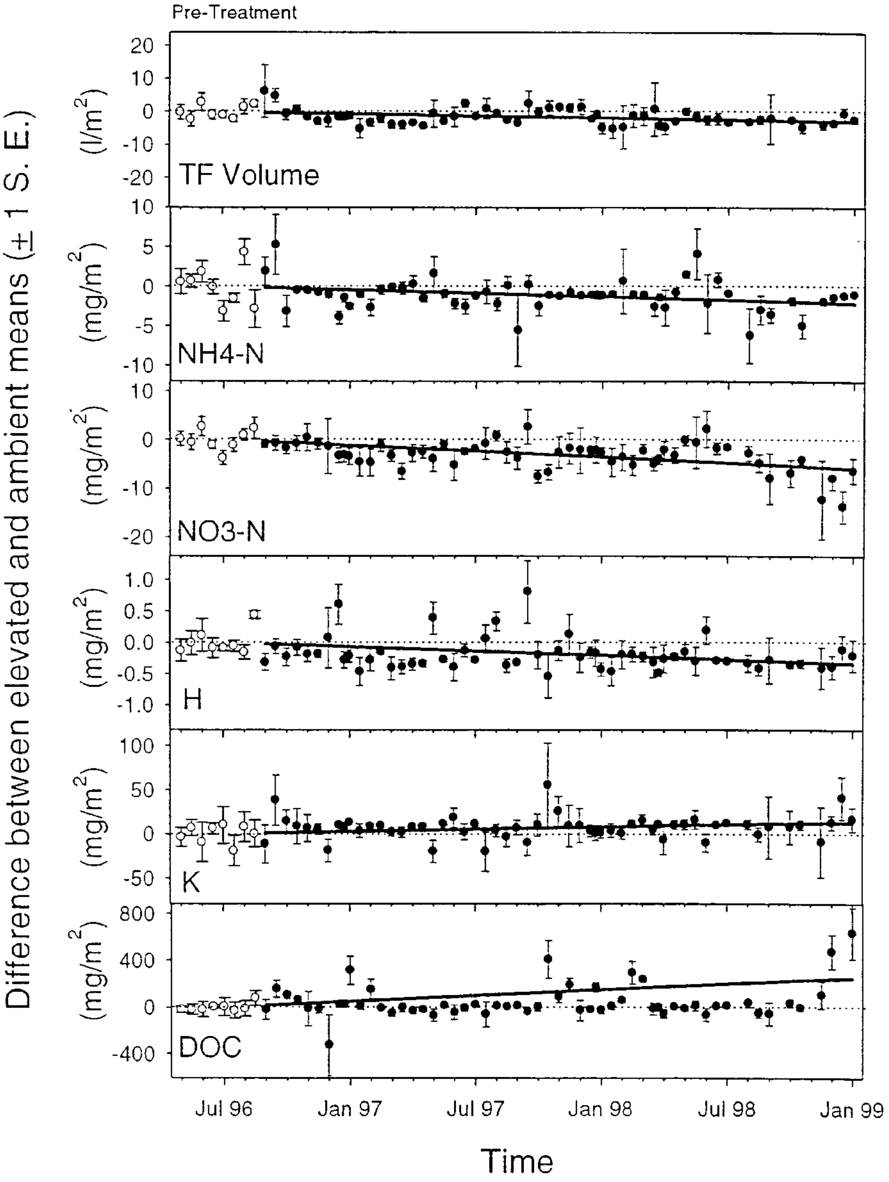

Figure 3. Time series showing trends in the difference between elevated CO_2 treatment and control means (±1. S.E.) in throughfall volume and deposition of several chemicals.

Net canopy exchange

Of 69 biweekly sample periods during the experiment, only 44 could be used to examine net canopy exchange because many incident precipitation samples were contaminated with bird feces. However, despite the incomplete data set, it was clear that NH_4^+ was absorbed by the canopy throughout the year at a rate approximating 1.2 kg N/ha/yr, whereas DOC, K^+, Ca^{2+}, and Mg^{2+} were released at rates approximating 163.7, 24.3, 3.1, and 1.7 kg/ha/yr, respectively (Figure 4). NO_3^- and H^+ were either absorbed by or leached/washed off from the canopy depending on the time of the year (Figure 5). Most foliar uptake of N and H^+ and foliar leaching of base cations and DOC occurred during the late summer and fall (Figure 5). Throughfall solutions were generally enriched by the canopy losses of SO_4^{-2}, but there was no clear seasonal pattern.

