

Variation in Forest Soil Properties along a Great Lakes Air Pollution Gradient

Neil W. MacDonald,* Andrew J. Burton, Martin F. Jurgensen, James W. McLaughlin, and Glenn D. Mroz

ABSTRACT

A pronounced air-pollution gradient exists across the Great Lakes region, with deposition of SO_4 , NO_3 , and H increasing from northern Minnesota to southern lower Michigan. Soils at six northern hardwood sites along this gradient were examined to characterize soil physical and chemical properties relevant to retention of pollutants, and to investigate the impact of differences in pollutant loading on soil chemical properties. Three randomly located pedons at each site were described and sampled. Soils at all sites were classified in closely related subgroups within the Spodosol order (Entic Haplorhods, Typic Haplorhods, Alfic Haplorhods, and Alfic Fragiorhods). Cation-exchange capacity and SO_4 -adsorption potential tended to decrease from north to south along the gradient, largely related to trends in inherent soil properties. In upper B horizons, additional significant positive deposition effects on water-soluble and adsorbed SO_4 , and negative deposition effects on SO_4 -adsorbing potentials were consistent with hypothesized pollutant impacts on soil SO_4 pools and soil capacities to retain additional atmospheric SO_4 . Exchangeable nutrient-cation contents (Ca, Mg, K) in upper B horizons tended to decrease as pollutant deposition increased. Regression analyses suggested that observed trends in nutrient-cation contents were primarily related to inherent soil properties such as clay, organic matter, and cation-exchange capacity. Differential effects of pollutant deposition and natural acidification processes on nutrient-cation reserves could not be separated at this time.

SOILS form the major biogeochemical link between the forest biota they support and atmospheric deposition. Soils function as nutrient reservoirs upon which forest ecosystems rely, but nutrient reserves and availability in soils may be altered by deposition of airborne pollutants. Probable effects of elevated pollutant (SO_4 , NO_3 , H) deposition on soils include accelerated acidification, solubilization of Al, and increased leaching of cations, resulting in reduced soil fertility with time (Reuss et al., 1987; Schulze, 1989; Johnson and Taylor, 1989; Nihlgard, 1990). The impacts of elevated NO_3 and NH_4 deposition on soil N pools are also of concern (Aber et al., 1989; Schulze, 1989; Nihlgard, 1990). The degree and rate at which pollutants alter nutrient cycles in forest ecosystems are greatly dependent on inherent soil properties (Johnson et al., 1982). Buffering of acidity (Johnson, 1979; Richter et al., 1983) and SO_4 adsorption (Johnson, 1984), both of which are dependent on inherent soil properties, modify the impacts of pollutant deposition on forest ecosystems. Complicating efforts to document pollutant effects is the superimposition of strong acid deposition on natural soil acidification processes (Reuss et al., 1987).

The northern Great Lakes region is currently experiencing a pronounced regional gradient of air-pol-

lutant deposition (Armentano and Loucks, 1983; Glass and Loucks, 1986). Annual wet SO_4 -S deposition ranges from $<3.5 \text{ kg ha}^{-1}$ in northern Minnesota to over 8 kg ha^{-1} in southern lower Michigan. Annual wet NO_3 -N deposition increases twofold across this same region, from $<2 \text{ kg ha}^{-1}$ in northern Minnesota to $>4 \text{ kg ha}^{-1}$ in southern Michigan. Precipitation pH follows a similar trend, ranging from >5 at the northern end of the gradient to ≈ 4 at the southern end (National Atmospheric Deposition Program, 1985a,b, 1986; Zemba et al., 1988). Historical evidence suggests that this gradient has persisted at current or higher rates of deposition for at least 20 to 30 yr (Glass and Loucks, 1986), raising concerns about potential impacts on forest ecosystems in the Great Lakes region.

The pollution gradient has provided an opportunity to study the effects of pollutant deposition on forest ecosystems under natural conditions on a regional basis. The otherwise extremely difficult problem of realistically applying pollutant treatments to entire ecosystems over multiyear periods was addressed by establishing study sites in geographic regions with documented differences in pollutant-deposition rates. A similar approach was used for extensive surveys of pollutant impacts in the Great Lakes region by Nichols and McRoberts (1986), David et al. (1988), and Grigal and Ohmann (1989). The presence of parallel gradients in climate and soil type are complicating factors (Lucier and Stout, 1988), but are a reflection of real-world conditions, not an artifact of study design. The use of site-specific measurements and long-term records of both pollutant deposition and climatic conditions will allow the separation of effects of climate; edaphic factors, and pollutant deposition on forest ecosystem processes (Witter, 1990; Burton et al., 1991). Following this rationale, the effects of airborne pollutants on the northern hardwood forest ecosystem were intensively studied at six sites located along the deposition gradient from northern Minnesota to central lower Michigan. This work was carried out as part of the Forest Response Program/Eastern Hardwoods Research Cooperative (Schroeder and Kiester, 1989).

The objective of the work reported here was to characterize soil physical and chemical properties relevant to ecosystem response to pollutant deposition, and to investigate the influence of pollutant loading on soil chemical properties at six northern hardwood sites. Primary hypotheses to be tested included (i) soil total S and N increase as pollutant deposition increases, (ii) water-soluble and adsorbed SO_4 increase and the potential to adsorb additional SO_4 decreases as pollutant deposition increases, and (iii) soil exchangeable nutrient-cation (Ca, Mg, and K) contents decrease as pollutant deposition increases.

N.W. MacDonald, School of Natural Resources, Univ. of Michigan, 430 E. Univ., Ann Arbor, MI 48109-1115; A.J. Burton, Dep. of Forestry, Michigan State Univ., E. Lansing, MI 48824-1222; and M.F. Jurgensen, J.W. McLaughlin, and G.D. Mroz, School of Forestry and Wood Products, Michigan Technological Univ., Houghton, MI 49931. Received 26 Oct. 1990. *Corresponding author.

Published in Soil Sci. Soc. Am. J. 55:1709-1715 (1991).

