Sulfate Adsorption in Forest Soils of the Great Lakes Region

Neil W. MacDonald,* Andrew J. Burton, John A. Witter, and Daniel D. Richter

ABSTRACT

Sulfate adsorption by forest soils modifies the impact of pollutant deposition on cation leaching processes. We examined relationships among SO$_3^-$ adsorption, soil properties, and seasonal variation in soil solution chemistry at 13 sites representing deciduous forest ecosystems common in the Great Lakes region. Objectives of the study were to test the validity of previously proposed SO$_3^-$ adsorption indices, to examine within- and among-site variability in SO$_3^-$ adsorption potential, and to investigate the effects of seasonal changes in soil solution chemistry on SO$_3^-$ retention. Mineral soils were sampled by horizon at all sites, and soil solutions were sampled at lower E and lower B horizon boundaries at 10 sites. Proposed indices overpredicted sulfate adsorption in certain SO$_3^-$ releasing subsurface horizons, seriously limiting the applicability of the published regression equations. We developed improved regression equations using the sum of initial extractable SO$_3^-$ and additional SO$_3^-$ adsorbed under laboratory conditions as the dependent variable. Sulfate retention indices predicted by the improved equations were independent of existing levels of extractable SO$_3^-$ and past history of atmospheric SO$_3^-$ deposition. Examination of within- and among-site variability in SO$_3^-$ adsorption potentials suggested that soils need to be grouped tightly on a taxonomic basis for modelling purposes. Seasonal variation in soil solution SO$_3^-$ concentrations and fluxes was consistent with an annual cycle of SO$_3^-$ retention and release. Although seasonal patterns in SO$_3^-$ concentrations and fluxes appeared to be controlled by hydrologic and S-cycling processes, the magnitude of SO$_3^-$ fluxes was primarily related to atmospheric SO$_3^-$ deposition rates.

Abbreviations: Fe$_{dc}$, dithionite-citrate extractable Fe; Al$_{dc}$, dithionite-citrate extractable Al; Fe$_{ox}$, ammonium oxalate extractable Fe; Al$_{ox}$, ammonium oxalate extractable Al. **, ***Significant at the 0.01 and 0.001 probability levels, respectively.

potential of a soil. A common thread uniting recent studies has been the attempt to statistically relate either indices of SO$_3^-$ adsorption (Johnson and Todd, 1983; Harrison et al., 1989; MacDonald and Hart, 1990) or adsorption isotherm parameters (Comfort et al., 1992) specifically tested the validity of the relationships presented. Shaffer and Stevens (1991) discussed the problems encountered when aggregating SO$_3^-$ adsorption isotherm data from soils within watersheds and the need to account for soil heterogeneity in predictive model development. However, few studies have quantified variability in SO$_3^-$ adsorption characteristics among similar soils.

Static, laboratory measures of the ability of a soil to adsorb SO$_3^-$ also need to be put in context with seasonal changes in soil solution chemistry. Foster (1985), Khanna et al. (1987), Mitchell et al. (1989), and Foster et al. (1992) reported pronounced seasonality in soil solution SO$_3^-$ concentrations in forest ecosystems in North America and Europe. Disturbance effects (Fuller et al., 1987; Nodvin et al., 1988) also may greatly modify patterns of SO$_3^-$ retention in forest ecosystems through soil acidification and alteration in soil solution chemistry. The dynamic nature of SO$_3^-$ adsorption and desorption needs to be considered when attempting to quantify ecosystem response to changes in pollutant deposition, but relatively few studies have examined temporal variation in soil solution SO$_3^-$ concentrations and fluxes.

We have studied the effects of atmospheric pollutant deposition on forest ecosystems at multiple sites in the Great Lakes region (Pregitzer et al., 1992; Burton et al., 1993; Liechty et al., 1993). Pollutant deposition effects on soil properties and ion leaching at these sites were previously considered (MacDonald et al., 1991, 1992, 1993). The objectives of the work reported here were to (i) test the validity of regression equations relating SO$_3^-$ adsorption potentials to soil properties proposed by MacDonald and Hart (1990), (ii) examine variability in soil SO$_3^-$ adsorption potentials within and among sites, and (iii) investigate the effects of seasonal changes in soil solution chemistry on SO$_3^-$ retention and flux in forest ecosystems in the Great Lakes region.