There were several significant correlations among chemicals in net deposition (Table 4). Notable were positive correlations among K^+, Ca^{2+}, and Mg^{2+}, and between each of these base cations and DOC, as well as negative correlations between these base cations and H^+. Net deposition of NH_4-N was negatively correlated with incident precipitation, whereas net deposition of K^+ was positively correlated with incident precipitation. Multiple regression analyses showed that net canopy exchange of H^+, NH_4^+, SO_4^{2-}, and DOC were significant predictors of net canopy exchange of K^+, whereas H^+, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, and DOC were significant predictors of Ca^{2+} and Mg^{2+} (Table 5). The regression coefficients were negative for cations and positive for anions, which is consistent with the release of base cations when H^+ and NH_4^+ are taken up by foliage and when strong or weak acid anions are released from foliage.

DOC charge density

A linear regression of anion deficit (i.e., the difference between the sum of measured positive charges and the sum of measured negative charges among inorganic constituents) on DOC mass in mg suggests a mean charge density of 4.4 μEq/mg DOC (Figure 6). This value is similar to the mean charge density of throughfall solutions in several French forests (i.e., 5.4 μEq/mg DOC; Fillion et al. 1998) and nearly identical to a theoretical value (i.e., 4.6 μEq/mg DOC) predicted for DOC in the waters of soft-water lakes (Hemond 1990). Throughfall solutions are similar to such lake waters in having low ionic strength. DOC charge density ranged seasonally between 0 and 15 μEq/mg DOC, and was inversely related to variation in the free acidity of throughfall solution (Figure 7). That is, foliar uptake of H^+ during the growing season reduces the free acidity of throughfall solution, which consequently increases

