

## Anion fluxes in three Indiana forests

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**Summary.** The major ions in soil solution in control and disturbed plots were measured over a year in three Indiana forests. The major ions in bulk precipitation were hydrogen and sulfate. Sulfate, calcium, and magnesium were the most important ions in the soil solution in control plots, while in disturbed plots nitrate, calcium, and magnesium were most important. Increase nitrate production and loss following disturbance caused a large increase in cation losses.

and reasonable arguments could be made for either sulfate or bicarbonate control in undisturbed forests. Moreover, the sites were included in a broader-scale study of nitrate production and mobility in disturbed forest soils (Vitousek et al. 1982), so substantial information on nitrate losses from disturbed plots was available.

### Introduction

The “anion mobility model” (cf. Johnson and Cole 1980) suggests that the leaching of both cations and anions through soil to streamwater and groundwater is controlled by the supply and mobility of anions. Moreover, it suggests that if the effects of perturbations (such as acid deposition) or management practices (such as clearfelling) on anion fluxes can be determined, their overall consequences for solution losses of ions will be understood. This general model was originally developed for individual anions (cf. McColl and Cole 1968; Johnson et al. 1977 for bicarbonate; Nye and Greenland 1960; Likens et al. 1969 for nitrate; and Cronan 1980 for sulfate); it was systematized by Johnson and Cole (1980) for all major anions.

The anion mobility model was applied to understanding leaching losses of ions in three forests in southern Indiana. No soil solution information for this region was available,

### Methods

The study sites were located on the unglaciated Norman Upland of southern Indiana, 10–15 km south of Bloomington 39°10' N, 86°20' W). The region has a humid continental climate, with mean January and July temperatures of 1 C and 26 C respectively. Mean annual precipitation is 1,120 mm, evenly distributed through the year (Visher 1944). Soil, site, and vegetation characteristics were reported by Vitousek et al. (1982); the most relevant of these are summarized in Table 1.

Soil solution anion and cation concentrations were determined in control and disturbed plots. Plots were disturbed by root trenching, which cuts off root uptake of water and nutrients without mixing the soil or altering microclimate (Vitousek et al. 1982). Porous cup soil water samplers (lysimeters) were installed at 55–70 cm depth in 10 trenched and 10 control plots in each site. Solution samples were collected weekly during the period May 1978–June 1979 whenever snow depth allowed access to the lysimeters; at least one collection was made in each month.

In order to reduce the number of chemical analyses, 10% of the volume of each lysimeter's collection was com-

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**Table 1.** Site characteristics of the three study sites. More complete information in Vitousek et al. (1982). Soil chemical properties refer to the 0–15 cm depth in mineral soil

	Maple	Oak	Pine
Dominant trees	<i>Acer saccharum</i> <i>Fagus grandifolia</i>	<i>Quercus rubra</i> <i>Q. velutina</i> <i>Q. alba</i>	<i>Pinus echinata</i>
Litterfall dry mass (Mg/ha)	5.2	6.8	5.0
Parent material	loess over siltstone over limestone	loess over siltstone	limestone
Soil subgroup	typic dystrochrept	typic dystrochrept	typic hapludalf
Soil series	Berks	Muskingum	Hagerstown
Forest floor mass (Mg/ha)	9.8	19.4	17.2
Soil pH	5.8	3.8	3.7
Cation exchange capacity ( $\mu\text{eq}/100\text{ g}$ )	16.6	11.1	14.4
Organic carbon (%)	1.8	1.8	1.1

**Table 2.** Coefficients of variation (standard deviation/mean) for within-treatment variation in soil solution chemistry. All lysimeters were analyzed individually for one collection (mid-May 1979); 10 lysimeters were in place in each treatment, but not all lysimeters yielded a sample

	Maple		Oak		Pine	
	Control	Trenched	Control	Trenched	Control	Trenched
NH <sub>4</sub>	1.75	1.75	1.12	0.66	1.50	1.05
Ca	0.40	0.15	0.33	0.43	0.80	0.54
Mg	0.35	0.07	0.32	0.38	0.40	0.48
Na	0.36	0.13	0.30	0.52	0.64	0.96
K	0.51	0.57	0.66	1.04	0.35	0.69
NO <sub>3</sub>	1.75	0.50	0.73	0.35	1.50	0.37
SO <sub>4</sub>	0.27	0.23	0.17	0.22	0.29	0.34
Cl	0.59	0.30	0.21	0.26	0.58	0.56

bin by site and treatment to yield a weekly composite sample. Each such sample was analyzed for pH and bicarbonate alkalinity (by potentiometric titration) the day of collection, then stored for at most a month at 4 C with 0.5 mg/kg phenylmercuric acetate added as a preservative. Samples were then analyzed for calcium, magnesium, sodium, and potassium by atomic absorption spectrophotometry (with LaCl<sub>2</sub> in HCl added to suppress interferences), and for ammonium, nitrate, sulfate, and chloride with a Technicon AutoAnalyzer II.

