Atmospheric Pollutants

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


ABSTRACT

A gradient of H⁺, SO₂⁻, and NO₃⁻ 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 SO₂⁻ deposition increases from less than 3.5 kg ha⁻¹ in northern Michigan to greater than 12 kg ha⁻¹ in northern Ohio. Annual wet NO₃⁻ 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 (>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; Anchebault 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.

*Corresponding author.


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

<table>
<thead>
<tr>
<th>Site</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4a</th>
<th>4b</th>
<th>5</th>
<th>6</th>
<th>7a</th>
<th>7b</th>
<th>8</th>
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<tbody>
<tr>
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<td>46°52'</td>
<td>45°33'</td>
<td>44°23'</td>
<td>44°21'</td>
<td>43°40'</td>
<td>42°27'</td>
<td>42°17'</td>
<td>42°17'</td>
<td>41°18'</td>
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<td>84°51'</td>
<td>85°50'</td>
<td>85°42'</td>
<td>86°09'</td>
<td>84°00'</td>
<td>83°39'</td>
<td>83°39'</td>
<td>81°35'</td>
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<td>Mean annual precipitation (cm)</td>
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<td>83</td>
<td>81</td>
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<td>85</td>
<td>77</td>
<td>77</td>
<td>77</td>
<td>90</td>
</tr>
<tr>
<td>Actual evapotranspiration (cm)</td>
<td>51</td>
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<td>55</td>
<td>57</td>
<td>57</td>
<td>57</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>64</td>
</tr>
<tr>
<td>Mean annual temperature (°C)</td>
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<td>4.2</td>
<td>4.2</td>
<td>5.8</td>
<td>5.8</td>
<td>7.6</td>
<td>9.3</td>
<td>9.3</td>
<td>9.3</td>
<td>9.8</td>
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<td>Stand age (yr)</td>
<td>78</td>
<td>79</td>
<td>73</td>
<td>74</td>
<td>76</td>
<td>78</td>
<td>47</td>
<td>119</td>
<td>104</td>
<td>105</td>
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<td>Total stand basal area (m² ha⁻¹)</td>
<td>31.4</td>
<td>32.0</td>
<td>29.7</td>
<td>30.3</td>
<td>30.8</td>
<td>30.1</td>
<td>23.5</td>
<td>37.9</td>
<td>39.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Dominant overstory species (%)</td>
<td>SM (90)</td>
<td>SM (86)</td>
<td>SM (87)</td>
<td>SM (83)</td>
<td>SM (78)</td>
<td>SM (75)</td>
<td>BO (99)</td>
<td>WO (51)</td>
<td>RO (47)</td>
<td>WO (45)</td>
</tr>
<tr>
<td>Soil texture</td>
<td>SL</td>
<td>LS</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>SL</td>
<td>L</td>
<td>CL</td>
</tr>
</tbody>
</table>

† 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.

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 Alfis 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 x 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 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 snowpack 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 HCO₃⁻, was determined on unfiltered soil solution samples by titration with H₂SO₄ 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-μm filters and stored at ≤5 °C prior to analysis. Anions (SO₄²⁻, NO₃⁻, F⁻, Cl⁻, PO₄³⁻) 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, Mg²⁺, and K⁺ were determined by atomic absorption spectrophotometry, either on fresh filtered samples within 4 wk of collection, or on HNO₃-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, ULV124, WEL149) and Ohio (DCF114, 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 colocated 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 SO₄²⁻, NO₃⁻, NH₄⁺, HNO₃, and SO₂ concentrations at Sites 2, 3, 5, and 7 could be predicted by latitude (r² = 0.88-0.97). Ambient Ca²⁺, Mg²⁺, 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 SO₂ (0.17), SO₄²⁻ (0.32), and NO₃ (0.57) were those calculated for the Turkish Lakes Watershed by Sirois and Vet (1988). The deposition velocity for HNO₃ (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 Ca²⁺ (0.74), Mg²⁺ (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 NH₄⁺ (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 HNO₃ and SO₂ deposition estimates, assuming complete conversion of dry deposited SO₂ to H₂SO₄ (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 ±10% of known values for all analyses. Repeated measurement errors for major ions determined from replicate sample analyses ranged from 1.2% for SO₄²⁻, NO₃⁻, and Ca²⁺, to 4.9% for Cl⁻ and NH₄⁺.