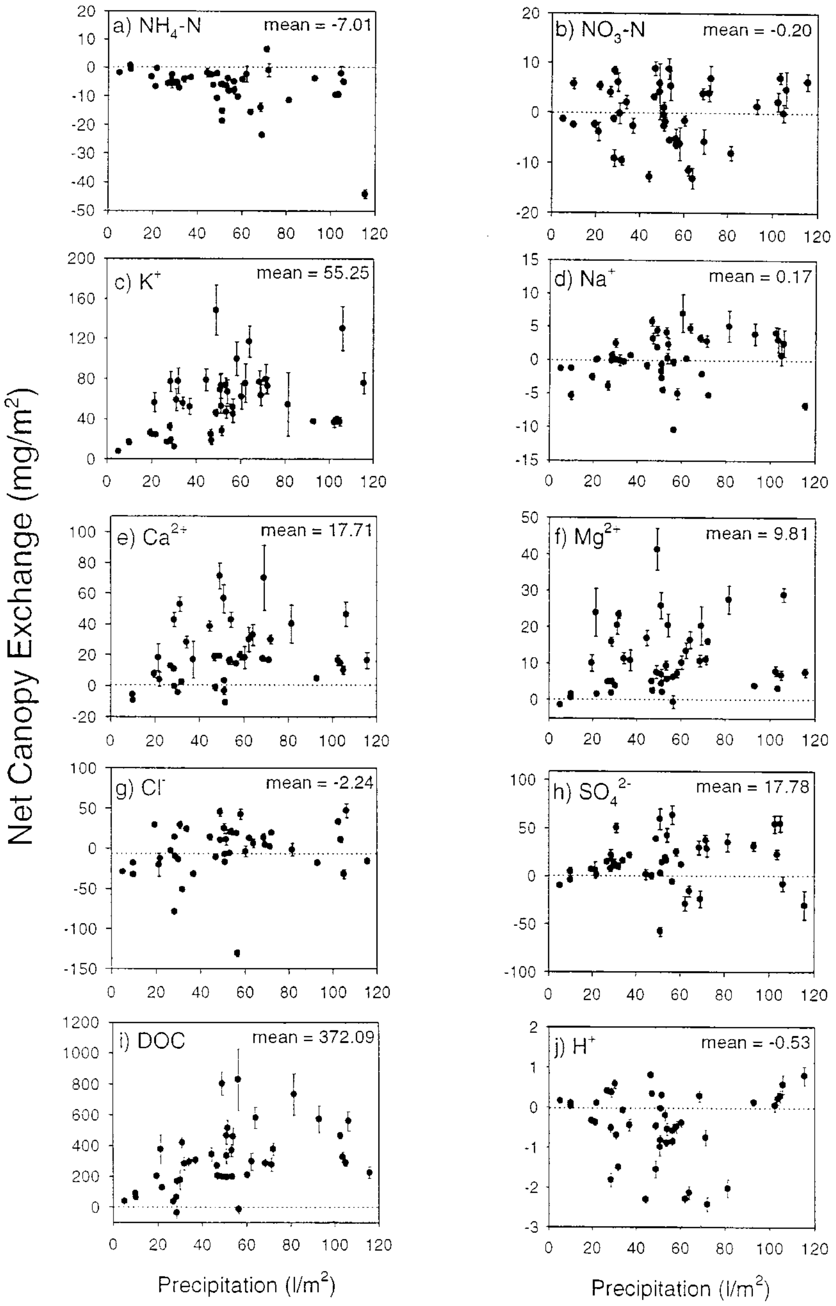

Figure 4. Net chemical exchange by the amount of incident precipitation. Data given as the mean (±1. S.E.) of the six experimental rings.

Table 4. Significant Pearson product-moment correlations among chemicals for net deposition.

Variable	Prec.	NH_4	NO_3	H	K	Na	Ca	Mg	Cl	PO_4	SO_4	DOC
Precip.	—	–0.43**	—	—	0.39**	—	—	—	—	—	—	—
NH_4		—	—	—	–0.31*	—	—	—	—	—	—	—
NO_3			—	0.45**	—	—	—	—	—	—	0.32*	–0.36*
H				—	–0.47***	—	–0.56***	–0.37*	—	—	—	—
K					—	0.66*	0.59***	0.41**	—	—	—	0.69***
Na						—	0.33*	—	0.35*	—	0.32*	—
Ca							—	0.80***	0.64***	—	0.40**	0.59***
Mg								—	0.56***	—	0.41**	0.67***
Cl									—	—	0.36*	—
PO_4										—	—	—
SO_4											—	—

$^{*}P < 0.05$, $^{**}P < 0.01$, $^{***}P < 0.001$.

