

Atmospheric Pollutants

Ion Leaching in Forest Ecosystems along a Great Lakes Air Pollution Gradient

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ABSTRACT

A gradient of H^+ , SO_4^{2-} , and NO_3^- deposition across the Great Lakes region raised concerns over impacts on soil solution chemistry and ion leaching in regional forest ecosystems. Ten study sites representing northern hardwood and oak ecosystems were established across the gradient of increasing deposition from Minnesota to Ohio. Lysimeters were installed at lower E and lower B horizon boundaries at each site and sampled over a 2-yr period. In soil solutions collected at lower E horizon boundaries, H^+ and SO_4^{2-} wet deposition were correlated with solution concentrations of SO_4^{2-} ($r = 0.82^{**}$ and 0.92^{**}) and Mg^{2+} ($r = 0.75^{**}$ and 0.85^{**}), and with the SO_4^{2-} /inorganic anion ratio ($r = 0.71^{**}$ and 0.70^{**}). In soil solutions collected at lower B horizon boundaries, SO_4^{2-} deposition was correlated with solution SO_4^{2-} concentrations ($r = 0.92^{**}$). Greater ionic outputs from B horizons than atmospheric inputs indicated that net losses of Ca^{2+} and Mg^{2+} were occurring from all sites. Sulfate outputs above background levels contributed 33 to 2367 mol SO_4^{2-} ha^{-1} yr^{-1} from north to south along the gradient, equal to 3.7 to 71.7% of annual cation outputs. Excess H^+ deposition accounted for 8 to 34% of annual cation outputs from north to south, and as much as 72% at one site with coarse-textured soils. Elevated cation losses related to H^+ and SO_4^{2-} deposition indicate that cation depletion remains a plausible consequence of pollutant deposition to forest ecosystems with poorly buffered soils.

ATMOSPHERIC POLLUTANT DEPOSITION has been a focal issue in forest ecosystem research for the past 20 yr. Much effort has centered on determining the extent to which elevated pollutant (H^+ , SO_4^{2-} , NO_3^-) deposition results in increased leaching of cations from forest ecosystems (e.g., Johnson et al., 1983; Binkley and Richter, 1987; Johnson and Taylor, 1989). Many site-specific studies of the effects of atmospheric deposition on soil solution chemistry and ion leaching in forest ecosystems have been conducted (e.g., Mollitor and Raynal, 1982; Foster, 1985; Johnson and Todd, 1990). Few previous studies have examined the effects of pollutant deposition on soil solution chemistry and ion leaching in forest ecosystems at multiple sites located across regional gradients of air pollutant deposition.

A pronounced gradient of atmospheric pollutant deposition exists across the Great Lakes region (Armentano and Loucks, 1983; Schwartz, 1989; MacDonald et al., 1991a). Annual wet SO_4^{2-} -S deposition increases from less than 3.5 kg ha^{-1} in northern Min-

nesota to greater than 12 kg ha^{-1} in northern Ohio. Annual wet NO_3^- -N deposition increases from less than 2 kg ha^{-1} in northern Minnesota to greater than 5 kg ha^{-1} in Ohio. Precipitation pH follows a similar trend, ranging from greater than 5.0 at the northern end of the gradient to around 4.3 at the southern end. Historical evidence suggests this gradient has persisted for at least 30 yr (Glass and Loucks, 1986).

We studied the effects of airborne pollutants on northern hardwood and oak forest ecosystems between 1987 and 1990 at multiple sites located along the deposition gradient from northern Minnesota to northern Ohio. The objectives of the study reported here were to determine the impacts of pollutant deposition on soil solution chemistry and ion leaching at six northern hardwood and four oak forest sites along the Great Lakes air pollution gradient. Overall hypotheses to be tested were that (i) soil solution chemistry is directly affected by atmospheric pollutant deposition, and (ii) cation leaching is directly related to atmospheric pollutant deposition.

METHODS

Site Selection and Description

Sites representing the northern hardwood ecosystem were selected for study based on (i) previously documented regional differences in pollutant deposition rates (Armentano and Loucks, 1983; Glass and Loucks, 1986), (ii) similarity of overstory species composition and structure ($\geq 75\%$ of total basal area as sugar maple, *Acer saccharum* Marsh.), (iii) stand age, (iv) physiography, and (v) soil (Table 1). Sites 1, 2, 3, 4a, and 5 were selected to be as similar as possible (Burton et al., 1991; MacDonald et al., 1991a). Site 4b represents a separate northern hardwood ecosystem in terms of species composition, N cycling, and productivity (Zak et al., 1986), but with similar atmospheric inputs to Site 4a. The northern hardwood site locations are shown in Fig. 1.

Oak forest sites were selected in southern lower Michigan and northern Ohio to extend the gradient study into areas experiencing higher pollutant deposition rates than in the northern hardwood forest region. The three oak sites in southern lower Michigan (Sites 6, 7a, 7b, Fig. 1) represent distinct oak ecosystems characterized by different overstory species compositions related to soil texture and physiography (Table 1; Archambault et al., 1990). The northern Ohio oak site (Site 8, Fig. 1) was selected as representative of an area with high rates of atmospheric pollutant deposition, but otherwise was similar in many respects to Sites 7a and 7b. Overstory compositions at the oak sites were dominated by one or more of the following species: black oak (*Quercus velutina* Lam.), red oak (*Q. rubra* L.), or white oak (*Q. alba* L.).

The study sites span 6° of latitude and 9° of longitude

Abbreviations: NADP, National Atmospheric Deposition Program; NDDN, National Dry Deposition Network.

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Table 1. Locations, climatic conditions, and stand characteristics of research sites in the Great Lakes region.

	Site									
	1	2	3	4a	4b	5	6	7a	7b	8
Latitude (N)	47°41'	46°52'	45°33'	44°23'	44°21'	43°40'	42°27'	42°17'	42°17'	41°18'
Longitude (W)	90°44'	88°53'	84°51'	85°50'	85°42'	86°09'	84°00'	83°39'	83°39'	81°35'
Mean annual precipitation†(cm)	67	87	83	81	81	85	77	77	77	90
Actual evapo-transpiration‡(cm)	51	52	55	57	57	57	60	60	60	64
Mean annual temperature†(°C)	3.7	4.2	5.2	5.8	5.8	7.6	9.3	9.3	9.3	9.8
Stand age (yr)	78	79	73	74	76	78	47	119	104	105
Total stand basal area (m ² ha ⁻¹)	31.4	32.0	29.7	30.3	30.8	30.1	23.5	37.9	39.0	40.0
Dominant overstory species§ (%)	SM (90)	SM (86)	SM (87)	SM (83)	SM (78)	SM (75)	BO (99)	WO (51)	RO (47)	WO (45)
Soil texture¶	SL	LS	S	S	S	S	S	SL	L	CL

† 30-yr means, National Oceanic and Atmospheric Administration (1983).