Abbreviations: NADP/NTN, National Atmospheric Deposition Program/National Trends Network; Fe_d and Al_d , dithionite-citrate-extractable Fe and Al, respectively; CEC, cation-exchange capacity; NBS, National Bureau of Standards; SRM, standard reference material; HSD, honestly significant difference; CV, coefficient of variation.

METHODS

Site Selection and Description

As part of the larger gradient project, analogous forest stands representing the northern hardwood ecosystem were selected for study based on (i) previously documented regional differences in pollutant-deposition rates, (ii) similarity of overstory species composition and structure, (iii) stand age, (iv) physiography, (v) soil, and, to the extent possible, (vi) climate. Sites were selected to maximize the sugar maple (*Acer saccharum* Marsh.) component of the overstory while minimizing the number of other hardwood species and eliminating any conifer component. Within the primary constraints of target deposition rates and desired overstory structure and composition, the site-selection criteria targeted soils that (i) were associated with morainal landforms, (ii) were well drained with udic moisture regimes, and (iii) had sand, loamy sand, or sandy loam textures. Following the criteria summarized above, northern hardwood stands were chosen for study in central lower Michigan (Site 5), in north-central lower Michigan (Sites 4a and 4b), in northern lower Michigan (Site 3), in northwestern upper Michigan (Site 2), and in northeastern Minnesota (Site 1, Fig. 1). Sites 1 to 5 represent regions that were expected to have different pollutant-deposition rates, increasing from north (Site 1) to south (Site 5). Sites 4a and 4b represent different soil conditions within an area of similar pollutant deposition, site 4b having higher moisture and fertility status than 4a. In Minnesota, limitations in the number of locations meeting both target deposition rate and desired overstory criteria necessitated selection of a site that deviated from optimal soil characteristics. Soils at Site 1 were coarse-loamy, mixed, frigid Alfic Haplorthods and Alfic Fragiorthods. Soils at the other sites were sandy, mixed, frigid Entic, Typic, and Alfic Haplorthods.

The study sites span 4° of latitude and 6° of longitude (Table 1, Fig. 1). Consequently, precipitation, temperature, and growing degree days vary with location (Table 1). Total stand basal areas ranged from 29.7 to 32.0 m² ha⁻¹, with at least 75% of basal area as sugar maple (Table 1). With the exception of Site 4b, all sites had combined sugar maple and red maple (*Acer rubrum* L.) basal areas of 86% or greater

Table 1. Locations, climate, and stand characteristics of northern hardwood study sites.

Variable	Site					
	1	2	3	4a	4b	5
Latitude (N)	47°41'	46°52'	45°33'	44°23'	44°21'	43°40'
Longitude (W)	90°44'	88°53'	84°52'	85°50'	85°42'	86°09'
Mean annual precipitation† (mm)	670	870	830	810	810	850
Mean annual temperature† (°C)	3.7	4.2	5.2	5.8	5.8	7.6
Growing degree days >5.6°C‡ (°C)	1319	1528	1736	1944	1944	2083
Total stand basal area (m ² ha ⁻¹)	31.4	32.0	29.7	30.3	30.8	30.1
Sugar maple basal area (%)	90	86	87	83	78	75
Other species basal area§ (%)	9 (PB)	7 (YB)	8 (WA)	8 (RM)	13 (WA)	13 (RM)
Stand biomass (Mg ha ⁻¹)	212	262	263	275	284	234
Stand age (yr)	78	79	73	74	76	78

† National Oceanic and Atmospheric Administration, 1983.

‡ Phillips and McCulloch, 1972.

§ Species with next highest percentage basal area, PB = paper birch (*Betula papyrifera* Marsh.), RM = red maple (*Acer rubrum* L.), WA = white ash (*Fraxinus americana* L.), YB = yellow birch (*Betula alleghaniensis* Britt.).

(Table 1). All stands were even aged, having originated after logging in the early 1900s, with minimal disturbance occurring during subsequent stand development.

To obtain site-specific estimates of pollutant deposition, wet/dry collectors (Aerochem Metrics, Bushnell, FL) and weighing rain gauges (Belfort Instrument Co., Baltimore, MD) were located in open areas within 15 km of each study site. Samples were collected on a weekly basis and analyzed for anions, cations, pH, and conductivity following NADP protocols. Deposition data from nearby NADP/NTN sites also were used where available (Sites 3 and 4). Climatic data were 30-yr means for the regions in which the sites occurred (Phillips and McCulloch, 1972; National Oceanic and Atmospheric Administration, 1983).

Soil Sampling and Analysis

Three soil pits, one associated with each of three overstory measurement plots per stand, were excavated and sampled at each site in August 1988. Pedon locations were selected following a random azimuth from plot center to a point five or more meters beyond the measurement-plot boundary. If a selected location fell on a soil area known to deviate from typical site conditions, such as a recent windthrow or animal burrow, it was rejected. Additional random locations were inspected until a suitable sampling spot was selected.

Soil pits were excavated to at least 1.6 m, with deeper C horizons sampled using a bucket auger. Soil profiles were described and sampled following standard soil-survey procedures. One or more bulk-density cores, totaling at least 70 cm³, were taken from each mineral horizon, dried at 105 °C, and weighed. Soil was air dried at 25 °C and then passed through a 2-mm sieve. The bulk soil sample was weighed prior to sieving and particles >2 mm were weighed after sieving to estimate percentage of coarse fragments on a volume basis in each mineral horizon. Analytical results expressed on a unit-area basis were adjusted to account for coarse-fragment volumes.

Forest floor was sampled in two layers (Oi and Oe+a) using a 30.5 by 30.5 cm steel frame. Five frames were sampled around each plot, one at the pit location and the remaining four at additional random locations. Forest-floor samples were dried at 65 °C, weighed, and then composited by plot. The Oi samples were ground in a Wiley mill (1-mm mesh openings) and Oe+a samples were crushed and passed through a 2-mm sieve prior to analysis.