**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, NO₃⁻ 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 SO₄²⁻ and NO₃⁻ deposition (Table 2) were similar to estimates made for Ontario, Canada, across the same regional pollution gradient (2.6-17.7 kg NO₃ ha⁻¹ yr⁻¹; 2.8-25.2 kg SO₄⁻ ha⁻¹ yr⁻¹; Barrie and Sirois, 1986; Sirois and
Barrie, 1988; Ro et al., 1988). Dry deposition estimates for \( \text{NH}_4^+ \), \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), and \( \text{Cl}^- \) 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 \( \text{K}^+ \) was calculated from a deposition velocity (8.3 cm \( \text{s}^{-1} \)) lower than that reported for \( \text{K}^+ \) dry deposition to an oak forest by Lovett and Lindberg (1984, 10.7-19.1 cm \( \text{s}^{-1} \)), so these estimates should be conservative. Estimates of \( \text{H}^+ \) dry deposition were consistent with estimates made by Lindberg et al. (1986), dry deposition of \( \text{H}^+ \) approximates equaling wet deposition of \( \text{H}^+ \).

The primary sources of free acidity in precipitation are \( \text{H}_2\text{SO}_4 \) and \( \text{HNO}_3 \), which form as the result of photochemical oxidation of anthropogenic \( \text{S} \) and \( \text{N} \) oxides in the atmosphere (Galloway et al., 1976; Barrie, 1981). Elevated levels of \( \text{H}^+ \), \( \text{NO}_3^- \), and \( \text{SO}_4^{2-} \) in incoming precipitation are all symptomatic of pollutant deposition. As \( \text{H}^+ \) and \( \text{NO}_3^- \) are readily consumed by a variety of forest ecosystem processes, \( \text{SO}_4^{2-} \) 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 \( \text{SO}_4^{2-} \) followed observed trends in \( \text{SO}_4^{2-} \) deposition. Elevated \( \text{SO}_4^{2-} \) content at Site 1 was related to high \( \text{SO}_4^{2-} \) adsorption ability combined with impeded drainage favoring \( \text{SO}_4^{2-} \) accumulation. High \( \text{SO}_4^{2-} \) deposition combined with both high \( \text{SO}_4^{2-} \) adsorption ability and impeded drainage accentuated soil \( \text{SO}_4^{2-} \) 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 B horizon boundaries, increases in solution conductivity, \( \text{SO}_4^{2-} \), and \( \text{Mg}^{2+} \) from Site 1 to Site 8 were statistically significant (Table 4, Fig. 2). Solution conductivity was correlated with wet deposition of \( \text{SO}_4^{2-} \) (\( r = 0.74** \)) and \( \text{H}^+ \) (\( r = 0.69** \)). Wet deposition of \( \text{SO}_4^{2-} \) was strongly correlated with solution concentrations of \( \text{SO}_4^{2-} \) (\( r = 0.92** \)) and \( \text{Mg}^{2+} \) (\( r = 0.85** \)). Sulfate and \( \text{Mg}^{2+} \) solution concentrations were similarly correlated with \( \text{H}^+ \) deposition (\( r = 0.82** \) and 0.75**). Both the \( \text{SO}_4^{2-} \) to total inorganic anion and the \( \text{SO}_4^{2-} \) to total cation ratios were correlated with \( \text{SO}_4^{2-} \) 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 \( \text{SO}_4^{2-} \) in soil solution as \( \text{H}^+ \) and \( \text{SO}_4^{2-} \) deposition increased across the gradient.