Variation within sites and treatments was assessed by analyzing the sample from each lysimeter individually for one collection in May 1979. The coefficients of variation obtained were relatively high (Table 2), especially for the minor constituents (i.e. ammonium) and for the pine site. If the variability in Table 2 is typical, standard errors for the composited samples were generally 10–25% of the means for the major ions.

Bulk precipitation was collected in two open polyethylene-lined collectors (surface area 163 cm<sup>2</sup>) in each site. The polyethylene liners containing the samples were removed each week and replaced with fresh liners. The chemical analysis of bulk precipitation followed the same procedures as for lysimeters. Litterfall was collected in each site as described in Vitousek et al. 1982, and calcium, magnesium, sodium, and potassium analysis of the litter followed the dry ashing procedure of Reiners and Reiners (1970).

## Results and discussion

The results for bulk precipitation chemistry are summarized in Table 3. Ion concentrations were similar in the sites, and as there was no reason to anticipate systematic differences among the sites, the mean of the 3 was used as the best estimate of precipitation chemistry in the region.

The charge balance calculated from the precipitation analyses was not close – cations totalled 191 µeq/liter, while anions totalled 150. Three possible explanations for this discrepancy are an unmeasured anion, analytical errors, and uncharged species analyzed as “cations.” The first was ruled out because there were no candidates, and because the sum of the equivalent conductances of individual ions was less than the measured conductivity. The second is unlikely because the charge balance in the lysimeter solutions was close. Uncharged particulates contributing to the “cations” measured are a reasonable possibility; the region is a mosaic of forested and agricultural land with many

**Table 3.** Precipitation chemistry in the 3 sites. All are volume-weighted mean concentrations in µeq/l

	Maple	Oak	Pine	Mean
H	96	79	86	87 (pH 4.06)
NH <sub>4</sub>	29	28	25	27
Ca	37	57	49	48
Mg	6	10	8	8
Na	7	13	7	9
K	14	15	9	13
NO <sub>3</sub>	38	38	35	37
SO <sub>4</sub>	95	107	96	99
Cl	14	12	14	13

unsurfaced roads, and dust would be trapped by the collectors used.

This problem aside, hydrogen ions were the dominant cation in precipitation, followed by calcium and ammonium. Sulfate was the dominant anion, followed by nitrate. Precipitation in the region can be viewed as a dilute solution of sulfuric acid; the hydrogen ion concentration corresponds to a pH of 4.1.

Results of the lysimeter sampling are summarized in Fig. 1. Arithmetic (unweighted) means are reported; the volume of water sampled each week could not be related to the volume percolating past that depth in the soil. The use of arithmetic means would introduce bias if solution chemistry varied seasonally or between collections; such variations were not systematically observed in the control plots, but there was a tendency towards higher concentrations in summer and fall in the trenched plots. The charge balances calculated for the lysimeter solutions were always within 10% and generally within 5% (Fig. 1).

The soil solution in control plots was similar to that in other acid precipitation-dominated areas (cf. Cronan 1980). Sulfate was the dominant anion in all 3 sites, and nitrate only contributed significantly to leaching in the maple site. Bicarbonate concentrations were also low – most cation leaching was driven by sulfate. Sulfate is relatively immobile in some temperate soils (Johnson et al. 1980), but it moved to below the rooting zone in these sites (Fig. 1) and apparently on to streams (Frey 1976). In fact, more sulfate was present in control lysimeters than could be accounted for by bulk precipitation inputs, even correcting for water lost in evapotranspiration. Gaseous and particulate sulfur inputs (Eaton et al. 1978) could have supplied the remainder.