### METHODS

We studied 13 sites at 10 locations representing deciduous forest ecosystems common in the Great Lakes region (Fig. 1). These sites are located along a gradient of atmospheric pollutant deposition extending from Minnesota to Ohio, with total estimated mean annual wet and dry SO$_3^-$ deposition ranging from 12 kg ha$^{-1}$ at Site 1 to 55 kg ha$^{-1}$ at Site 10 (MacDonald et al., 1992). Overstory species composition at Sites 1, 2, 3, 4a, 4b, and 5 was predominantly sugar maple (Acer saccharum Marshall; Pregitzer et al., 1992). Overstory composition at Sites 6c, 6, 7, 8, 9a, 9b, and 10 was dominated by one or more of the following species: black oak (Quercus velutina Lam.), red oak (Quercus rubra L.), or white oak (Quercus alba L., MacDonald et al., 1993). Soils at Sites 1 to 5 were Fragipodams or Hapludalfs (Table 1).

Table 1. Classification of soils present at research sites in the Great Lakes region.

<table>
<thead>
<tr>
<th>Site</th>
<th>Family</th>
<th>Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>coarse-loamy, mixed, frigid</td>
<td>Sarona</td>
</tr>
<tr>
<td></td>
<td>Alfic Haplorthod</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>coarse-loamy, mixed, frigid</td>
<td>Wakefield</td>
</tr>
<tr>
<td></td>
<td>Alfic Fragiorthod</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>sandy, mixed, frigid Typic</td>
<td>Kalkaska</td>
</tr>
<tr>
<td></td>
<td>Haplorthod</td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>sandy, mixed, frigid Typic</td>
<td>Blue Lake</td>
</tr>
<tr>
<td></td>
<td>Haplorthod</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>sandy, mixed, mesic Typic</td>
<td>Kalkaska</td>
</tr>
<tr>
<td></td>
<td>Haplorthod</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>coarse-loamy, mixed, mesic</td>
<td>Oshtemo</td>
</tr>
<tr>
<td></td>
<td>Typic Hapludalf</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>sandy, mesic Psammentic</td>
<td>Oshtemo</td>
</tr>
<tr>
<td></td>
<td>Hapludalf</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>mixed, mesic Typic Haplorthod</td>
<td>Oakville</td>
</tr>
<tr>
<td>9a</td>
<td>coarse-loamy, mixed, mesic</td>
<td>Oshtemo</td>
</tr>
<tr>
<td></td>
<td>Typic Hapludalf</td>
<td></td>
</tr>
<tr>
<td>9b</td>
<td>fine-loamy, mixed, mesic</td>
<td>Miami</td>
</tr>
<tr>
<td></td>
<td>Typic Hapludalf</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>fine, illitic, mesic Aquic</td>
<td>Ellsworth</td>
</tr>
<tr>
<td></td>
<td>Hapludalf</td>
<td></td>
</tr>
</tbody>
</table>

† No mesic zone Typic Haplorthod series is currently recognized in Michigan. The closest equivalent Typic Haplorthod is Kalkaska (W.E. Frederick, USDA-SCS, E. Lansing, MI, 1993, personal communication).

Soils at each site were sampled by horizon to a depth of at least 150 cm from three randomly located soil pits (MacDonald et al., 1991, 1993). Soil samples were air dried at 25°C and passed through a 2-mm sieve prior to analysis. All samples were analyzed for pH (1:1 soil/H$_2$O and 1:2 soil/0.01 M CaCl$_2$); texture (hydrometer); H$_2$O and PO$_4^{2-}$ [0.008 M Ca(H$_2$PO$_4$)$_2$, H$_2$O] extractable SO$_3^-$; NH$_4$Cl exchangeable Ca$^{2+}$, Mg$^{2+}$, and K$^+$; KCl exchangeable Al$^3+$; NH$_4$F-HCl extractable P, and Fe$_{OC}$ and Al$_{OC}$. To provide data for mesic zone prediction equations, samples from Sites 6 to 10 also were analyzed for organic C (H$_2$SO$_4$-K$_2$Cr$_2$O$_7$ oxidation) and Fe$_{OC}$ and Al$_{OC}$. Cations were determined by atomic absorption spectrophotometry; SO$_3^-$ by ion chromatography, organic C by titration with FeSO$_4$, and P by automated colorimetry (phosphomolybdate). Analyses were performed using air-dry samples with results corrected to an oven-dry weight basis. Analytical methods are docu-
Sulfate adsorption potentials were determined by shaking 10-g samples for 24 h in 0.05 L of 0.01 M CaCl₂ containing 0.312 mmol SO₄²⁻ L⁻¹ as detailed by MacDonald and Hart (1990). Solutions were filtered through Whatman no. 42 filter paper and analyzed for SO₄²⁻ by automated BaSO₄ turbidimetry (Wall et al., 1980) or by ion chromatography. Turbidimetry was used for soils collected from northern hardwood sites in 1988, whereas ion chromatography was used for soils collected from oak sites in early 1989 and 1990. Both methods were used routinely to analyze quality control and quality assurance samples and achieved comparable accuracy and precision (MacDonald et al., 1991, 1992, 1993). Sulfate adsorbed was calculated as the difference in SO₄²⁻ concentration before and after the 24-h shaking period.