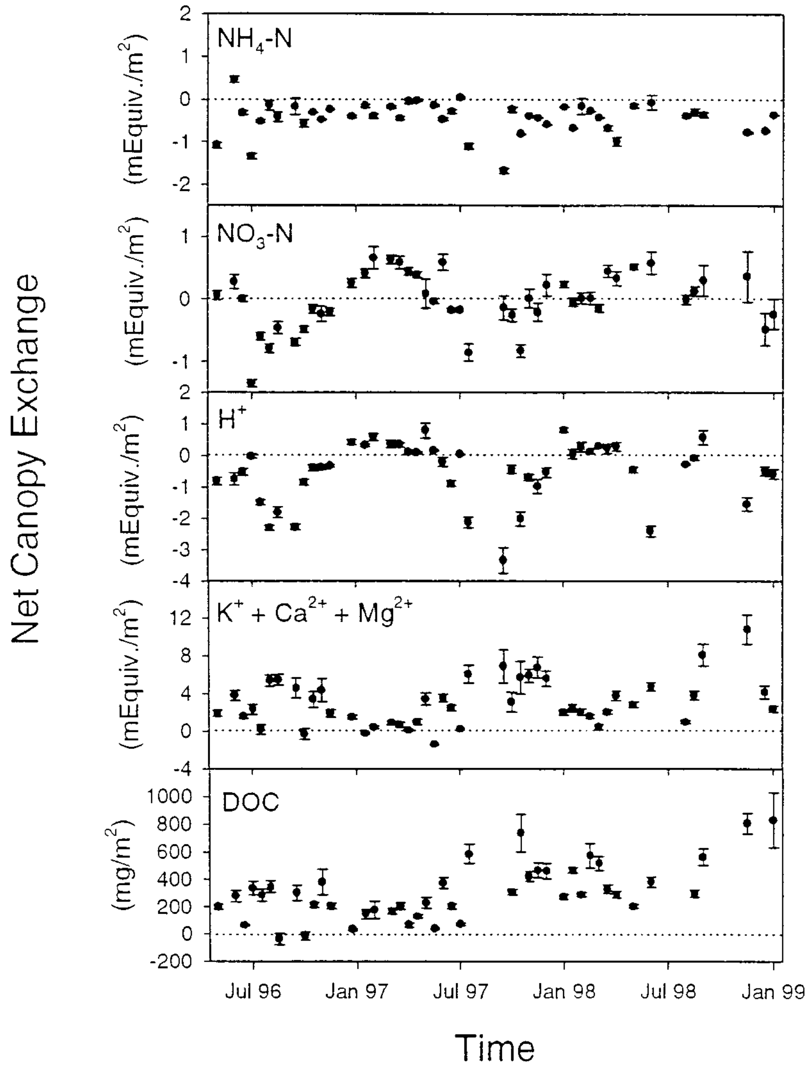

Figure 5. Seasonal variability in net canopy exchange. Data given as the mean (±1 S.E.) of the six experimental rings.

the charge density of DOC. The inverse relationship between DOC charge density and throughfall free acidity is markedly nonlinear (Figure 7), suggesting that factors other than throughfall pH may influence the charge density of DOC. There were no statistically significant differences in DOC charge density associated with the elevated CO_2 treatment.

Table 5. Results of multiple regression analyses of net chemical deposition.

Variable	K		Na		Ca		Mg	
	Coeff.	*P*	Coeff.	*P*	Coeff.	*P*	Coeff.	*P*
Constant	0.457	0.002	–0.023	0.593	–0.335	0.004	–0.084	0.494
H	–0.240	0.005	0.014	0.594	–0.570	<0.001	–0.194	0.013
NH_4	–0.384	0.004	0.038	0.338	–0.446	<0.001	–0.211	0.069
Cl	0.127	0.126	0.051	0.052	0.507	<0.001	0.314	<0.001
NO_3	0.084	0.662	0.005	0.932	0.554	0.001	0.331	0.064
SO_4	0.256	0.026	0.046	0.187	0.372	<0.001	0.333	0.002
DOC	0.303	<0.001	0.024	0.103	0.038	<0.001	0.343	<0.001
Adj. R^2	0.705		0.184		0.907		0.700	
Regression *P*	<0.001		0.035		<0.001		<0.001	

Discussion

Two and a half years after the initiation of Duke Forest FACE experiment, total net primary production under elevated CO_2 concentrations increased by 25 percent relative to ambient CO_2 concentrations (DeLucia et al. 1999). Trees receiving the elevated CO_2 treatment had greater woody increment growth, litterfall mass, and fine-root turnover (DeLucia et al. 1999). Although the differences were not statistically significant, estimates of plant area index (i.e., leaf area index + light intercepted by stems as estimated with the Li-Cor Canopy Analyzer hemispherical sensor, D.S. Ellsworth, pers. comm.) suggest canopy growth is also accelerated under the elevated CO_2 treatment relative to the control. Our measurements and analyses of throughfall chemistry show that these increases in tree growth and productivity were paralleled by a substantial increase in throughfall deposition of DOC and significant trends in throughfall volume and in deposition of NH_4-N, NO_3-N, H^+, and K^+.

The large increase in DOC deposition to the forest floor is attributed to increased availability of soluble C in leaf tissues grown under the elevated CO_2 treatment. Although accelerated canopy growth under elevated CO_2 may also have contributed to increased leaching of DOC, the increase in plant area index under the treatment relative to the control was small between 1997 and 1998 (i.e., 3% versus 2%; D.S. Ellsworth, pers. comm.), which seems insufficient to explain the substantial increase in DOC deposition. Plants commonly respond to elevated CO_2 by accumulating labile sugars and starch in leaves (Körner & Arnone 1992; Körner & Miglietta 1994; Wurth et al. 1998), which