‡ 30-yr means, Phillips and McCulloch (1972).

§ Dominant overstory species and percentage of total basal area. BO = black oak, RO = red oak, SM = sugar maple, WO = white oak.

¶ Dominant texture of the upper 75 cm of mineral soil. CL = clay loam, L = loam, LS = loamy sand, S = sand, SL = sandy loam.

(Table 1, Fig. 1). Climatic conditions thus differ unavoidably across locations (Table 1). Soil texture in the upper 75 cm at the northern hardwood sites varied from sand to sandy loam; soil texture at the oak sites varied from sand to clay loam (Table 1). Soils were well drained, with the exception of soils at Sites 1 and 8 that were moderately well drained. Soils were classified as follows: Site 1, coarse loamy, mixed, frigid Alfic Haplorthods and Alfic Fragiorthods; Sites 2 to 5, sandy, mixed, frigid Entic, Typic, and Alfic Haplorthods; Site 6, mixed, mesic Typic Udipsamments and sandy, mixed, mesic Psammentic Hapludalfs; Sites 7a and 7b, respectively, coarse loamy and fine loamy, mixed, mesic Typic Hapludalfs; and Site 8, fine, illitic, mesic Aquic Hapludalfs.

Plot Instrumentation and Sample Collection

Estimates of annual wet pollutant deposition at Sites 3 and 4 were obtained from existing National Atmospheric Deposition Program (NADP) sites at Pellston and Wellston, MI. To obtain site-specific estimates of wet pollutant deposition at Sites 1, 2, 5, 7, and 8, wet/dry precipitation collectors (Model 301, Aerochem Metrics Inc., Bushnell, FL) and weighing rain gauges (Model 5-780, Belfort Instrument Co., Baltimore MD) were located in open areas within 15 km of each study site. Wet deposition at Site 6 was estimated from precipitation collected between April and November in two bulk collectors consisting of 4-L polyethylene bottles fitted with 17-cm diam. polyethylene funnels. Bulk collectors also were colocated with the wet/dry collector at Site 7 to provide a means of comparison. Precipitation samples were collected on a weekly basis from July 1987 to September 1990, except at Site 8 where collection started in June 1988, and at Sites 1 and 2 where collection was terminated in March 1990.

Three 0.09-ha (30 m × 30 m) measurement plots were established at each site. Throughfall was collected at all sites from July to November in 1987, and from April to November in 1988 and 1989. Throughfall was collected weekly at all sites using five collectors per plot similar to the bulk precipitation collectors. At Sites 1 to 5, monthly (December–March) snowfall samples were collected on each plot in four 25-cm diam. galvanized steel tubes fitted with polyethylene collection bags. Snowfall was not collected at Sites 6 to 8 on measurement plots, but contribution of snowfall to annual throughfall was estimated from wet/dry collectors. Wet/dry collectors at these southern sites had 93

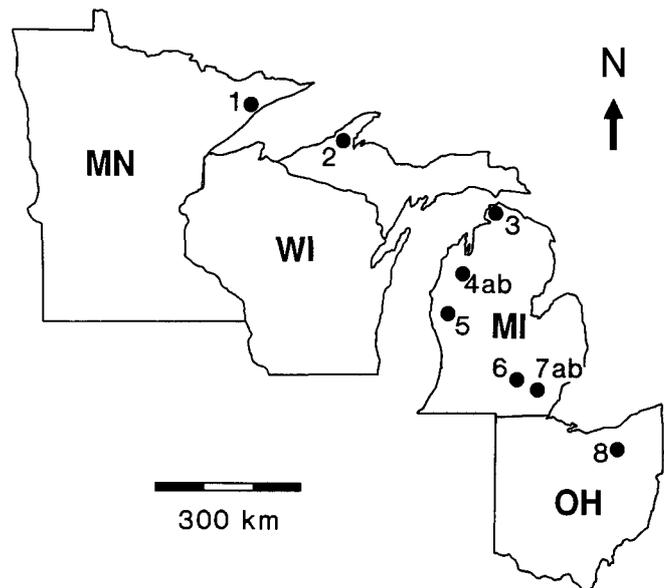


Fig. 1. Locations of forest research sites in the Great Lakes Region.

to 95% overall collection efficiencies during winter collection periods.

Four tension lysimeters (Model 1900, Soilmoisture Equipment Corp., Santa Barbara, CA) were installed at each of two soil depths on all measurement plots (24 total per site, 12 at each depth). Upper lysimeters were installed at 15 cm at northern hardwood sites and 30 cm at oak sites, approximating the lower boundary of soil E horizons. Lower lysimeters were installed at 75 cm at all sites except Site 1, where the presence of a fragipan necessitated installation at 60 cm. These depths approximated the lower boundary of soil B horizons. Lysimeters were installed during spring 1987 at the southern Michigan oak sites (Sites 6, 7a, 7b), during late fall and early winter of 1987 at the northern hardwood sites (Sites 1 to 5), and in May 1988 at the Ohio site (8). After an initial test period to permit equilibration, lysimeters were sampled every 2 wk during spring, summer, and fall from September 1988 to June 1990 at all sites. Lysimeters also were sampled approximately once per month

during December to March at the oak sites where a snow-pack did not develop. For each collection date, individual lysimeter volumes were measured and samples were composited by depth on each plot for analysis.

Three soil pits were sampled at each site, one pit associated with each measurement plot. Soils were sampled by horizon to a depth of 150 cm. MacDonald et al. (1991a) describe the soil sampling procedures employed, soil analyses performed, and analytical methods followed.

Water Sample Analysis

All water samples were returned to the laboratory and analyzed for pH and conductivity within 24 h if possible. For remote locations without laboratory facilities (Sites 1 and 8), samples were shipped to central laboratories in coolers for all analyses. Alkalinity, as HCO_3^- , was determined on unfiltered soil solution samples by titration with H_2SO_4 to pH 4.5 as soon after collection as possible (24 h–1 wk). Subsamples analyzed for anions and cations were filtered through 0.45- μ filters and stored at $\leq 5^\circ\text{C}$ prior to analysis. Anions (SO_4^{2-} , NO_3^- , F^- , Cl^- , PO_4^{3-}) were determined by ion chromatography within 4 wk of collection. Ammonium was determined by automated colorimetry (autoanalyzer/rapid flow analyzer) within 3 wk of collection. Calcium, Mg^{2+} , and K^+ were determined by atomic absorption spectrophotometry, either on fresh filtered samples within 4 wk of collection, or on HNO_3 -acidified samples if longer storage was required. All analyses included aqueous quality assurance and quality control samples provided by the U.S. Geological Survey and the USEPA/USFS Forest Response Program. All analyses included 10% replication as an internal quality control check.