Tension lysimeters (Model 1900, Soilmoisture Equipment Corp., Santa Barbara, CA) were installed at two soil depths on three measurement plots per site (four per plot at each depth), with the exception of Sites 4c, 6, and 7 where soil solutions were not collected. Upper lysimeters were installed at depths approximating the lower boundary of soil E horizons (15–30 cm deep), whereas lower lysimeters were installed at depths approximating the lower boundary of soil B horizons (60–75 cm). Lysimeters were equilibrated for periods of from 16 wk to more than 1 yr prior to initiation of routine collections. Soil solutions were sampled from September 1988 to June 1990, and samples were analyzed for pH, conductivity, alkalinity, anions, and cations as detailed by MacDonald et al. (1992).

Validity of Adsorption Prediction Equations

RESULTS AND DISCUSSION

Validity of Adsorption Prediction Equations

To test the validity of Eq. [1], [2], and [3], the relationships between predicted indices and observed adsorption potentials were evaluated using regression. Residuals were examined for patterns indicating departure from linearity, nonhomogeneity of variance, and presence of outliers. Improved regression equations were developed for subsurface horizons using the sum of native PO₄³⁻ extractable SO₄²⁻ (adsorbed + soluble SO₄²⁻) and additional SO₄²⁻ adsorbed during laboratory equilibration as an index of SO₄²⁻ retention ability. This SO₄²⁻ retention index allowed inclusion of samples that released SO₄²⁻ during equilibration, the sum giving an estimate of the total SO₄²⁻ retaining ability of the soil under the specific laboratory conditions employed. In nine of 389 total cases, SO₄²⁻ release exceeded extractable SO₄²⁻. Discrepancies were mostly <0.5 mg SO₄²⁻ S kg⁻¹, and the samples involved were from deep subsurface (BC, C) horizons where additional SO₄²⁻ release during the 24-h shaking period may have occurred from slow dissolution of SO₄²⁻ bearing minerals (e.g., CaSO₄, present in calcareous C horizons). These nine samples had no net SO₄²⁻ retention ability, and the negative numbers were set to zero. For regression analyses, SO₄²⁻ retention indices were transformed to ln[(mg SO₄²⁻ S kg⁻¹) + 1] to control variance. Transformation of predictor variables other than pH measures took the form ln(X). For simplicity, we limited the number of predictor variables to two. The new equations incorporated both the data of MacDonald and Hart (1990) and that from the current study (total frigid zone n = 226, total mesic zone n = 163).

Data from frigid zone A, AE, E, and mesic zone A horizons were excluded a priori from all regression analyses because these surface horizons are relatively inactive in SO₄²⁻ adsorption processes under laboratory conditions (MacDonald and Hart, 1990; Randlett et al., 1992). Studies of precipitation, throughfall, and soil solution SO₄²⁻ concentrations and fluxes at these sites (MacDonald et al., 1992) also have not detected any measurable net adsorption or retention of SO₄²⁻ occurring in these surface horizons. Because surface horizons differ greatly in organic C content, microbial activity, and mechanisms of SO₄²⁻ cycling from underlying horizons, including both surface and subsurface horizon data in prediction equations serve only to obscure relationships between SO₄²⁻ adsorption and other physical and chemical soil properties.
Table 2. Improved regression equations for SO$_3^{–}$ retention in subsurface horizons of forest soils in the Great Lakes region.