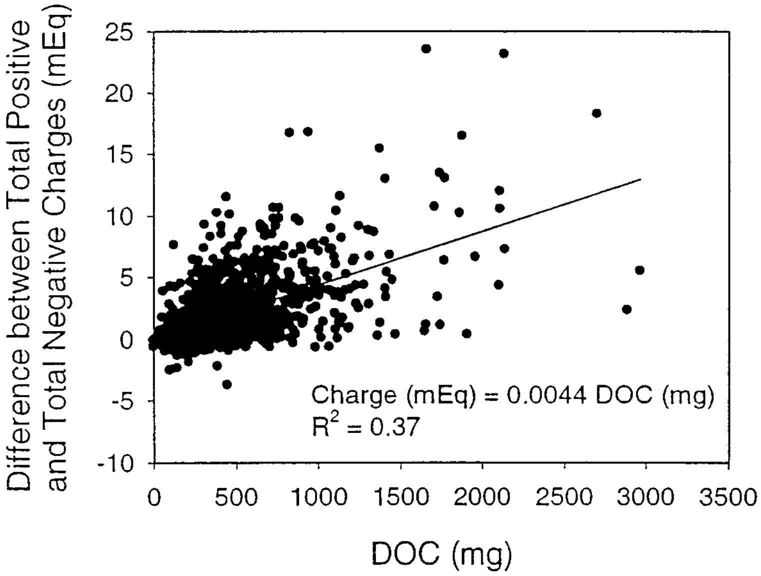

Figure 6. DOC charge density of each throughfall collector for each two-week time step during the experiment. The overall mean charge density is given as the slope of the linear regression.

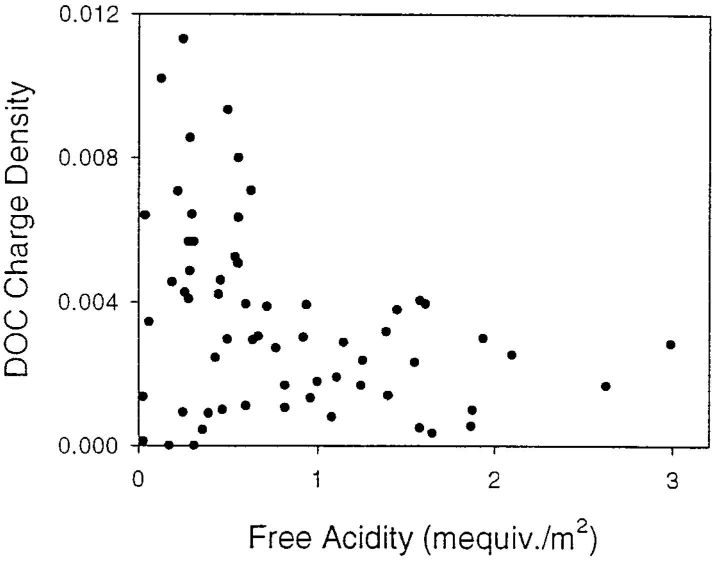

Figure 7. The relationship between DOC charge density and free acidity of throughfall solution.

may result in greater leaching of carbohydrates relative to organic acids. However, inasmuch as we detected no difference between the charge density of DOC in throughfall collected under elevated CO_2 from that of the ambient CO_2 controls, there does not seem to have been a shift in the relative abundance of carbohydrates and organic acids in solutions. Moreover, the mean DOC charge density was similar to values reported for throughfall solutions in forests not exposed to elevated atmospheric CO_2 concentrations (Fillion et al. 1998) and for soft-water lakes (Marmorek et al. 1996). Epiphytes and microbes could account for part of the observed changes; however, we have no data distinguishing their role from that of plant foliage.

The net increase in throughfall deposition of DOC in plots maintained at elevated CO_2 was $\sim$43 kg ha^{-1} during 1998. This increase represents a small proportion (i.e., $\sim$1%) of the total amount of C available for microbial use in soils. However, throughfall DOC contains metabolically labile forms of C (i.e., sugars, starch, and organic acids). Because soil microbial biomass and activity are generally limited by C availability (Zak et al. 1994), this small increase in labile C may lead to greater microbial biomass and eventually greater N mineralization and turnover after a period of immobilization during which microbial growth occurs. A similar hypothesis has been proposed by Zak et al. (1993) to explain the effects of increased exudation of labile C from the roots of plants grown under elevated atmospheric CO_2 concentrations. Although the increase in N turnover may be relatively small compared with total mineralization, it represents a mechanism that may contribute to sustained growth under elevated atmospheric CO_2 concentrations.