Total N of organic and mineral horizons was determined by automated colorimetry following H₂SO₄ digestion. Organic horizons were analyzed for total Ca, Mg, K, and Al by direct-current Ar plasma atomic emission spectrometry following HNO₃-HClO₄ digestion. Total S in Oi horizons was determined by automated turbidimetry following HNO₃-HClO₄ digestion (Wall et al., 1980). Total S in Oe+a and mineral soil horizons was determined by inductively coupled plasma atomic emission spectrometry following HNO₃-HClO₄ digestion. Organic matter in the Oe+a layer and

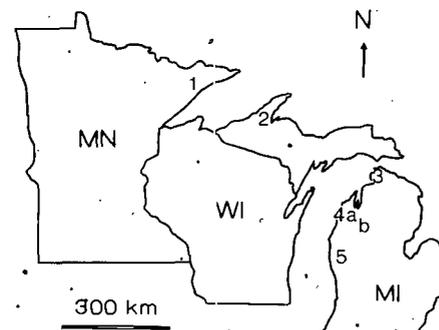


Fig. 1. Locations of northern hardwood forest study sites across the Great Lakes region.

mineral horizons was determined by loss-on-ignition (500 °C for 4 h). Mineral horizons were analyzed for KCl-exchangeable Al; NH₄Cl-exchangeable Ca, Mg, and K; and water- and PO₄-extractable SO₄. For these analyses, cations were determined by atomic absorption and SO₄ by ion chromatography. Mineral soils also were analyzed for texture (hydrometer), Fe_d and Al_d, and CEC. Analytical methods followed were standard methods documented by the Soil Conservation Service (1972, 1982) and Page et al. (1982). Sulfate adsorption indices were determined by equilibrating 10-g samples in 0.01 M CaCl₂ solutions containing 0.312 mmol SO₄-S L⁻¹, as detailed in MacDonald and Hart (1990). All analyses included 10% replication as an internal quality control check. Total elemental analyses included National Bureau of Standards (NBS) standard reference material (SRM) samples as quality assurance checks (SRM 1572 citrus leaves; SRM 1575 pine needles; SRM 1646 estuarine sediment).

Analyses of variance were performed on untransformed data unless transformation improved homogeneity of variance. Mean separation was accomplished using Tukey's HSD test. Correlations among forest floor, mineral soil, and environmental variables were based on site means ($n = 6$) unless otherwise specified. Mineral soil regression analyses employed plot means ($n = 18$).

RESULTS AND DISCUSSION

Mean percent recoveries determined from total elemental analyses of NBS samples were as follows: 101 to 114% for S, 96 to 97% for N, and 104 to 116% for Ca. Mean recoveries for Mg, K, and Al were lower: respectively, 86, 80, and 82%. Coefficients of variation for total elemental analyses of NBS samples ranged from 0.8 to 5.1%, with an overall mean CV of 2.7%.

Results from 3 yr of precipitation sampling (1987–1990) confirmed the presence of a pronounced pollutant deposition gradient extending from northern Minnesota to central lower Michigan (Table 2). Sulfate and H deposition increased significantly from north (Site 1) to south (Site 5). Nitrate deposition followed a similar, though less pronounced trend. Deposition of H, SO₄, and NO₃ were negatively correlated (-0.73^{**} to -0.87^{**} [significant at $P = 0.01$]) with both latitude and longitude, conforming to a strict definition of a regional gradient across the sites being studied. Our 3-yr record of pollutant deposition corresponded both in magnitude and trend to past patterns of deposition reported by the National Atmospheric Deposition Program (1985a,b, 1986).

Inherent Soil Properties

Inherent soil properties are relatively fixed and unaffected by pollutant deposition, but greatly modify the impacts of pollutant deposition on soil chemistry.

Table 2. Mean annual wet deposition of pollutants at five sites in the Great Lakes region, 1 Oct. 1987 to 30 Sept. 1990.

Element	Site				
	1	2	3	4	5
	kg ha ⁻¹ yr ⁻¹				
H ^{**}	0.07b	0.09b	0.31a	0.35a	0.30a
SO ₄ -S ^{**}	3.23b	3.64b	5.33ab	6.33a	6.16a
NO ₃ -N ^{**}	1.98b	2.23b	3.16ab	4.06a	3.41ab
NH ₄ -N	2.43	2.40	2.35	2.92	2.94

** Means not followed by the same letter differ significantly at $P = 0.01$; letters compare deposition rates across sites.

Inherent soil properties represent the influences of parent material, topography, climate, and vegetation integrated over time through the processes of soil formation. These properties are expected to change only gradually over periods of centuries or millenia. Although our sites were selected to be as similar as possible in an ecosystem sense, significant differences among sites were present in several inherent soil properties (Fig. 2).

Surface mineral horizons (A and E) differed in CEC, largely related to thicker surface horizons at the southern sites. Variation in upper B horizon (to 75 cm) physical and chemical characteristics also was present, Site 1 having higher amounts of organic matter, silt, and Fe_d than any of the other sites. Similar trends in Al_d and Fe_d were present in deeper B and C horizons (75–150 cm). In subsurface horizons, CEC tended to decrease from north to south. Variation in clay content among sites was not statistically significant.

Properties Susceptible to Pollutant Deposition

Properties susceptible to pollutant deposition include those soil properties that are subject to change over relatively short time periods (years to decades) as a result of both natural processes and pollutant deposition. These properties include total S, N, and other elements in forest floor and mineral soil, water-soluble and adsorbed SO₄, potential to adsorb additional SO₄, and exchangeable Ca, Mg, K, and Al contents. These properties could be directly affected by pollutant deposition, or could change indirectly as a result of pollutant effects on overstory nutrient cycling (Johnson et al., 1982).