<table>
<thead>
<tr>
<th>Predictor variable†</th>
<th>Parameter estimate</th>
<th>Standard error</th>
<th>$R^2$</th>
<th>SE</th>
<th>df‡</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Frigid zone Fragiorthods and Haplorthods</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Constant</td>
<td>-0.0578</td>
<td>0.3747</td>
<td></td>
<td>0.5401***</td>
<td>0.0550</td>
</tr>
<tr>
<td>ln(AL$_2$)</td>
<td>-0.6326***</td>
<td>0.0323</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH in CaCl$_2$</td>
<td>-0.4206***</td>
<td>0.0469</td>
<td>0.78***</td>
<td>0.456</td>
<td>223</td>
</tr>
<tr>
<td><strong>Mesic zone Udiumpsments and Hapludalfs</strong></td>
<td></td>
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<td></td>
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<tr>
<td><strong>Regression A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Constant</td>
<td>0.7597</td>
<td>0.5205</td>
<td></td>
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<tr>
<td>ln(Fe$_i$)</td>
<td>0.5401***</td>
<td>0.0550</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH in CaCl$_2$</td>
<td>-0.6489***</td>
<td>0.0318</td>
<td>0.77***</td>
<td>0.471</td>
<td>160</td>
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<tr>
<td><strong>Regression B</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Constant</td>
<td>4.7906</td>
<td>0.2066</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>ln(clay)</td>
<td>0.3329***</td>
<td>0.0430</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH in CaCl$_2$</td>
<td>-0.6460***</td>
<td>0.0346</td>
<td>0.74***</td>
<td>0.509</td>
<td>160</td>
</tr>
</tbody>
</table>

*** Significant at $P < 0.001$.
† Dependent variable = ln((mg SO$_3^{–}$-S kg$^{-1}$) + 1); AL$_2$ and Fe$_i$ in mg kg$^{-1}$; clay in percent.
‡ Standard error of the estimate (In units).
§ Error degrees of freedom.

6 to 10) were significantly but less strongly predicted by the regressed indices from Eq. [2] ($r^2 = 0.43$*** and [3] ($r^2 = 0.56$***). Examination of residuals from these two equations revealed the presence of outliers characterized by SO$_3^{–}$ release under laboratory conditions and overprediction of SO$_3^{–}$ adsorption. These outliers were samples from fine-textured Bt$_2$, BC, and C horizons with high base saturation (>99%). Unlike Eq. [1], removal of outliers having this combination of properties did not greatly improve $r^2$ values compared with those reported above, suggesting that Eq. [2] and [3] have further limitations.

The greatest overprediction of adsorption occurred for BC and C horizons at Site 10, which released up to 33 mg SO$_3^{–}$-S kg$^{-1}$ during laboratory equilibrations. Desorption from these horizons at Site 10 was associated with high ambient solution SO$_3^{–}$ concentrations (>0.4 mmol L$^{-1}$) resulting from high rates of atmospheric SO$_3^{–}$ deposition (MacDonald et al., 1993). The occurrence of SO$_3^{–}$ releasing subsurface horizons in both mesic and frigid zone soils limited the applicability of previously published regression equations. Specifically, the equations proposed by MacDonald and Hart (1990) overpredicted adsorption in fine-textured subsurface horizons with base saturation >99% and overpredicted adsorption in soils with ambient solution SO$_3^{–}$ concentrations >0.3 mmol L$^{-1}$.

Development of Improved Adsorption Prediction Equations

Improved regression equations, where the dependent variable was the ln-transformed SO$_3^{–}$ retention index, were developed for frigid and mesic zone soils using a few commonly measured soil properties as predictor variables (Table 2). This index provided a more reliable measure of the ability of a soil to retain SO$_3^{–}$ because it accounted for native adsorbed and soluble SO$_3^{–}$ in the soil as well as additional amounts of SO$_3^{–}$ that could be adsorbed. The $R^2$ values and standard errors of the esti-
Sources of data needed to apply these prediction equations include published soil survey investigations reports (Soil Conservation Service, 1980) and regionally available soil characterization data (Michigan Technological University, 1982–1984). A limitation for application of these and similar equations is that Al and Fe4 and, to a lesser extent, pH measured in CaCl2, are not consistently available in existing soil characterization data sets. In instances where the necessary soil characterization data is lacking or for research related to specific sites, it is necessary to directly measure the SO3~ adsorption properties of the soil in question using a method appropriate to the objectives of the research being performed. Although subject to the caveats and limitations discussed above, the results do support the validity of using previously measured soil properties to predict SO3~ retention characteristics within groups of taxonomically related soils.