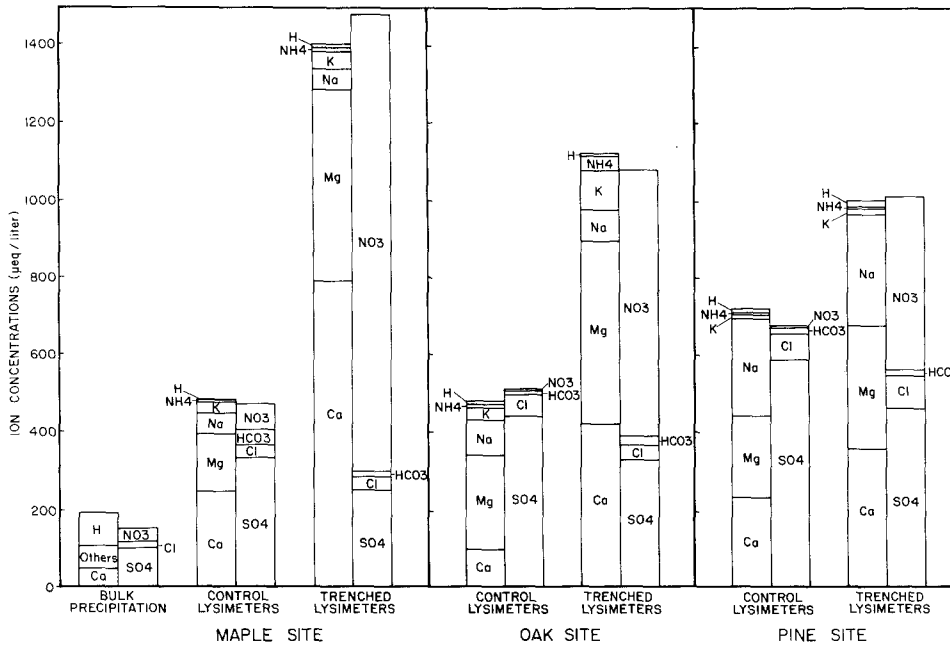


Fig. 1. Mean cation and anion concentrations ( $\mu\text{eq/l}$ ) in bulk precipitation and in control and trenched plot lysimeters in the study sites

The cations in lysimeter leachate in control plots were different from those in bulk precipitation. Hydrogen ion was largely retained within the sites, as was ammonium. Calcium and magnesium were major cations in all 3 sites; sodium was of equal importance in the pine site. These cations were mobilized from the exchange complex in association with sulfate; they were probably replaced (in the short term) with hydrogen ions.

Trenching caused large increases in nitrate concentrations below the rooting zone in all 3 sites (Fig. 1). Water flux through the trenched plots was also increased, so the results reported understate the true magnitude of the increase in nitrate losses following trenching. The concentrations of anions other than nitrate generally decreased in trenched plots. This decrease could be explained as dilution of a constant amount of anion by an increased water flux, but it has also been suggested that high nitrate levels affect sulfur transformations or sulfate mobility (Nodvin 1982).

Nitrate concentrations increased more rapidly and to higher levels in the relatively fertile maple site than in the others; concentrations were lowest in the relatively infertile pine plantation (Vitousek et al. 1982). Nitrate production eventually led to greater total anion strength in trenched plots in all sites, however, and cation leaching was increased equivalently. The relative importance of individual cations leached from trenched plots was similar to that in control plots, except that the divalent cations were a relatively greater proportion of the total cation strength following trenching.

Because vegetation regrowth was excluded from the trenched plots, these results exaggerate the nitrate losses that could be observed after clearfelling or most other large-scale disturbances. Losses of nitrate and associated cations comparable to those observed here have been reported in large-scale experiments only where revegetation was inhibited with herbicides (Likens et al. 1970). In contrast, commercial clearfelling generally increased nitrate losses, but the increases are substantial in relatively few sites (Vitousek and Melillo 1979). Commercial clearfelling increased nitrate

production in southern Indiana soils (Matson and Vitousek 1981), but no information on leaching losses from such clearcut sites is available.

The magnitude of sulfate-driven leaching in the control plots and nitrate-driven leaching in trenched plots is compared with other element pools and fluxes in these sites in Table 4. A number of assumptions were necessary to calculate areal estimates for leaching; these are described in Table 4. While inexact, the calculated fluxes are useful in showing the relative magnitude of leaching. They show that the exchangeable pool of metallic cations in these sites was large relative to inputs, outputs, or biotic cycling of cations. The cations in this pool could be readily leached if enough mobile anions (and associated hydrogen ions) were added. In contrast, the nitrate pool sizes in the soils were small relative to either nitrogen cycling or to nitrogen losses upon disturbance. These pools were maintained by mineralization, nitrification, and plant nitrogen uptake in the intact forests, and when uptake was disrupted both nitrate and cation losses increased.