Significant differences in total N and S occurred among sites, but trends in forest-floor and mineral-soil total S and N were not directly related to the pollutant-deposition gradient (Table 3, Fig. 3). No trends in total Ca, Mg, K, or Al concentrations were noted in Oi layers (Table 3). In Oe+a layers, total Mg, K, and Al were highest at Site 1, and significantly lower at all other sites (Table 3). In surface mineral horizons, nutrient-cation (Ca, Mg, and K) saturation was least at Sites 4a and 5 (Fig. 3). In upper B horizons and deeper mineral horizons (75–150 cm), exchangeable Ca, Mg, and K tended to decrease from north to south across the gradient (Fig. 3). Water-soluble SO₄ and adsorbed SO₄ were highest in subsurface mineral horizons at Site 1 (Fig. 3). Water-soluble and adsorbed SO₄-S made up a relatively small portion of total S pools at all sites, ranging from 1.5 to 3% in A and E horizons, and from 5 to 9% in upper B horizons. This is in contrast to more highly weathered soils in unglaciated regions where adsorbed and soluble SO₄-S make up >30% of total S (Johnson, 1984). Potential to adsorb additional SO₄ was highest at Site 1 and tended to decrease from north to south (Fig. 3).

Factors Affecting Soil Properties

Interpretation of pollutant-deposition effects on soil properties by direct site-to-site comparisons is difficult because of unavoidable soil differences related to climate and parent material. For this reason, correlation and regression analyses were used to identify dominant factors affecting those soil properties hypothe-

sized to be susceptible to pollutant deposition. Independent variables included 30-yr means of climatic factors, mean annual deposition rates, inherent soil properties, and forest stand characteristics. Susceptible soil properties were also used as independent variables to explain observed variation in related soil properties where appropriate.

The Oi organic-matter weight was positively correlated with growing degree days (Table 4), and was consistent with a measured increase in litter production from north to south in 1987 (K.S. Pregitzer, 1991, unpublished data). However, Oi weight also was correlated with total $\text{NO}_3\text{-N}$ plus $\text{NH}_4\text{-N}$ deposition, possibly related to a combined effect of climate and atmospheric-N deposition on Oi weight through effects on litter production. Total N, S, K, and Mg concentrations in the Oi layer were correlated with one another and with overstory biomass, suggesting a strong dependence on internal nutrient-cycling processes in the overstory and overall site productivity (Table 4). Total Ca and Al concentrations in the Oi horizon directly reflected soil supplies of these elements or soil conditions related to their solubility and availability.

Oe+a organic-matter weight was negatively correlated with growing degree days and positively correlated

with levels of soil organic matter, related to increased podzolization in the northern soils (Table 4). With the exception of total S, Oe+a elemental concentrations were exclusively related to mineral soil properties (Table 4). Total S was positively correlated with Oe+a total N as expected, but additional variability in Oe+a total S concentration was explained by SO_4 deposition (Table 4). David et al. (1988) also found that forest-floor total S concentration, when adjusted for total N concentration, increased with increasing SO_4 deposition across the northern Great Lakes region. Trends in Oe+a total Mg and K, decreasing from northwest to southeast, were consistent with the findings of Grigal and Ohmann (1989), who found decreasing forest-floor cation concentrations related to decreasing cation deposition from west to east across the states of Minnesota, Wisconsin, and Michigan.

In mineral soil horizons, examination of standardized regression coefficients revealed that the primary predictors of soil nutrient contents were inherent soil properties (Table 5). Neither total $\text{NO}_3\text{-N}$ plus $\text{NH}_4\text{-N}$ deposition nor SO_4 deposition were significantly related to mineral-soil total N and S contents. Certain nutrients were related to climatic factors in addition to soil properties. Exchangeable K in A and E horizons