**Variation in Adsorption Within and Among Sites**

The variance of SO3~ adsorption potentials of major soil horizons sampled within sites (Table 4) in most cases was not significantly different from the variance of similar genetic horizons sampled within soil series across a much larger region by MacDonald and Hart (1990). This suggests that a large proportion of the variation in SO3~ adsorption potential among similar soils occurs at local, not regional scales. Within-site variance was significantly less than within-series variance only in one horizon at Site 9b. Within-site variance was significantly greater than within-series variance at Sites 2, 6, 7, and 8 where Bt horizon development or C horizon characteristics varied greatly within a site. At Sites 2, 7, and 8, soils were classified in divergent families as a result of variation in these subsurface properties. This suggests that soils should be grouped tightly on a taxonomic basis when aggregating SO3~ adsorption data for modelling purposes.

In Fragiorthods and Haplorthods, adsorption potentials were highest in Bhs and Bs horizons (Fig. 2a–2f). Adsorption peaks in upper B horizons of Spodosols have previously been reported (Johnson and Todd, 1983; Fuller et al., 1985). Sulfate adsorption potentials in these soils tended to decrease as soil pH levels increased and extractable Al decreased (Fig. 2a–2f). Highly developed Spodosols (Fig. 2a and 2b) had substantial capacities to adsorb additional SO3~.

Sulfate adsorption potentials were highest in Bt horizons of mesic zone Hapludalfs (Fig. 3a–3f). In Udipsamm and Hapludalfs developed in acidic sands, adsorption potentials increased with clay content (Site 8 < 7 < 6, Fig. 3a–3c). Adsorption potentials in upper E and Bt horizons of Hapludalfs having shallow calcareous C horizons increased with acidity (Site 9b < 9a < 10, Fig. 3e, 3d, 3f) but were less related to clay content, which increased in the order Site 9a < 9b < 10.

These results illustrate the consistent relationship between soil properties and SO3~ adsorption characteristics of forest soils in the Great Lakes region. The magnitude of SO3~ retention is determined by the amounts of Al, Fe, and clay in the soil, as modified by the degree of acidity. To the extent that physical and chemical properties can be quantified for a given soil taxon from a statistically representative sample, SO3~ retention characteristics of soils should be predictable within a soil taxonomic framework. Such predictions need to take into consideration the past history of SO3~ input, as noted by Johnson and Todd (1983) and illustrated earlier in this paper. The need to maximize similarity in soil properties while aggregating soil SO3~ adsorption characteristic data (Shaffer and Stevens, 1991) suggests that regional characterizations should take place at the lowest taxonomic level possible, e.g., the family or series level.

**Seasonal Sulfate Concentrations and Fluxes**

Analysis of variance of soil solution SO3~ concentration data revealed significant (P < 0.05) site and season effects, as well as significant two-way interactions among site, depth, and season. Sulfate concentrations in soil solutions collected at lower E horizon boundaries generally were higher in fall than in spring (Fig. 4a). Elevated SO3~ concentrations in the fall apparently were related to the combined effects of reduced soil water content resulting from evapotranspiration (e.g., Foster et al., 1992), accumulation of mineralized SO3~ in surface soils during the summer, and the autumnal flux of SO3~ leached from foliar litter. Soil solution SO3~ concentrations in the upper sola then declined during late fall, winter, and early spring as a result of soil water recharge and snowmelt. Sulfate concentrations in solutions collected at lower B horizon boundaries displayed much less seasonal variation (Fig. 4b). In the fall, solution SO3~ concentrations tended to decrease from lower E to lower B horizons, whereas in the spring, SO3~ concentrations increased with depth in the soil profile. Similar seasonal fluctuations in soil solution SO3~ concentrations were reported for northern hardwood forests at the Turkey Lakes Watershed, Ontario, Canada (Foster, 1985; Foster et al., 1992).

Estimated SO3~ fluxes, incorporating variation in both SO3~ concentrations and hydrologic fluxes, display seasonal differences in SO3~ release and retention more clearly. During the fall, lower B horizon SO3~ fluxes were less than E horizon SO3~ fluxes (Fig. 4c), which

**Table 4. Sites and soil horizons with significantly different within-site and within-series estimates of variance for SO3~ adsorption potential of major soil horizons.**

| Site | Horizon | Within-site variance | Within-series variance | F
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Bt/BC</td>
<td>43.5</td>
<td>0.6-4.4</td>
<td>72.5**</td>
</tr>
<tr>
<td>6</td>
<td>2C</td>
<td>3.4</td>
<td>0.4</td>
<td>22.5**</td>
</tr>
<tr>
<td>7</td>
<td>Bt/E' and Bt</td>
<td>21.9</td>
<td>0.8-49.0</td>
<td>27.4**</td>
</tr>
<tr>
<td>2C</td>
<td>3.7</td>
<td>0.4-0.8</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>E' and Bt</td>
<td>6.8</td>
<td>0.8</td>
<td>8.5*</td>
</tr>
<tr>
<td>9b</td>
<td>Bt1</td>
<td>0.2</td>
<td>28.1</td>
<td>140.5*</td>
</tr>
</tbody>
</table>