Acceleration in canopy growth under elevated CO_2 must solely account for the trend toward decreasing throughfall volume in elevated CO_2 relative to control rings, and may account for the trends toward decreased deposition of NH_4-N, NO_3-N, and H^+, and increased deposition of K^+. Increased canopy growth would provide more leaf surface area for diffusion, uptake, and ion exchange. Because the forest canopy absorbed more NH_4^+, NO_3^-, and H^+ than it released, and conversely, released more K^+ than it absorbed, an increase in leaf area should enhance absorption of N and H^+ and release of K^+.

Plants may also respond to elevated CO_2 concentrations by becoming more efficient in their use of limiting nutrients (Drake et al. 1997). Several studies have shown increased C:N ratios of leaf tissue for trees grown under elevated atmospheric CO_2, which is indicative of greater N-use efficiency (e.g., Norby et al. 1986; Eamus & Jarvis 1989; Cuelemans & Mousseau 1994; Zak et al. 2000). Reduced tissue concentrations should place a greater premium on N retention and reduce rates of diffusion and leaching of N as leaf concentrations decrease. The trends toward decreased throughfall N deposition under elevated CO_2 are consistent with increased N-use efficiency although we have not seen significant differences in tissue N concentrations associated with the elevated CO_2 treatment in the Duke Forest FACE experiment (Finzi et al. 2000). It is therefore not clear whether increased N-use efficiency contributed to the trend toward decreased N deposition under elevated CO_2, or whether the trend was related solely to the increase in canopy growth.

Increased leaching of K^+ may result from greater uptake of NH_4^+ and H^+ and greater leaching of organic acids as well as greater leaf area. Results of our multiple regression analyses are consistent with several studies showing that K^+ and other base cations are released from foliage as NH_4^+ and H^+ are taken up, and as Cl^- and organic acids are released from foliage. K^+ moves freely in plant tissue and may diffuse readily in response to charge imbalances. K^+ may also be actively exchanged for NH_4^+ and H^+ (Schaefer & Reiners 1989).

If the current trends persist, significant alterations of throughfall N, H^+, and K^+ fluxes to the soil system will occur after only a few years. Assuming that the net removal of N from the canopy declines at a constant rate of 0.059 g N/m^2/yr -as observed between 1996 and 1998 under the elevated CO_2 treatment (Table 1), it would require only 3.9 years for throughfall N flux in elevated CO_2 rings to reach levels one-half of the mean annual throughfall N flux in ambient CO_2 controls. Similarly, it will require only 2.2 years for throughfall H^+ flux under elevated CO_2 to reach levels one-half of the mean annual throughfall H^+ flux under ambient CO_2, and only 8.3 years for throughfall DOC flux elevated CO_2 to reach levels twice the annual mean for ambient CO_2 controls.

Although the linear trends are not likely to continue indefinitely, these changes may have substantial consequences for forest nutrient cycling and soil solution chemistry. Spatial variation in soil water and ion fluxes may be strongly correlated with throughfall inputs to soils. Manderscheid and Matzner (1995) found that the spatial heterogeneity in soil water, Mg, Cl, and SO_4-S fluxes in a spruce forest was largely explained by the spatial heterogeneity of throughfall fluxes. Berg et al. (1997) showed that throughfall inputs altered soil ionic strength and nitrate leaching in an experiment with reciprocal transplants of soil across a climate and N and S deposition gradient. In addition to contributing to chemical fluxes to soils, throughfall inputs of water can strongly influence soil solution chemistry as well as the distribution of understory plants (Anderson et al. 1969).

Seasonal variability in throughfall chemistry is associated with plant growth as well as nutrient translocation and leaf senescence (e.g., Miller 1963; Carlisle et al. 1966, 1967; Henderson 1977). Although leaf senescence probably explains the peak deposition of base cations and DOC in the autumn

(Carlisle et al. 1966; Tukey 1970), seasonal fluctuations in the net canopy exchange of NO_3^- and H^+ indicate that foliar uptake during the summer controls variability of these ions in throughfall. Seasonal ion exchange of H^+ across leaf surfaces appears to influence variability in the charge density of DOC.