Ionic Flux Estimates

Wet deposition was calculated on a weekly basis using analytical concentrations and measured rain gauge volumes. Throughfall ionic flux was similarly calculated from analytical concentrations and throughfall collector volumes. Missing precipitation and throughfall ionic concentrations were replaced with volume-weighted mean annual concentrations. Annual wet deposition and throughfall ionic fluxes were calculated by summing weekly deposition values by collection year.

Dry deposition fluxes were estimated by multiplying mean annual ambient gaseous and particulate concentrations by deposition velocities obtained from the literature. A multiyear (1984–1988) record of air concentration data from four dry deposition monitoring sites in northern Minnesota was provided by the Minnesota Pollution Control Agency, Air Quality Division (E.J. Orr, 1991, personal communication). Ambient gaseous and particulate concentrations at Site 1 were estimated as the mean of values measured at the Minnesota sites. A 2-yr record (1989–1990) of ambient air concentration data for three sites each in lower Michigan (ANA115, UVL124, WEL149) and Ohio (DCP114, OXF122, LYK123) was obtained from the National Dry Deposition Network (NDDN; Edgerton et al., 1991; B.R. Whitmire, 1991, personal communication). The NDDN site WEL149 is collocated with the NADP site at Wellston near Sites 4a and 4b, while NDDN Site ANA115 is located within 14 km of Site 6. Ambient gaseous and particulate concentrations at Site 8 were estimated as the mean of values determined at the three Ohio NDDN sites. Based on the Minnesota and NDDN data, ambient SO_4^{2-} , NO_3^- , NH_4^+ , HNO_3 , and SO_2 concentrations at Sites 2, 3, 5, and 7 could be predicted by latitude ($r^2 = 0.88\text{--}0.97$). Ambient Ca^{2+} , Mg^{2+} , and K^+ concentrations at Sites 2, 3, 4, 5, 7, and 8 were estimated from known ambient concentrations at Sites 1 and 6 using site/site cation ratios determined from wet deposition.

Deposition velocities (cm s^{-1}) for SO_2 (0.17), SO_4^{2-} (0.32), and NO_3^- (0.57) were those calculated for the Turkey Lakes Watershed by Sirois and Vet (1988). The deposition velocity for HNO_3 (2.47) was taken as the average of deposition velocities calculated for the Algoma and Experimental Lakes Area sites by Sirois and Barrie (1988). Deposition velocities for Ca^{2+} (0.74), Mg^{2+} (0.91), and K^+ (8.33) were calculated from dry deposition rates determined by Liechty et al. (1990) following methods used by Lovett and Lindberg (1984). The deposition velocity for NH_4^+ (0.30) was taken from Dasch (1986) and the deposition velocity for Cl^- (0.95) was taken from Hofken et al. (1983). Dry deposition of H^+ was calculated from HNO_3 and SO_2 deposition estimates, assuming complete conversion of dry deposited SO_2 to H_2SO_4 (Lindberg et al., 1986).

Soil solution ionic fluxes were estimated for the period October 1987 to October 1990 from volume-weighted mean seasonal (January–June, July–December) soil solution concentrations and monthly leaching losses calculated using the Thornthwaite water balance equation (Thornthwaite and Mather, 1957).

Statistical Analyses

Analyses of variance for soil property, wet deposition, and soil solution chemical concentration data were performed on untransformed data, with mean separation accomplished using Tukey's HSD test. Wet deposition analyses of variance were calculated from annual deposition values. Soil solution analyses of variance were calculated using volume-weighted plot means. Correlations among soil solution chemistry, soil property, and pollutant deposition variables were based on plot means ($n = 30$) and mean annual pollutant deposition for each site. Correlations among pollutant deposition inputs, throughfall fluxes, and soil solution ionic outputs were based on site means ($n = 10$). Dry deposition and ionic leaching flux estimates were not statistically compared among sites because of the uncertainties and assumptions involved in their calculation.

RESULTS AND DISCUSSION

Analytical accuracy, as determined from U.S. Geological Survey and USEPA/U.S. Forest Service Forest Response Program aqueous quality assurance and quality control samples, was typically within $\pm 10\%$ of known values for all analyses. Repeated measurement errors for major ions determined from replicate sample analyses ranged from 1.2% for SO_4^{2-} , NO_3^- , and Ca^{2+} , to 4.9% for Cl^- and NH_4^+ .

Pollutant Deposition

Results from 3 yr of precipitation sampling confirmed the presence of a pollution deposition gradient extending from Minnesota to Ohio (Table 2), corresponding both in magnitude and trend to past patterns of wet deposition reported for the Great Lakes region (Glass and Loucks, 1986; Zemba et al., 1988). Sulfate, NO_3^- and H^+ wet deposition increased significantly from north to south (Table 2), and were negatively correlated ($r = -0.72^{**}$ to -0.92^{**}) with both latitude and longitude, consistent with a regional gradient across the study sites.

Estimates of annual total dry SO_4^{2-} and NO_3^- deposition (Table 2) were similar to estimates made for Ontario, Canada, across the same regional pollution gradient (2.6–17.7 $\text{kg NO}_3^- \text{ ha}^{-1} \text{ yr}^{-1}$; 2.8–25.2 $\text{kg SO}_4^{2-} \text{ ha}^{-1} \text{ yr}^{-1}$; Barrie and Sirois, 1986; Sirois and

Table 2. Mean annual ionic deposition at eight sites in the Great Lakes region, 1 Oct. 1987 to 30 Sept. 1990.