In soil solutions collected at lower B horizon boundaries, deposition effects were less noticeable, but still present. Soil solution \( \text{SO}_4^{2-} \) concentrations were highly correlated with both \( \text{SO}_4^{2-} \) deposition (\( r = 0.92** \)) and water extractable \( \text{SO}_4^{2-} \) 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 (\( r = 0.92** \)), \( \text{Ca}^{2+} \) (\( r = 0.96** \)), \( \text{Mg}^{2+} \) (\( r = 0.82** \)), and pH (\( r = 0.59** \)) were positively correlated with \( \text{HCO}_3^- \) (Table 4, Fig. 2). Solution \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) concentrations also were correlated with upper 75 cm soil exchangeable \( \text{Ca}^{2+} \) (\( r = 0.89** \)) and \( \text{Mg}^{2+} \) (\( r = 0.86** \)) contents.

Sites with finer-textured soils (1, 7a, 7b, 8) tended to have higher solution \( \text{SO}_4^{2-} \) concentrations (Fig. 2), a result of lower leaching rates related to soil texture and structure favoring \( \text{SO}_4^{2-} \) accumulation. This effect is most apparent when comparing Sites 6, 7a, and 7b where soil textures varied from sand to loam (Table

<table>
<thead>
<tr>
<th>Site</th>
<th>Mean Annual Ionic Deposition at Eight Sites in the Great Lakes Region, 1 Oct. 1987 to 30 Sept. 1990.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion</td>
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</tr>
<tr>
<td>------</td>
<td>---</td>
</tr>
<tr>
<td>( \text{H}^+ )</td>
<td>0.08</td>
</tr>
<tr>
<td>( \text{NO}_3^- )</td>
<td>3.70</td>
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<tr>
<td>( \text{SO}_4^{2-} )</td>
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<tr>
<td>( \text{Ca}^{2+} )</td>
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<tr>
<td>( \text{Mg}^{2+} )</td>
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<tr>
<td>( \text{K}^+ )</td>
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</tr>
<tr>
<td>( \text{Cl}^- )</td>
<td>2.23</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Site</th>
<th>Property</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4a</th>
<th>4b</th>
<th>5</th>
<th>6</th>
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<th>7b</th>
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<tbody>
<tr>
<td></td>
<td>Mg ha⁻¹</td>
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</tr>
<tr>
<td></td>
<td>Silt***</td>
<td>2624bc</td>
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<td>731d</td>
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<td>610d</td>
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<td>H₂O extractable</td>
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<td>SO₄⁻S adsorption potential***</td>
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<td>96b</td>
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<td>9276ab</td>
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<td>Exchangeable Mg²⁺***</td>
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<td>390c</td>
<td>69c</td>
<td>189c</td>
<td>81c</td>
<td>138c</td>
<td>180c</td>
<td>2893ab</td>
<td>4097a</td>
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</table>

*** 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 (Johnston, 1980; Reuss et al., 1987). While this may not be the controlling force behind cation leaching (Henderson 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.

<table>
<thead>
<tr>
<th>Site</th>
<th>Depth†</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4a</th>
<th>4b</th>
<th>5</th>
<th>6</th>
<th>7a</th>
<th>7b</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH LE***</td>
<td>5.3bc</td>
<td>5.6abc</td>
<td>5.9ab</td>
<td>5.1c</td>
<td>5.6abc</td>
<td>5.2bc</td>
<td>5.6abc</td>
<td>6.2a</td>
<td>5.9ab</td>
<td>5.3bc</td>
</tr>
<tr>
<td></td>
<td>Conductivity (mS m⁻¹) LE***</td>
<td>3.94</td>
<td>5.5c</td>
<td>6.9a</td>
<td>6.3abc</td>
<td>6.1abc</td>
<td>6.6ab</td>
<td>6.0abc</td>
<td>6.7a</td>
<td>6.8a</td>
<td>5.7b</td>
</tr>
<tr>
<td></td>
<td>SO₄²⁻/anion ratio LE***</td>
<td>0.34e</td>
<td>0.24e</td>
<td>0.36de</td>
<td>0.52cd</td>
<td>0.24e</td>
<td>0.58abc</td>
<td>0.72ab</td>
<td>0.52cd</td>
<td>0.54bc</td>
<td>0.75a</td>
</tr>
<tr>
<td></td>
<td>SO₄²⁻/cation ratio LE***</td>
<td>0.44cd</td>
<td>0.29d</td>
<td>0.24d</td>
<td>0.35cd</td>
<td>0.19d</td>
<td>0.40cd</td>
<td>0.86ab</td>
<td>0.57c</td>
<td>0.60bc</td>
<td>0.97a</td>
</tr>
</tbody>
</table>