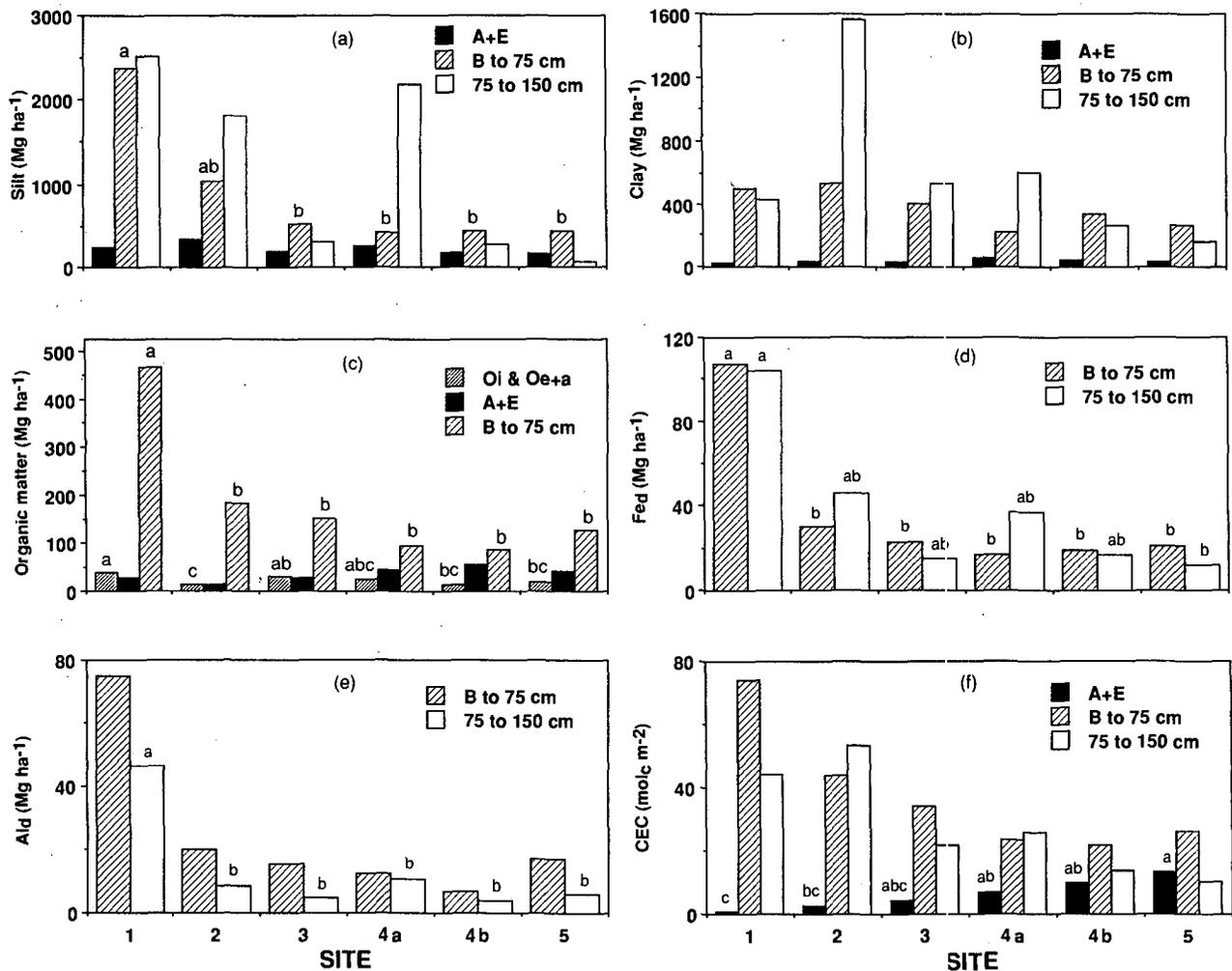


Fig. 2. Soil properties related to inherent soil characteristics at six northern hardwood sites in the Great Lakes region. Bars without common letters differ significantly at $P \leq 0.05$; letters compare means across sites within a single soil layer. Al_e and Fe_e are dithionite-citrate extractable Al and Fe, respectively; CEC is cation-exchange capacity.

and exchangeable Ca and Mg in the 75- to 150-cm depths were negatively related to mean annual precipitation, suggesting a leaching effect related to precipitation amount (Table 5).

Water-extractable and adsorbed SO₄ contents in upper B horizons were strongly related to total S contents, but additional variability in both measures was explained by SO₄ deposition (Table 5). As a percent of total S, water-soluble SO₄-S in upper B horizons increased significantly from 1.5% at Site 1 to 4.1% at Site 5. This trend was positively correlated with SO₄ deposition ($r = 0.70^{**}$). Significant negative effects of SO₄ deposition on SO₄-adsorbing potentials in upper B horizon soils also were present (Table 5). These statistical relationships support the hypothesis that atmospheric SO₄ deposition has had a measurable impact on soil SO₄ pools and capacities of soils to retain additional

Table 3. Forest floor total elemental concentrations.

Element	Horizon	Site					
		1	2	3	4a	4b	5
g kg ⁻¹							
N	Oi*	15.2b	19.0ab	16.7ab	19.6ab	20.3a	15.2b
	Oe+a	13.9	11.0	11.9	11.5	12.2	10.8
S	Oi	1.5	1.7	1.8	1.9	2.0	1.5
	Oe+a	1.7	1.2	1.8	1.5	1.8	1.5
Ca	Oi**	22.4ab	16.5b	24.1a	17.7b	26.5a	20.3ab
	Oe+a*	8.5ab	5.6b	10.0ab	6.0ab	12.2a	7.6ab
Mg	Oi**	1.2b	1.1b	1.1b	1.1b	1.5a	1.2b
	Oe+a**	2.3a	1.0b	0.9b	0.8b	1.1b	1.1b
K	Oi**	1.6b	1.8b	1.8b	2.0ab	2.4a	1.6b
	Oe+a**	2.8a	1.4b	1.2b	1.1b	1.4b	1.3b
Al	Oi	0.8	0.7	0.7	0.8	0.8	0.8
	Oe+a**	19.0a	6.6b	5.5b	4.7b	5.5b	7.7b

*** Means without common letters differ significantly at $P = 0.05$ and 0.01 , respectively; letters compare concentrations across sites within a single horizon.