Ion	Site							
	1	2	3	4	5	6†	7	8
	kg ha ⁻¹ yr ⁻¹							
	<u>Wet deposition</u>							
H ⁺ ***	0.07c	0.08c	0.31b	0.35b	0.30b	0.39	0.40b	0.64a
NO ₃ ⁻ **	8.78c	9.87bc	13.97bc	17.96abc	15.32bc	13.24	18.63ab	24.56a
SO ₄ ²⁻ ***	9.69c	10.59c	15.98bc	18.96bc	18.52bc	19.46	24.09b	36.55a
NH ₄ ⁺	3.14	3.01	3.02	3.76	3.78	3.53	4.44	4.60
Ca ²⁺	1.80	2.05	1.61	2.32	1.87	1.95	2.72	2.95
Mg ²⁺	0.50	0.69	0.29	0.46	0.74	0.31	0.53	0.57
K ⁺	0.91	0.82	0.16	0.20	0.52	0.42	0.45	0.84
Cl ⁻ *	1.27ab	1.51ab	0.86b	1.29ab	1.04ab	2.26	2.46ab	3.86a
	<u>Dry deposition</u>							
H ⁺	0.08	0.14	0.24	0.32	0.38	0.47	0.58	0.66
NO ₃ ⁻	3.70	7.08	11.79	16.40	18.47	23.63	30.73	29.34
SO ₄ ²⁻	2.60	4.26	6.87	8.14	10.62	11.84	13.54	18.81
NH ₄ ⁺	0.49	0.80	1.14	1.35	1.64	1.96	2.29	2.54
Ca ²⁺	0.32	0.35	0.55	0.65	0.62	0.95	1.23	1.07
Mg ²⁺	0.09	0.11	0.16	0.21	0.38	0.29	0.45	0.39
K ⁺	2.23	1.92	1.31	1.29	4.02	5.68	5.65	8.51
Cl ⁻	0.06	0.06	0.05	0.06	0.06	0.15	0.15	0.19

*, **, *** Means without common letters differ significantly at the probability levels 0.05, 0.01, and 0.001, respectively. Letters compare wet deposition rates across sites for a single ion. Dry deposition estimates were not statistically analyzed.

† Site 6 deposition values were estimated from a bulk collector and data were not included in the overall statistical analysis.

Barrie, 1988; Ro et al., 1988). Dry deposition estimates for NH₄⁺, Ca²⁺, Mg²⁺, and Cl⁻ were of the same order of magnitude as total annual dry deposition estimates for these ions from a network of Minnesota monitoring sites (E.J. Orr, 1991, personal communication). Estimated dry deposition of K⁺ was calculated from a deposition velocity (8.3 cm s⁻¹) lower than that reported for K⁺ dry deposition to an oak forest by Lovett and Lindberg (1984, 10.7–19.1 cm s⁻¹), so these estimates should be conservative. Estimates of H⁺ dry deposition were consistent with estimates made by Lindberg et al. (1986), dry deposition of H⁺ approximately equaling wet deposition of H⁺.

The primary sources of free acidity in precipitation are H₂SO₄ and HNO₃, which form as the result of photochemical oxidation of anthropogenic S and N oxides in the atmosphere (Galloway et al., 1976; Barrie, 1981). Elevated levels of H⁺, NO₃⁻, and SO₄²⁻ in incoming precipitation are all symptomatic of pollutant deposition. As H⁺ and NO₃⁻ are readily consumed by a variety of forest ecosystem processes, SO₄²⁻ tends to remain as a marker that can be used to assess the overall magnitude of deposition impacts, however.

Soil Properties

Soil properties, summed for the upper 75 cm of the soil profile, varied among sites (Table 3). Silt content was high at Sites 1, 7b, and 8, with high clay content in the Alfisols at Sites 7b and 8. Trends in both water soluble and adsorbed SO₄²⁻-S followed observed trends in SO₄²⁻ deposition. Elevated SO₄²⁻-S content at Site 1 was related to high SO₄²⁻ adsorption ability combined with impeded drainage favoring SO₄²⁻ accumulation. High SO₄²⁻ deposition combined with both high SO₄²⁻ adsorption ability and impeded drainage accentuated soil SO₄²⁻-S content at Site 8. Exchangeable cation contents were correlated with clay content ($r = 0.76^{**}$ – 0.97^{**}), largely reflecting soil parent material influences.

Soil Solution Chemistry

In soil solution collected at lower E horizon boundaries, increases in solution conductivity, SO₄²⁻, and Mg²⁺ from Site 1 to Site 8 were statistically significant (Table 4, Fig. 2). Solution conductivity was correlated with wet deposition of SO₄²⁻ ($r = 0.74^{**}$) and H⁺ ($r = 0.69^{**}$). Wet deposition of SO₄²⁻ was strongly correlated with solution concentrations of SO₄²⁻ ($r = 0.92^{**}$) and Mg²⁺ ($r = 0.85^{**}$). Sulfate and Mg²⁺ solution concentrations were similarly correlated with H⁺ deposition ($r = 0.82^{**}$ and 0.75^{**}). Both the SO₄²⁻ to total inorganic anion and the SO₄²⁻ to total cation ratios were correlated with SO₄²⁻ deposition ($r = 0.70^{**}$ and 0.68^{**}) and increased significantly from Site 1 to Site 8 (Table 4). Trends in these ratios clearly demonstrate the increasing dominance of SO₄²⁻ in soil solution as H⁺ and SO₄²⁻ deposition increased across the gradient.

In soil solutions collected at lower B horizon boundaries, deposition effects were less noticeable, but still present. Soil solution SO₄²⁻ concentrations were highly correlated with both SO₄²⁻ deposition ($r = 0.92^{**}$) and water extractable SO₄²⁻ in the upper 75 cm of mineral soil ($r = 0.91^{**}$), and increased significantly across the gradient (Fig. 2). As a result of neutralization, exchange, and dissolution reactions within the soil profile, conductivity ($r = 0.92^{**}$), Ca²⁺ ($r = 0.96^{**}$), Mg²⁺ ($r = 0.82^{**}$), and pH ($r = 0.59^{**}$) were positively correlated with HCO₃⁻ (Table 4, Fig. 2). Solution Ca²⁺ and Mg²⁺ concentrations also were correlated with upper 75 cm soil exchangeable Ca²⁺ ($r = 0.89^{**}$) and Mg²⁺ ($r = 0.86^{**}$) contents.

Sites with finer-textured soils (1, 7a, 7b, 8) tended to have higher solution SO₄²⁻ concentrations (Fig. 2), a result of lower leaching rates related to soil texture and structure favoring SO₄²⁻ accumulation. This effect is most apparent when comparing Sites 6, 7a, and 7b where soil textures varied from sand to loam (Table

Table 3. Mineral soil properties in the upper 75 cm at forest research sites in the Great Lakes region.