Our results suggest that elevated atmospheric CO_2 concentrations can substantially affect throughfall water and chemical fluxes to soils in forests over a period of several years. Trees responded with greater canopy growth, greater foliar uptake of N and H^+, and greater foliar leaching of DOC and K^+. Although the magnitudes of these alterations were minor compared to chemical fluxes to soils in litterfall and fine-root turnover, if these trends persist, significant changes in soil solution chemistry will lead to significant changes in forest nutrient cycling. Most important among these changes is a potential priming effect of increased deposition of DOC on N cycling (e.g., Zak et al. 1993).

Acknowledgements

The authors kindly thank Heather Hemric, Mike Hofmockel, Neung-Hwan Oh, Anthony Mace, and Rajpreet Singh for the laboratory chemical analyses, and Andy Allen, Jim Clark, David Ellsworth, Miguel Gonzalez-Meler, and Roser Matamala for helpful discussion and comments on earlier drafts of this manuscript. The comments of Michael Bredemeier, Christian Körner, and an anonymous referee greatly improved this paper. Financial support for this research was provided by the U.S. Department of Energy and the National Science Foundation.

References

Anderson RC, Loucks, OL & Swain AM (1969) Herbaceous response to canopy cover, light intensity, and throughfall precipitation in coniferous forests. Ecology 50: 255–263

Berg MP, Verhoff HA, Bolger T, Anderson JM, Beese F, Couteaux MM, Ineson P, McCarthy F, Palka L, Raubuch M, Splatt P & Willison T (1997) Effects of air pollutant-temperature interactions on mineral-N dynamics and cation leaching in reciprocal forest soil transplantation experiments. Biogeochem. 39: 295–326

Bredemeier M (1988) Forest canopy transformation of atmospheric deposition. Water, Air Soil Pollut. 40: 121–138

Carlisle AA, Brown HF & White EJ (1966) The organic matter and nutrient elements in the precipitation beneath a sessile oak canopy. J. Ecol. 54: 87–98

Carlisle AA, Brown HF & White EJ (1967) The nutrient content of tree stemflow and ground flora litter and leachates in a Sessile Oak (Quercus petraea) woodland. J. Ecol. 55: 615–627

Cronan CS & Reiners WA (1983) Canopy processing of acidic precipitation by coniferous and hardwood forests in New England. Oecologia 59: 216–223

Cuelmans R & Mousseau M (1994) Effects of elevated atmospheric CO_2 on woody plants. New Phytologist 127: 425–446

DeLucia EH, Hamilton JG, Naidu SL, Thomas RB, Andrews JA, Finzi A, Lavine M, Matamala R, Mohan JE, Hendrey GR & Schlesinger WH (1999) Net primary production of a forest ecosystem with experimental CO_2 enrichment. Science 284: 1177–1179

Drake BG, Gonzalez-Mejer MA & Long SP (1997) More efficient plants: a consequence of rising atmospheric CO_2. Ann. Rev. Plant Physiol. Plant Mol. Biol. 48: 609–639

Eamus D and Jarvis PG (1989) The direct effects of increase in the global atmospheric CO_2 concentration on natural and commercial temperate trees and forests. Adv. Ecol. Res. 19: 1–55

Fillion N, Probst A & Probst JL (1998) Natural organic matter contribution to throughfall acidity in French forests. Environ. Int. 24: 547–558

Finzi AC, Allen AS, DeLucia EH, Ellsworth DS & Schlesinger WH (2000) Forest litter production, chemistry, and decomposition following two years of free-air CO_2 enrichment. Ecology, in press.

Foster NW (1974) Annual macroelement transfer from Pinus banksiana (Lamb.) forest to soil. Can. J. Forest Res. 2: 448–455

Hemond HF (1990) Acid neutralizing capacity, alkalinity, and acid-base status of natural waters containing organic acids. Environ. Sci. Technol. 24: 1486–1489

Henderson GS, Harris WF, Todd Jr DE & Grizzard T (1977) Quantity and chemistry of throughfall as influenced by forest-type and season. J. Ecol. 65: 365–374

Hendrey GR & Kimball BA (1994) The FACE program. Agricult. Forest Meteorol. 70: 3–14

Hendrey GR, Ellsworth DS, Lewin KF & Nagy J (1999) A free-air enrichment system for exposing tall forest vegetation to elevated atmospheric CO_2. Global Change Biol. 5: 293–309

Hoffman WA Jr., Lindberg SE & Turner RR (1980) Precipitation acidity: the role of forest canopy in acid exchange. J. Environ. Quality 9: 95–100