These results demonstrate the usefulness of the anion mobility model in understanding leaching losses. External sulfate loading caused cation leaching prior to disturbance. When nitrate (and associated hydrogen ion) production and loss were elevated by disturbance, the consequent increase in total anion strength caused an equivalent increase in total cation losses. The particular cations lost were controlled by ion exchange processes, but total losses were controlled by the supply of mobile anions.

Despite increased anion supply, the large exchangeable pool of cations buffers these sites against rapid nutrient depletion. Cation losses in the control plots were probably elevated over preindustrial levels due to excess sulfate depositions, but they were still only 1–2% of the exchangeable cation pools on the site. The increased cation losses caused by nitrate losses were greater, but less than 10% of the exchangeable pools. Of course, excess sulfate deposition is a chronic phenomenon, while disturbance is episodic.

The long-term consequences of cation removals result-

**Table 4.** Annual fluxes of ions (in meq/m<sup>2</sup>) in the 3 sites in comparison with available pools in the soil. Fluxes of ions in bulk precipitation calculated as concentrations (Table 3) times precipitation volume for the 14-month sample period, converted to an annual basis (127.6 cm). Fluxes past lysimeters calculated as volume times mean concentrations, assuming 60 cm of water flux past control lysimeters (with the remainder lost to evapotranspiration), and 94 cm past trenched-plot lysimeters (with the remainder lost to interception and evaporation). Litterfall is tree and shrub stratum litterfall alone in the oak and pine sites, but it includes spring ephemerals (Blank et al. 1980) for the maple site (where they were abundant). Soils data from Vitousek et al. (1982); pool sizes to 70 cm depth in the soil

	Precipitation	Available in Soil	Circulated in Litterfall	Control Lysimeters	Trenched Lysimeters
<b>Maple</b>					
H	110			2	9
NH <sub>4</sub>	34	180		3	6
Ca	61	18,000	450	150	740
Mg	10	3,700	89	89	470
Na	11	1,100	18	31	50
K	15	1,700	100	17	43
NO <sub>3</sub>	47	67		38	1,100
SO <sub>4</sub>	130			200	230
Cl	17			20	33
HCO <sub>3</sub>	–			24	13
Total N	81 <sup>a</sup>	43,000 <sup>b</sup>	380	41 <sup>a</sup>	1,109 <sup>a</sup>
<b>Oak</b>					
H	110			7	8
NH <sub>4</sub>	34	290		3	32
Ca	61	13,000	380	59	390
Mg	10	7,300	91	140	440
Na	11	1,100	22	54	76
K	15	4,000	110	20	98
NO <sub>3</sub>	47	18		2	650
SO <sub>4</sub>	130			260	310
Cl	17			32	35
HCO <sub>3</sub>	–			7	23
Total N	81 <sup>a</sup>	44,000 <sup>b</sup>	440	5 <sup>a</sup>	682 <sup>a</sup>
<b>Pine</b>					
H	110			8	16
NH <sub>4</sub>	34	79		2	4
Ca	61	28,000	170	140	340
Mg	10	12,100	66	130	300
Na	11	2,400	18	150	270
K	15	2,800	64	6	13
NO <sub>3</sub>	47	7	1	420	
SO <sub>4</sub>	130			350	430
Cl	17			42	79
HCO <sub>3</sub>	–			10	17
Total N	81 <sup>a</sup>	23,400 <sup>b</sup>	360	3 <sup>a</sup>	424 <sup>a</sup>

<sup>a</sup> Ammonium-nitrogen plus nitrate-nitrogen only – dissolved organic nitrogen not determined

<sup>b</sup> Total organic nitrogen pool, not available nitrogen. Available nitrogen (by incubation) in Vitousek et al. (1982)

ing from either atmospheric deposition or disturbance are difficult to predict. Magnesium appears to be more likely to become depleted than calcium or potassium, a result which has previously been reported in north Germany (Ulrich et al. 1980). Weathering of soil minerals could replace cations if losses are slower than weathering. In these sites estimated sulfate losses (200–350 meq·m<sup>-2</sup>·yr<sup>-1</sup>) are greater than normal weathering rates for silicate minerals (20–200 meq·m<sup>-2</sup>·yr<sup>-1</sup>) (Ulrich et al. 1980), and there is a potential for cation depletion of surface soils in the long run.

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