Property	Site									
	1	2	3	4a	4b	5	6	7a	7b	8
	Mg ha ⁻¹									
Silt***	2624bc	1375cd	731d	670d	610d	590d	752d	1858bcd	3383b	5063a
Clay***	531b	570b	442b	287b	377b	303b	312b	1274b	2859a	3342a
	kg ha ⁻¹									
H ₂ O extractable SO ₄ ²⁻ -S***	31bc	12c	13c	11c	15c	21c	37bc	38bc	65b	172a
Adsorbed SO ₄ ²⁻ -S***	74ab	13bc	7bc	8bc	5c	20bc	23bc	16bc	19bc	138a
SO ₄ ²⁻ -S adsorption potential***	221a	127ab	69b	70b	64b	104b	78b	96b	73b	134a
Exchangeable Ca ²⁺ ****	3064cd	1724cd	2055cd	588d	1918cd	740d	576d	9276ab	13698a	6851bc
Exchangeable Mg ²⁺ ****	402c	449c	390c	69c	189c	81c	138c	1808bc	2893ab	4097a
Exchangeable K ⁺ ****	441cd	205d	126d	132d	139d	101d	189d	638bc	1203a	869ab

*** Means without common letters differ significantly at the probability level of 0.001. Letters compare means across sites for a single soil property.

1) but where SO₄²⁻ deposition was similar. The presence of calcareous C horizons produced increases in conductivity, Ca²⁺, Mg²⁺, and HCO₃⁻ with depth at Sites 3, 7a, 7b, and 8. High NO₃⁻ concentrations at both depths at Site 4b (Fig. 2) resulted from episodic defoliation by the forest tent caterpillar (*Malacosoma disstria* Hübner) and high nitrification rates typical in this northern hardwood ecosystem (Zak et al., 1986). Elevated NO₃⁻ concentrations at Sites 1 and 7b also were related to higher nitrification rates (Hua, 1990; Spiguel, 1990).

The relationships observed in soil solution chemistry at both sampling depths were consistent with hypothesized effects of acidic deposition, overriding effects related to underlying variation in ecosystem properties. Removal of acidity as water moved through the soil profile occurred as expected (Table 4; Richter et al., 1983; Reuss et al., 1987), resulting in mobilization of nutrient cations. Increased soil solution SO₄²⁻ and cation concentrations and increased conductivity resulting from elevated H⁺ and SO₄²⁻ deposition were evident (Fig. 2, Table 4; Reuss, 1983; Abrahamsen and Stuanes, 1986; Richter et al., 1988). The strong relationships among H⁺ and SO₄²⁻ deposition, SO₄²⁻ solution concentration, and Mg²⁺ solution concentration were consistent with the results of Johnson and Todd (1990), who concluded that SO₄²⁻-

dominated leaching was the major cause of Mg²⁺ export in three out of four deciduous forest sites studied in Tennessee. While Ca²⁺ was the dominant cation in soil solution, the ratio of Mg²⁺/Ca²⁺ in B horizon soil solution (0.27–1.22) was consistently higher than the Mg²⁺/Ca²⁺ ratio on the soil exchange complex (Table 3, 0.17–1.09). This suggests a preferential leaching of Mg²⁺, possibly related to ion selectivity differences.

The mobile anion concept holds that SO₄²⁻ concentrations elevated above background levels require an equivalent net increase in cation concentrations (Johnson, 1980; Reuss et al., 1987). While this may not be the controlling force behind cation leaching (Hendershot et al., 1991), the relative dominance of SO₄²⁻ in soil solution is a strong indicator of the magnitude of pollution deposition impacts on solution chemistry. On a charge basis, SO₄²⁻ balanced 24 to 44% of cations in solution at less polluted northern sites as compared to 57 to 97% of cations in solution at more polluted southern sites (Table 4). We do not imply that "cation leaching is caused by SO₄²⁻ leaching," but it is clear that leaching of cations displaced by H⁺ is facilitated by abundant mobile SO₄²⁻ at the more polluted sites. It is also important to recognize that the observed changes in solution chemistry are not simply ecosystem differences between northern hard-

Table 4. Mean soil solution chemical characteristics at two depths at forest research sites across the Great Lakes region.

Property	Depth†	Site									
		1	2	3	4a	4b	5	6	7a	7b	8
pH	LE**	5.3bc	5.6abc	5.9ab	5.1c	5.6abc	5.2bc	5.6abc	6.2a	5.9ab	5.3bc
	LB***	5.4c	5.5c	6.9a	6.3abc	6.1abc	6.6ab	6.0abc	6.7a	6.8a	5.7bc
Conductivity (mS m ⁻¹)	LE***	2.9b	3.2b	3.7b	4.1b	8.1a	4.3b	3.7b	7.4a	7.3a	8.2a
	LB***	3.3cd	2.6d	6.7bcd	3.4cd	5.7bcd	3.7cd	4.1cd	13.1b	22.3a	11.8bc
SO ₄ ²⁻ /anion ratio	LE***	0.34e	0.24e	0.36de	0.52cd	0.24e	0.58abc	0.72ab	0.52cd	0.54bc	0.75a
	LB***	0.27c	0.24c	0.22c	0.44abc	0.24c	0.47abc	0.70a	0.36bc	0.20c	0.66ab
SO ₄ ²⁻ /cation ratio	LE***	0.44cd	0.29d	0.24d	0.35cd	0.19d	0.40cd	0.86ab	0.57c	0.60bc	0.97a
	LB***	0.28b	0.36b	0.23b	0.47ab	0.24b	0.55ab	0.85a	0.38b	0.23b	0.80a

** , *** Means without common letters differ significantly at the probability levels of 0.01 and 0.001, respectively. Letters compare means across sites within the same depth.

† Sampling depth: LE = 15 cm at Sites 1 to 5, 30 cm at Sites 6 to 8. LB = 60 cm at Site 1, 75 cm at all other sites.