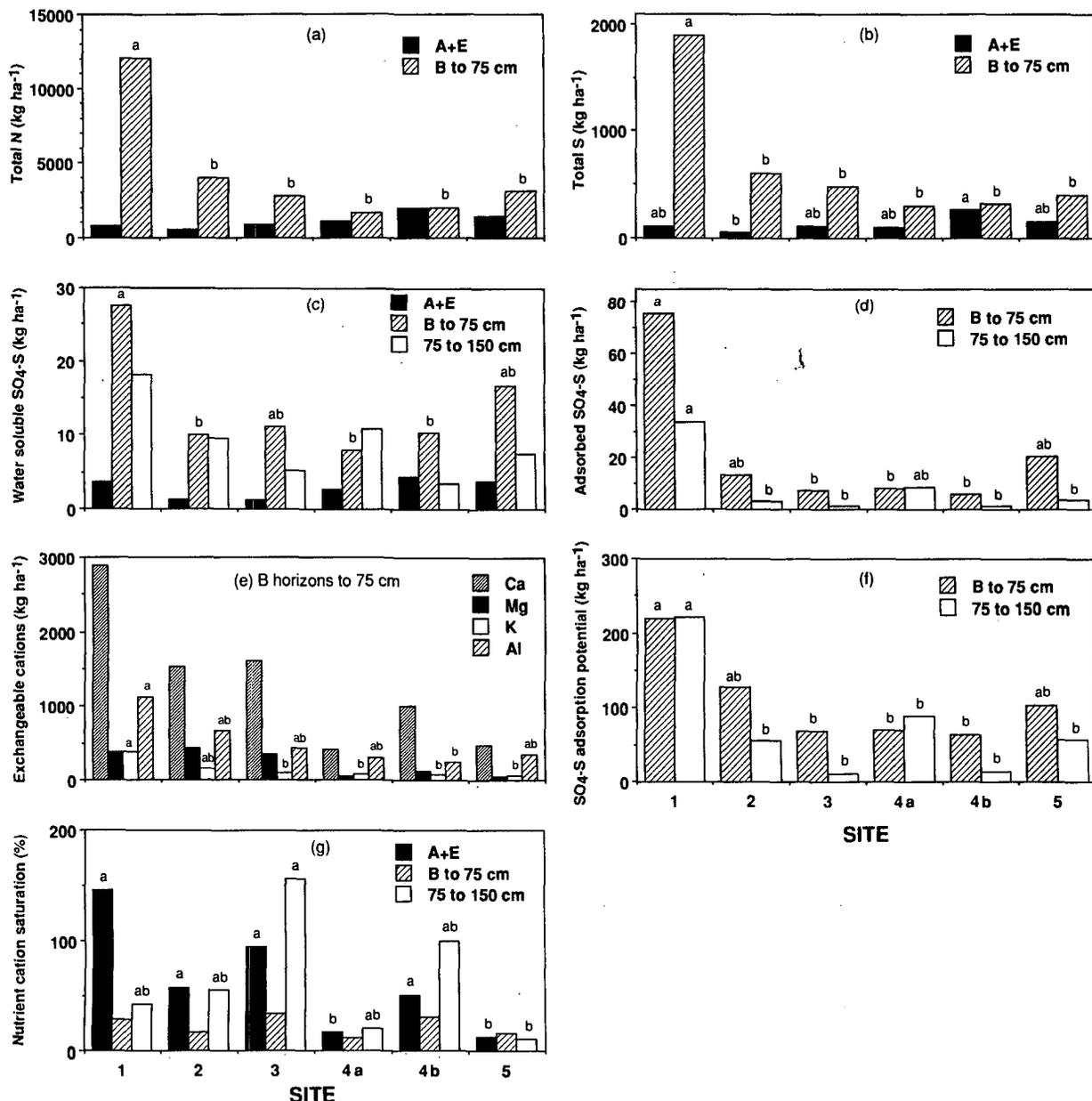


Fig. 3. Mineral soil properties susceptible to pollutant deposition at six northern hardwood sites in the Great Lakes region. Bars without common letters differ significantly at $P \leq 0.05$; letters compare means across sites within a single soil layer. Nutrient-cation saturation $> 100\%$ (g) indicates the presence of soluble salts (Site 1, A and E horizons) or calcareous C horizons (Site 3, 75–150-cm depth).

Table 4. Correlations among forest-floor properties, mineral-soil properties, climatic factors, and pollutant deposition.

Property†	Related variables and correlations (r)‡
<u>Oi</u>	
Organic matter	GDDAYS (0.85*), NO ₃ -N + NH ₄ -N dep. (0.85*)
N	Stand biomass (0.90**), total S (0.91**)
S	Stand biomass (0.95**), total K (0.97**)
K	Stand biomass (0.84*), total N (0.86*)
Mg	Total K (0.80*)
Ca	0-150-cm soil effective Ca saturation (0.97**)
Al	0-150-cm soil effective Mg saturation (-0.86*)
<u>Oe+a</u>	
Organic matter	GDDAYS (-0.75*), 0-75-cm SOM (0.84*)
N	0-150-cm soil total N (0.85*), 0-75-cm SOM (0.84*)
S	Total N (0.83*, R§ with SO ₄ dep. = 0.87**)
K	0-75-cm SOM (0.98**)
Mg	0-75-cm SOM (0.96**)
Ca	0-150-cm soil effective Ca saturation (0.96**)
Al	0-150-cm Al _d content (0.98**)

*,** Significant at $P = 0.05$ and 0.01 , respectively.

† Organic-matter weight, total elemental concentrations.

‡ Correlations based on site means, $n = 6$, unless otherwise noted. GDDAYS = growing degree days > 5.6 °C; SOM = mineral soil organic-matter content to 75 cm, dep. = atmospheric deposition, Al_d = dithionite-citrate-extractable Al.

§ R = multiple correlation coefficient ($n = 18$) of Oe+a total S with Oe+a total N and SO₄ deposition. In regression form, Oe+a total S = $-455.4 + 0.134(\text{total N}) + 29.73(\text{SO}_4 \text{ deposition})$, $R^2 = 0.76^{**}$.

atmospheric SO₄. These relationships were consistent with the observation (MacDonald, 1987) that mean SO₄-S contents in the upper 1.5 m of mineral soil in southern lower Michigan forest soils (11.6 g S m⁻²) were significantly higher than in northern lower Michigan forest soils (4.2 g S m⁻²). The occurrence of deposition impacts on soil S pools in the Great Lakes region also is supported by David et al. (1988), who found increased total S concentrations in both forest floor and surface mineral soils as atmospheric SO₄ deposition increased across Minnesota, Wisconsin, and Michigan. Evidence of regional SO₄ deposition impacts on soil S pools supports the plausibility of other commonly hypothesized regional pollutant-deposition impacts on soil nutrient reserves and soil-mediated processes (e.g., Johnson et al., 1982; Reuss et al., 1987; Aber et al., 1989; Johnson and Taylor, 1989; Schulze, 1989).

Observed trends in exchangeable Ca, Mg, and K contents in the upper B horizons from Site 1 to Site 5 (Fig. 3) were consistent with hypothesized nutrient-cation leaching effects related to pollutant deposition (Johnson and Taylor, 1989). However, results of regression analyses suggest that cation levels were primarily related to inherent soil properties such as clay content, organic-matter content, and CEC, along with climatic factors such as annual precipitation (Table 5). Coarse texture, low CEC, and low SO₄-adsorption potential predispose Sites 4a and 5 to accelerated nutrient losses resulting from both natural acidification processes and pollutant deposition (Johnson et al., 1982; Johnson and Taylor, 1989). Low nutrient-cation saturation in all mineral soil levels at Sites 4a and 5 indicate cation impoverishment (Fig. 3). The relative contribution of natural processes and more recent anthropogenic impacts cannot be separated on the basis of soil properties alone (Johnson et al., 1983; Binkley and Richter, 1987). Strong dependence on inherent

Table 5. Relationships among mineral soil properties, climatic factors, and pollutant deposition.