*** 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.
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 $\text{SO}_4^{2-}$ in solution as $\text{SO}_2^-$ deposition increased across the gradient strongly supports the hypothesis that soil solution chemistry has been directly affected by pollutant deposition. Significant relationships among $\text{H}^+$ and $\text{SO}_2^-$ deposition, soil solution $\text{SO}_4^{2-}$ 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 $\text{H}^+$, $\text{NO}_3^-$, $\text{Ca}^{2+}$, and $\text{SO}_4^{2-}$ ($r = 0.81^{**}-0.99^{**}$). Increases in $\text{SO}_4^{2-}$ in throughfall are highly related to total $\text{SO}_2^-$ dry deposition (Garten et al., 1988; Lindberg and Garten, 1988. In comparison, $\text{NO}_3^-$ tends to be absorbed in the canopy (Lindberg et al., 1986; Shepard et al., 1989); while $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, and $\text{K}^+$ 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 $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ were lost from all sites along the gradient. Outputs of $\text{K}^+$ were variable, with sites having high estimated dry deposition of $\text{K}^+$ displaying net gains. Sulfate outputs from both E and B horizons were strongly correlated with wet plus dry $\text{SO}_2^-$ deposition and throughfall $\text{SO}_4^{2-}$ flux ($r = 0.95^{**}-0.98^{**}$). Estimated $\text{SO}_4^{2-}$ outputs were slightly less than inputs at Sites 1 to 3, but equaled or exceeded inputs at Sites...
4a to 8. Site 1 exhibited slight net losses of NO₃ as a result of nitrification, similar to the Turkey Lakes Watershed in Ontario (Foster et al., 1989). Site 4b experienced extremely high rates of NO₃ loss related to severe defoliation coupled with inherently high rates of nitrification. At this site, internal H⁺ and NO₃ production as a result of nitrification was the driving force behind high rates of cation leaching (Fig. 3). Immobilization of atmospherically deposited NO₃ at the majority of our sites suggests that NO₃ deposition had little or no direct influence on cation leaching (Johnson et al., 1985). All sites had close to 100% retention of NH₄⁺ (N.W. MacDonald, 1992, unpublished data).

Greater output than input of Ca²⁺, Mg²⁺, and SO₄²⁻ 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 SO₄²⁻ 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 \( SO_4^{2-} \) ha⁻¹ yr⁻¹ from E horizons; 218 mol \( SO_4^{2-} \) 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 \( SO_4^{2-} \) ha⁻¹ yr⁻¹ leaching from E horizons, and 33 to 2367 mol \( SO_4^{2-} \) 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 (\( Ca^{2+} + Mg^{2+} + K^+ \)) 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 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 ha⁻¹ yr⁻¹ at Site 2 to 1137 mol 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 ha⁻¹ yr⁻¹ at Site 2 to 195 mol ha⁻¹ yr⁻¹ at Site 8.

Driscoll et al. (1989) determined that 77 to 82% of stream efflux of basic cations (\( Ca^{2+} + Mg^{2+} + K^+ + Na^+ \)) 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 ≤ 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 (\( Ca^{2+} + Mg^{2+} + K^+ + Na^+ \)) 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.
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 inputs 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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