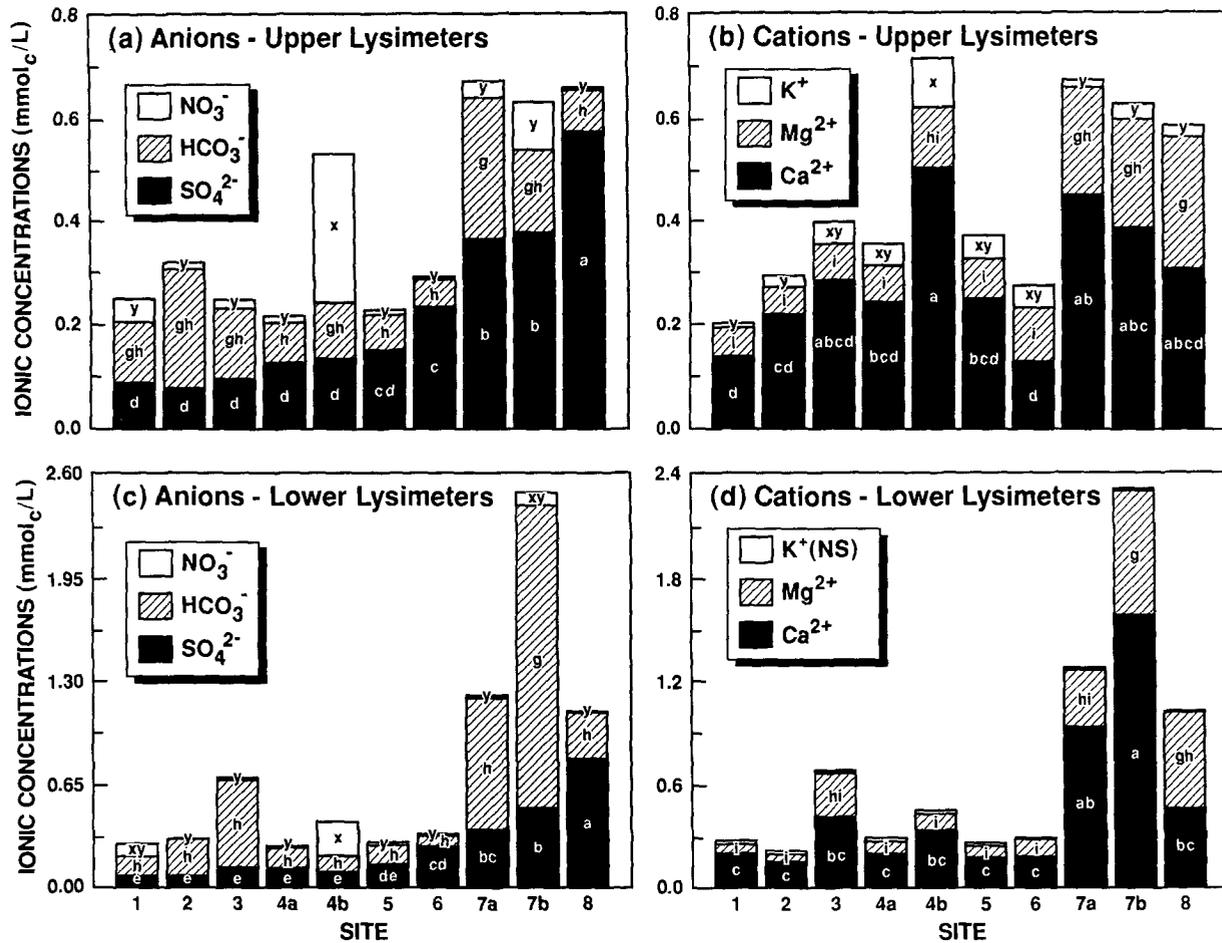


Fig. 2. Volume-weighted mean annual soil solution ionic concentrations at forest research sites across the Great Lakes region. Bars without common letters differ significantly at $P \leq 0.01$; letters compare means across sites for a single ion.

wood and oak forests. Similar relationships between pollutant deposition and soil solution chemistry were apparent and statistically significant when only data for the analogous northern hardwood sites (1, 2, 3, 4a, 5) were considered (MacDonald et al., 1991b).

The increasing dominance of SO_4^{2-} in solution as SO_4^{2-} deposition increased across the gradient strongly supports the hypothesis that soil solution chemistry has been directly affected by pollutant deposition. Significant relationships among H^+ and SO_4^{2-} deposition, soil solution SO_4^{2-} concentrations, and soil solution cation concentrations are consistent with the hypothesis that nutrient cation leaching has been increased by pollutant deposition. Similar conclusions were reached by Johnson et al. (1985) for two deciduous forest ecosystems in Tennessee and by Foster et al. (1986) for a northern hardwood ecosystem in Ontario, Canada.

Ecosystem Ionic Fluxes

Ecosystem fluxes of major ions were categorized as inputs or outputs relative to the movement of solution into or out of the soil (Fig. 3). Inputs included measured wet deposition plus estimated dry deposition to the canopy. Throughfall fluxes represent the net effect of dry deposition, leaching, and exchange reactions in the canopy on ionic inputs to the soil. Outputs in soil

solution were calculated for ionic constituents exiting from E horizons and from B horizons. B horizon output less than total input indicates a net retention of an ion within the ecosystem; output greater than input indicates a net loss of an ion.

Throughfall fluxes (Fig. 3) were positively correlated with total wet plus dry inputs for H^+ , NO_3^- , Ca^{2+} , and SO_4^{2-} ($r = 0.81^{**}$ – 0.99^{**}). Increases in SO_4^{2-} in throughfall are highly related to total SO_4^{2-} dry deposition (Garten et al., 1988; Lindberg and Garten, 1988). In comparison, NO_3^- tends to be absorbed in the canopy (Lindberg et al., 1986; Shepard et al., 1989); while Ca^{2+} , Mg^{2+} , and K^+ are enriched in throughfall from dry deposition and foliar leaching (Lovett and Lindberg, 1984; Johnson et al., 1985). Hydrogen is consumed in the canopy as a result of exchange reactions (Richter et al., 1983; Foster, 1985).

Comparison of total estimated atmospheric ionic inputs with ionic outputs from B horizons (Fig. 3) showed that Ca^{2+} and Mg^{2+} were lost from all sites along the gradient. Outputs of K^+ were variable, with sites having high estimated dry deposition of K^+ displaying net gains. Sulfate outputs from both E and B horizons were strongly correlated with wet plus dry SO_4^{2-} deposition and throughfall SO_4^{2-} flux ($r = 0.95^{**}$ – 0.98^{**}). Estimated SO_4^{2-} outputs were slightly less than inputs at Sites 1 to 3, but equaled or exceeded inputs at Sites