Property†	Significant predictors‡	R ²	P
<u>Surface eluviated horizons (A+E)</u>			
Total N	SOM(0.88) + Al _d (0.37) + Clay(-0.36)	0.90	0.000
Total S	SOM(0.85)	0.73	0.000
H ₂ O-S§	Total S(0.77)	0.59	0.000
Ex. Ca	Ex. Al(-0.89) + SOM(0.55) + Clay(0.34) + CEC(0.33)	0.94	0.000
Ex. Mg	SOM(0.93) + Ex. Al(-0.45)	0.77	0.000
Ex. K	Silt(0.51) + SOM(0.50) + MAPRE(-0.50)	0.81	0.000
Ex. Al	Ex. Ca(-0.95) + Clay(0.46) + SOM(0.44) + CEC(0.37)	0.93	0.000
<u>Upper B horizons to 75 cm (Bhs, Bs, Bw)</u>			
Total N	SOM(0.97)	0.95	0.000
Total S	SOM(0.99)	0.98	0.000
H ₂ O-S	Total S(1.10) + SO ₄ dep.(0.32)	0.83	0.000
Ads-S¶	Total S(1.14) + SO ₄ dep.(0.31)	0.91	0.000
S-Ads#	Al _d (0.67) + SO ₄ dep.(-0.39)	0.87	0.000
Ex. Ca	Clay(0.50) + Silt(0.49)	0.84	0.000
Ex. Mg	Clay(0.92)	0.84	0.000
Ex. K	Silt(0.53) + SOM(0.49)	0.95	0.000
Ex. Al	Silt(0.89)	0.80	0.000
<u>Lower B and C horizons from 75 to 150 cm</u>			
H ₂ O-S	Fe _d (0.89)	0.79	0.000
Ads-S	Al _d (0.95)	0.90	0.000
S-Ads	Al _d (0.74) + Ex. Al(0.40)	0.81	0.000
Ex. Ca	Clay(1.33) + Silt(-0.62) + MAPRE(-0.43)	0.87	0.000
Ex. Mg	Clay(1.34) + Silt(-0.58) + MAPRE(-0.31)	0.96	0.000
Ex. K	Clay(0.75) + Fe _d (0.36)	0.97	0.000
Ex. Al	Silt + Clay(0.86) + BASEMOL(-0.71)	0.50	0.006

† Total and exchangeable (Ex.) elemental content, kg ha⁻¹, by major soil layers.

‡ All predictors significant at $P \leq 0.05$. Standardized regression coefficients in parentheses. Soil predictors = horizon content (kg, Mg) on a ha⁻¹ basis unless otherwise specified. SOM = soil organic matter; Al_d and Fe_d = dithionite-citrate-extractable Al and Fe, respectively; CEC = cation-exchange capacity, mol_c m⁻²; BASEMOL = Ca, Mg, and K, mol_c ha⁻¹. MAPRE = mean annual precipitation, cm; dep. = atmospheric deposition, kg ha⁻¹.

§ H₂O-extractable SO₄-S (water-soluble SO₄-S).

¶ Adsorbed SO₄-S.

SO₄-S-adsorption potential.

soil properties and lack of significant relationships between soil cation levels and pollutant-deposition variables suggest that pollutant deposition has not measurably impacted soil nutrient-cation reserves to date. However, long-term deleterious consequences of continued pollutant deposition on nutrient-cation reserves at Sites 4a and 5 cannot be ruled out.

Limitations encountered during this study of soil properties included the small number of sites sampled and the relatively limited sampling performed within sites. Concentrating on only a few sites along the gradient, however, allowed intensive study of other ecosystem processes related to atmospheric deposition (e.g., Burton et al., 1991). More extensive regional soil sampling (e.g., MacDonald, 1987; David et al., 1988; Grigal and Ohmann, 1989) has greater power to detect subtle differences in soil properties related to pollutant deposition. Because of the site-specific nature of our study, variation in inherent soil properties became a complicating factor. Trends in inherent soil properties, including those under climatic influence, could be removed statistically. Remaining variation in soil properties attributed to pollutant deposition is both conservative in a statistical sense and consistent with findings of extensive regional soil-sampling efforts.

CONCLUSIONS

At the six northern hardwood sites studied, no evidence was found to support the hypothesis that forest-floor total N or mineral-soil total S and N had increased as a result of pollutant deposition. Mineral-soil total S and N contents were exclusively related to soil organic-matter levels. Total S concentration in forest floor (Oe+a) was strongly related to total N concentration, but SO₄ deposition was a secondary significant predictor. Water soluble and adsorbed SO₄ primarily reflected soil total S contents, but additional variability also was explained by a positive effect of SO₄ deposition. Similarly, after accounting for effects of inherent soil properties, a significant negative effect of SO₄ deposition on the SO₄-adsorption potential of upper B horizons existed. These relationships support the hypothesis that soil SO₄-S contents increased and the capacity to retain additional SO₄ decreased as SO₄ deposition increased. Observed trends in exchangeable-cation contents were consistent with hypothesized pollutant effects but were largely explainable by similar trends in inherent soil properties. Differential effects of pollutant deposition and natural acidification processes on nutrient-cation reserves could not be separated at this time.

ACKNOWLEDGMENTS

The authors would like to thank S. Alexander, L. Ashford, R. Brooks, C. Butler, S. Hoffmann, M. Jaeger, N. Mullett, D. Oles, C. Schewlander, J. Stoker, and K. Tschirhart for their assistance in soil description, sampling, and analysis. This research was supported by the Northeastern Forest Experiment Station, Eastern Hardwoods Research Cooperative, within the joint USEPA-USDA Forest Service Forest Response Program. This paper has not been subject to EPA or Forest Service policy review and should not be construed to represent the policies of either agency.