Johnson DW & Lindberg SE (Eds) (1992) Atmospheric Deposition and Nutrient Cycling in Forest Ecosystems. Springer-Verlag, New York

Körner C & Arnone III JA (1992) Responses to elevated carbon dioxide in artificial tropical ecosystems. Science 257: 1672–1675

Körner C & Miglietta F (1994) Long term effects of naturally elevated CO_2 on mediterranean grassland and forest trees. Oecologia 99: 343–351

Kimmins JP (1973) Some spatial aspects of sampling throughfall precipitation in nutrient cycling studies in British Columbian coastal forests. Ecology 54: 1008–1019

Kostelnik KM, Lynch JA, Grimm, JW & Corbett ES (1989) Sample size requirements for estimation of throughfall chemistry beneath a mixed hardwood forest. J. Environ. Quality 18: 274–280

Lewin KF, Hendrey GR, Nagy J & LaMorte RL (1994) Design and application of a free-air carbon dioxide enrichment facility. Agricultural and Forest Meteorology 70: 15–29

Lindberg SE & Garten Jr CT (1988) Sources of sulphur in forest canopy throughfall. Nature 336: 148–151

Lindberg SE, Lovett GM, Richter DD & Johnson DW (1986) Atmospheric deposition and canopy interactions of major ions in a forest. Science 231: 141–145

Lovett GM & Lindberg SE (1993) Atmospheric deposition and canopy interactions of nitrogen in forests. Can. J. Forest Res. 23: 1603–1616

Mahendrappa, MK (1989) Impacts of forests on water chemistry. Water, Air Soil Pollut. 46: 61–72

Manderscheid B & Matzner E (1995) Spatial and temporal variation of soil solution chemistry and ion fluxes through the soil in a mature Norway spruce (*Picea abies* (L.) Karst.) stand. Biogeochem. 30: 99–114

Marmorek DR, MacQueen RM, Wedeles CHR, Blancher PJ & McNicol DK (1996) Improving pH and alkalinity estimates for regional-scale acidification models: incorporation of dissolved organic carbon. Can. J. Fishery Aquatic Sci. 53: 1602–1608

Miller RB (1963) Plant nutrients in hard beech III: the cycle of nutrients. New Zealand J. Sci. 6: 388–413

Neary AJ & Gizyn WI (1994) Throughfall and stemflow chemistry under deciduous and coniferous forest canopies in south-central Ontario. Can. J. Forest Res. 24: 1089–1100

Norby RJ, Pastor J & Melillo JM (1986) Carbon-nitrogen interactions CO_2 enriched white oak: physiological and long-term perspectives. Tree Physiol. 2: 233–241

Parker GG (1983) Throughfall and stemflow in the forest nutrient cycle. Adv. Ecol. Res. 13: 57–133

Puckett LJ (1991) Spatial variability and collector requirements for sampling throughfall volume and chemistry under a mixed-hardwood canopy. Can. J. Forest Res. 21: 1581–1588

Schaefer DA & Reiners WA (1989) Throughfall chemistry and canopy processing mechanisms. In: Lindberg SE, Page AL & Norton SA (Eds) Acidic Precipitation. Vol. 3 Sources, Deposition, and Canopy Interactions. Springer-Verlag

Tukey Jr HB (1970) The leaching of substances from plants. Ann. Rev. Plant Physiol. 21: 305–324

Wurth MKR, Winter K, & Körner C (1998) Leaf carbohydrate responses to CO_2 enrichment at the top of a tropical forest. Oecologia 116: 18–25

Zak DR, Pregitzer KS, Curtis PS, Teeri JA, Fogel R & Randlett DL (1993) Elevated CO_2 and feedback between carbon and nitrogen cycles. Plant and Soil 151: 105–117

Zak DR, Tilman D, Parmenter RR, Rice CW, Fisher FM, Vose J, Milchunas D & Martin CW (1994) Plant production and soil microorganisms in late-successional ecosystems: A continental scale study. Ecology 75: 2333–2347

Zak DR, Pregitzer KS, Curtis PS & Holmes WE (2000) Atmospheric CO_2 and ecosystem feedback between carbon and nitrogen cycles: synthesis of an integrated experiment. Ecological Applications, in press