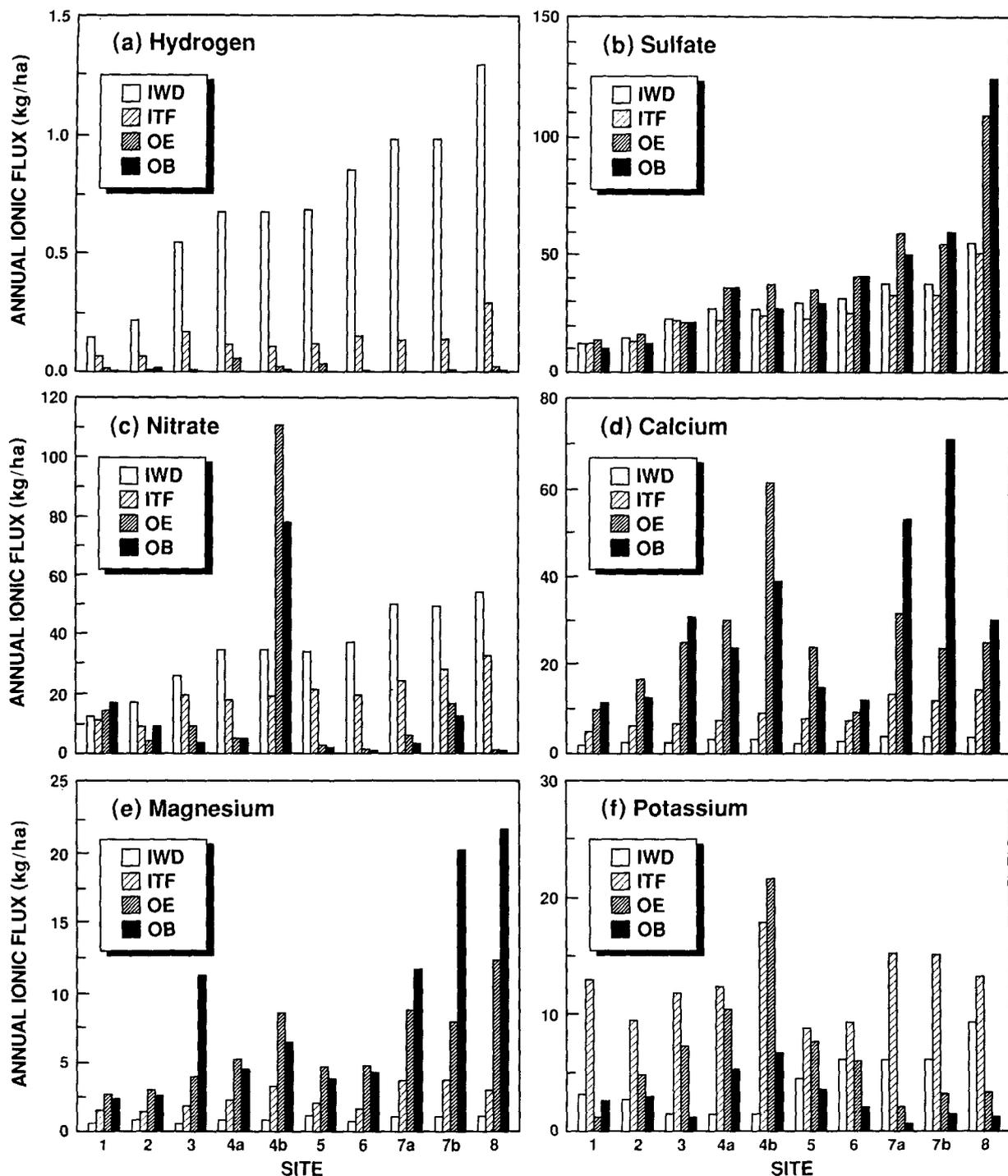


Fig. 3. Mean annual ionic input/output balances for forest research sites across the Great Lakes region, 1987 to 1990. IWD = total wet plus dry deposition ionic input, ITF = ionic input in throughfall, OE = ionic output below lower E horizon boundary, OB = ionic output below lower B horizon boundary.

4a to 8. Site 1 exhibited slight net losses of NO_3^- as a result of nitrification, similar to the Turkey Lakes Watershed in Ontario (Foster et al., 1989). Site 4b experienced extremely high rates of NO_3^- loss related to severe defoliation coupled with inherently high rates of nitrification. At this site, internal H^+ and NO_3^- production as a result of nitrification was the driving force behind high rates of cation leaching (Fig. 3). Immobilization of atmospherically deposited NO_3^- at the ma-

jority of our sites suggests that NO_3^- deposition had little or no direct influence on cation leaching (Johnson et al., 1985). All sites had close to 100% retention of NH_4^+ (N.W. MacDonald, 1992, unpublished data).

Greater output than input of Ca^{2+} , Mg^{2+} , and SO_4^{2-} were consistent with findings for other hardwood ecosystems in the northeastern USA and Canada (Foster et al., 1986; Lynch and Corbett, 1989; Shepard et al., 1989). Greater SO_4^{2-} outputs than inputs at the more

southerly sites might be related to mineralization of stored organic S or desorption of previously adsorbed SO_4^{2-} in response to reduced S deposition (Dillon et al., 1988; Driscoll et al., 1989) over the past decade. Outputs of SO_4^{2-} greater than inputs also could represent underestimation of dry S deposition (Richter et al., 1983), overestimation of annual leaching losses by the water balance method, or tension lysimeter samples not accurately reflecting true soil solution SO_4^{2-} concentrations in finer-textured soils.

Since SO_4^{2-} inputs are strongly tied to H^+ inputs, the proportion of cation outputs balanced by SO_4^{2-} is one indication of the overall effect of pollutant deposition on cation leaching. Assuming SO_4^{2-} outputs from Site 1 represent background levels of SO_4^{2-} output (294 mol_c SO_4^{2-} ha⁻¹ yr⁻¹ from E horizons; 218 mol_c SO_4^{2-} ha⁻¹ yr⁻¹ from B horizons; as suggested by Johnson et al., 1985), then atmospheric deposition, mineralization of organic S, and desorption of SO_4^{2-} contributed from 43 to 1978 mol_c SO_4^{2-} ha⁻¹ yr⁻¹ leaching from E horizons, and 33 to 2367 mol_c SO_4^{2-} ha⁻¹ yr⁻¹ leaching from B horizons at Sites 2 to 8. These excess mobile anions balanced 3.6 (Site 2) to 84.8% (Site 8) of nutrient cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+$) leaching from below E horizons, and 3.7 to 71.7% of nutrient cations leaching from below B horizons. In comparison, Foster et al. (1986) estimated excess SO_4^{2-} contribution of 330 mol_c ha⁻¹ yr⁻¹ associated with 21% of annual base cation leaching for the Turkey Lakes Watershed in Ontario. The degree to which cation leaching has been facilitated by SO_4^{2-} outputs is uncertain, since SO_4^{2-} added to soils may interact with organic anions or HCO_3^- so that increased leaching is not directly equivalent to SO_4^{2-} losses (Hendershot et al., 1991). In addition, we do not have any true baseline data to determine with certainty how much SO_4^{2-} was present in these ecosystems in a preindustrial unpolluted state.