REFERENCES

- Aber, J.D., K.J. Nadelhoffer, P. Steudler, and J.M. Melillo. 1989. Nitrogen saturation in northern forest ecosystems. *BioScience* 39:378-386.
- Armentano, T.V., and O.L. Loucks. 1983. Air pollution threats to US national parks in the Great Lakes region. *Environ. Conserv.* 10:303-313.
- Binkley, D., and D.D. Richter. 1987. Nutrient cycles and H⁺ budgets of forest ecosystems. *Adv. Ecol. Res.* 16:1-51.
- Burton, A.J., K.S. Pregitzer, and D.D. Reed. 1991. Leaf area and foliar biomass relationships in northern hardwood forests located along an 800 km acid deposition gradient. *For. Sci.* 37:1041-1059.
- David, M.B., D.F. Grigal, L.F. Ohmann, and G.Z. Gertner. 1988. Sulfur, carbon, and nitrogen relationships in forest soils across the northern Great Lake states as affected by atmospheric deposition and vegetation. *Can. J. For. Res.* 18:1386-1391.
- Glass, G.E., and O.L. Loucks. 1986. Implications of a gradient in acid and ion deposition across the northern Great Lakes states. *Environ. Sci. Technol.* 20:35-43.
- Grigal, D.F., and L.F. Ohmann. 1989. Spatial patterns in elemental concentrations of the forest floor across the north central USA. *J. Environ. Qual.* 18:368-373.
- Johnson, D.W. 1984. Sulfur cycling in forests. *Biogeochemistry* 1:29-43.
- Johnson, D.W., D.D. Richter, H. Van Miegroet, and D.W. Cole. 1983. Contributions of acid deposition and natural processes to cation leaching from forest soils: A review. *J. Air Pollut. Control Assoc.* 33:1036-1041.
- Johnson, D.W., and G.E. Taylor. 1989. Role of air pollution in forest decline in eastern North America. *Water Air Soil Pollut.* 48:21-43.
- Johnson, D.W., J. Turner, and J.M. Kelly. 1982. The effects of acid rain on forest nutrient status. *Water Resour. Res.* 18:449-461.
- Johnson, N.M. 1979. Acid rain: Neutralization within the Hubbard Brook ecosystem and regional implications. *Science (Washington, DC)* 204:497-499.
- Lucier, A.A., and B.B. Stout. 1988. Changes in forests and their relationships to air quality. *Tappi J.* 71(4):103-107.
- MacDonald, N.W. 1987. Sulfate adsorption in Michigan forest soils. Ph.D. diss. Michigan State Univ., East Lansing (Diss. Abstr. 87-22859).
- MacDonald, N.W., and J.B. Hart, Jr. 1990. Relating sulfate adsorption to soil properties in Michigan forest soils. *Soil Sci. Soc. Am. J.* 54:238-245.
- National Atmospheric Deposition Program. 1985a. NADP annual summary, precipitation chemistry in the United States, 1982. *Nat. Resour. Ecol. Lab., Colorado State Univ., Fort Collins.*
- National Atmospheric Deposition Program. 1985b. NADP/NTN annual summary, precipitation chemistry in the United States, 1983. *Nat. Resour. Ecol. Lab., Colorado State Univ., Fort Collins.*
- National Atmospheric Deposition Program. 1986. NADP/NTN annual summary, precipitation chemistry in the United States, 1984. *Nat. Resour. Ecol. Lab., Colorado State Univ., Fort Collins.*
- National Oceanic and Atmospheric Administration. 1983. Climate normals for the U.S. (Base: 1951-1980). National Climatic Center, Environ. Data Inf. Serv. Gale Research Co., Detroit, MI.
- Nichols, D.S., and R.E. McRoberts. 1986. Relations between lake acidification and sulfate deposition in northern Minnesota, Wisconsin, and Michigan. *Water Air Soil Pollut.* 31:197-206.
- Nihlgard, B. 1990. Relationship of forest damage to air pollution in the nordic countries. *Agric. For. Meteorol.* 50:87-98.
- Page, A.L., R.H. Miller, and D.R. Keeney. (ed.) 1982. Methods of soil analysis. Part 2. 2nd ed. *Agron. Monogr.* 9. ASA and SSSA, Madison, WI.
- Phillips, D.W., and J.A.W. McCulloch. 1972. The climate of the Great Lakes basin. *Atmospheric Environ., Climatol. Stud.* no. 20. Environment Canada, Toronto, ON, Canada.
- Reuss, J.O., B.J. Cosby, and R.F. Wright. 1987. Chemical processes governing soil and water acidification. *Nature (London)* 329:27-32.
- Richter, D.D., D.W. Johnson, and D.E. Todd. 1983. Atmospheric sulfur deposition, neutralization, and ion leaching in two deciduous forest ecosystems. *J. Environ. Qual.* 12:263-270.
- Schroeder, P., and A.R. Kiestler. 1989. The Forest Response Program: National research on forest decline and air pollution. *J. For.* 87(1):27-32.
- Schulze, E.-D. 1989. Air pollution and forest decline in a spruce (*Picea abies*) forest. *Science (Washington, DC)* 244:776-783.
- Soil Conservation Service. 1972. Soil survey laboratory methods and procedures for collecting soil samples. USDA-SCS Soil Surv. Invest. Rep. 1. U.S. Gov. Print. Office, Washington, DC.
- Soil Conservation Service. 1982. Procedures for collecting soil samples and methods of analysis for soil survey. USDA-SCS Soil Surv. Invest. Rep. 1. Revised ed. U.S. Gov. Print. Office, Washington, DC.
- Wall, L.L., C.W. Gehrke, and J. Suzuki. 1980. An automated turbidimetric method for total sulfur in plant tissue and sulfate sulfur in soils. *Commun. Soil Sci. Plant Anal.* 11:1087-1103.
- Witter, J.A. 1990. Effects of multiple interactions on forests: Approaches and examples. p. 142-147. *In* Are forests the answer? Proc. 1990 SAF Natl. Conv., Washington, DC. 29 July-1 Aug. 1990. Soc. Am. Foresters, Bethesda, MD.
- Zemba, S.G., D. Golomb, and J.A. Fay. 1988. Wet sulfate and nitrate deposition patterns in eastern North America. *Atmos. Environ.* 22:2751-2761.