Total estimated wet plus dry H^+ deposition in excess of background levels (Site 1) increased from 74 mol_c ha⁻¹ yr⁻¹ at Site 2 to 1137 mol_c ha⁻¹ yr⁻¹ at Site 8, suggesting that accelerated cation leaching of at least these magnitudes has been induced by H^+ exchange in the canopy and soil coupled with mobility of excess SO_4^{2-} in solution. Excess H^+ input explains 8 to 34% of cation leaching from Site 2 to Site 8, and as much as 72% at Site 6. To the extent that NH_4^+ in precipitation represents NH_3 combined with H^+ in the atmosphere (Munger, 1982), NH_4^+ deposition represents an additional input of H^+ to the ecosystem. At the sites we studied, NH_4^+ was largely taken up by plants either directly or after conversion to NO_3^- , since both NH_4^+ and NO_3^- losses were minimal at the majority of sites. Under these conditions, one H^+ would be generated in the ecosystem for each NH_4^+ deposited (Johnson et al., 1983; Binkley and Richter, 1987). Additional H^+ input in this form above background levels increased from 10 mol_c ha⁻¹ yr⁻¹ at Site 2 to 195 mol_c ha⁻¹ yr⁻¹ at Site 8.

Driscoll et al. (1989) determined that 77 to 82% of stream efflux of basic cations ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+$) at Hubbard Brook could be accounted for by cation inputs in bulk precipitation. In our study, total

estimated wet plus dry nutrient cation inputs could account for 7 to 35% of total nutrient cation outputs from B horizons. While estimated cation inputs tended to increase from north to south (Table 2), total cation outputs were significantly correlated with SO_4^{2-} and H^+ inputs ($r = 0.64^* - 0.68^*$), but not with total cation inputs. Our results suggest that differential rates of cation leaching at sites across the deposition gradient were most strongly related to H^+ and SO_4^{2-} inputs. Contribution of atmospheric cation deposition to total cation output was greatest at Sites 5 and 6 (30–35%), where soil nutrient cation reserves were low. This does lend support to the idea that the magnitude of atmospheric base cation input may be more important to rates of cation export in nutrient-poor forest ecosystems (Driscoll et al., 1989).

As a percentage of total exchangeable nutrient cation pools in the upper 75 cm of mineral soil, annual cation outputs below B horizons ranged from 1.9 to 4.5% at Sites 2 to 6, but $\leq 0.6\%$ at the other sites. On this basis, relative cation outputs were elevated where soils were coarse textured and nutrient cation pools were limited (Table 3). As a percentage of exchangeable nutrient cation pools in the upper 15 cm of mineral soil, annual cation outputs below E horizons averaged 1.2% at Sites 1, 7a, and 7b, but greater than 5% at all other sites. Upper 15 cm relative cation export at Sites 4a (15.0%), 6 (22.2%), and 8 (8.3%) were noticeably elevated. On this basis, relative cation outputs were again highest at sites with coarse-textured soils that were receiving moderately high pollutant loadings. Relative cation outputs also were elevated at Site 8, which has finer-textured soils but is experiencing high rates of pollutant deposition. In comparison, Richter et al. (1983) present data showing annual relative cation outputs ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+$) of 4.6 and 5.1% from the upper 15 cm of mineral soil in two deciduous forest ecosystems experiencing extremely high rates of SO_4^{2-} deposition (44 kg SO_4^{2-} ha⁻¹ yr⁻¹).

In the northern hardwood and oak sites studied, Mg^{2+} appeared to be preferentially leached relative to Ca^{2+} , with annual outputs of 0.5 to 6.4% of upper 75 cm soil exchangeable reserves, as compared to annual Ca^{2+} outputs of 0.4 to 4.0%. Annual losses of Mg^{2+} were highest (>3%) at sites with coarse-textured soils that were receiving moderately high pollutant loading (Sites 4a–6). In comparison to weathering rates reported for other eastern U.S. forest soils (Johnson et al., 1968; Likens et al., 1977; Adams and Boyle, 1979), K^+ losses appeared to be within the range than can be replaced by weathering (1–7 kg ha⁻¹ yr⁻¹). Magnesium losses exceeded estimated weathering rates (1–8 kg ha⁻¹ yr⁻¹) only at Sites 3, 7a, 7b, and 8, where calcareous C horizons were present. In contrast, Ca^{2+} losses from the majority of sites approached or exceeded maximum estimated weathering rates (1–21 kg ha⁻¹ yr⁻¹). Elevated Ca^{2+} losses from the poorly buffered soils at Sites 4a, 4b, 5, and 6 combined with preferential leaching of Mg^{2+} suggest that depletion of cation reserves from sites with susceptible soils remains a plausible consequence of pollutant deposition over long time periods.

CONCLUSIONS

Three years of precipitation sampling confirmed the presence of a regional gradient of H^+ , SO_4^{2-} , and NO_3^- deposition extending across the Great Lakes region from Minnesota to Ohio. Soil solution SO_4^{2-} concentrations, Mg^{2+} concentrations, conductivity, SO_4^{2-} /inorganic anion ratios, and SO_4^{2-} /cation ratios were strongly related to H^+ and SO_4^{2-} deposition at multiple sites representing a variety of forest ecosystems located along this gradient. These trends in soil solution chemistry were clear despite underlying variation in soil properties and ecosystem type. Solution Ca^{2+} and Mg^{2+} concentrations also were related to trends in inherent soil properties, but the proportion of cations in solution associated with SO_4^{2-} increased from north to south as H^+ and SO_4^{2-} deposition increased. These observations support the hypotheses that (i) soil solution chemistry has been directly affected by pollutant deposition, and (ii) nutrient cation leaching has been increased by pollutant deposition in the Great Lakes region.

Comparison of total atmospheric ionic inputs with ionic outputs from B horizons suggests that net losses of Ca^{2+} and Mg^{2+} occurred from all sites along the gradient. Sulfate outputs equaled or exceeded inputs at the southern sites receiving higher SO_4^{2-} deposition. Immobilization of atmospherically deposited NO_3^- at the majority of sites indicated that NO_3^- deposition had little direct effect on cation leaching. Elevated losses of Ca^{2+} and preferential leaching of Mg^{2+} from sites with coarse-textured soils in response to H^+ and SO_4^{2-} deposition suggest that depletion of cation reserves at such poorly buffered sites remains a likely consequence of pollutant deposition. While this may be deemed only an acceleration of natural cation leaching processes, it still must be viewed as an additional negative stress on forest ecosystems that are nutrient limited, drought prone, and potentially subject to both rapid climate change and insect defoliation in the near future.

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