*, **Significant at P < 0.05 and 0.01 (two-tailed test).
† Estimates of within-series variance (s2) taken from MacDonald and Hart (1990). Where a range of variance estimates are given, the smallest within-series variance was used to calculate F.
‡ F values calculated as larger s2/smaller s2 with appropriate numerator and denominator degrees of freedom.
is consistent with adsorption or retention in B horizons. During the spring, lower B horizon SO$_4^{2-}$ fluxes were greater than E horizon SO$_4^{2-}$ fluxes at Sites 3 to 10 (Fig. 4d), which is consistent with SO$_4^{2-}$ desorption or release from B horizons. Sites 1 and 2, which have low rates of atmospheric SO$_4^{2-}$ deposition and soils with high adsorption potentials, retained small amounts of SO$_4^{2-}$ in both spring and fall.

Both spring and fall SO$_4^{2-}$ fluxes calculated at lower E and lower B horizon boundaries (Fig. 4c and 4d) were positively correlated ($r = 0.63^{**}$ to $0.95^{**}$) with total annual wet plus dry SO$_4^{2-}$ deposition. Net SO$_4^{2-}$ flux in the fall of 1990 also was positively correlated ($r = 0.77^{**}$) with total SO$_4^{2-}$ deposition. Net spring SO$_4^{2-}$ fluxes were negatively correlated ($r = -0.79^{**}$ to $-0.81^{**}$) with total SO$_4^{2-}$ deposition. Additional varia-
tion in net spring $\text{SO}_4^{2-}$ fluxes was explained by either B horizon $\text{SO}_4^{2-}$ adsorption potential ($R = 0.82^{**}$) or $\text{SO}_4^{2-}$ retention index ($R = 0.83^{**}$ to $0.88^{**}$). These relationships are consistent with the magnitude of seasonal $\text{SO}_4^{2-}$ fluxes in these forest ecosystems being driven by rates of atmospheric $\text{SO}_4^{2-}$ input. The magnitude of seasonal fluxes within these ecosystems appears to be modified to a lesser extent by the inherent ability of the soil to adsorb or otherwise retain $\text{SO}_4^{2-}$. On an ecosystem level, annual input-output balances (MacDonald et al., 1992) suggested that $\text{SO}_4^{2-}$ outputs below B horizons equalled or exceeded atmospheric $\text{SO}_4^{2-}$ inputs, supporting the contention that adsorption does not represent a significant net sink for $\text{SO}_4^{2-}$ in forest ecosystems that
have a long previous history of elevated atmospheric SO$_4^{2-}$ deposition (Fuller et al., 1985; Randlett et al., 1992).

Fuller et al. (1987) and Nodvin et al. (1988) documented links among nitrification, soil acidification, and SO$_4^{2-}$ adsorption in both undisturbed and clearcut watersheds at Hubbard Brook, New Hampshire. Relationships between soil solution NO$_3^-$ and SO$_4^{2-}$ concentrations consistent with nitrification effects also were reported for the Turkey Lakes watershed by Foster et al. (1992) and Yin et al. (1993). In contrast to these reports, seasonal patterns of soil solution SO$_4^{2-}$ were not strongly tied to nitrification at the majority of sites we studied. Site 4b experienced elevated NO$_3^-$ loss as a result of nitrification following defoliation by the forest tent caterpillar (*Malacosoma disstria* Hübner), but NO$_3^-$ and SO$_4^{2-}$ concentrations in soil solution were positively correlated ($r = 0.57^{**}$, $n = 89$), not negatively correlated as reported by Nodvin et al. (1988) and Foster et al. (1992). Only one of the other sites we studied (9b) displayed a negative correlation ($r = -0.35^{**}$, $n = 97$) between NO$_3^-$ and SO$_4^{2-}$ in soil solutions collected at 30 cm, with spring increases in NO$_3^-$ coinciding with decreases in SO$_4^{2-}$. At this same site, NO$_3^-$ concentrations and pH in soil solutions collected at 75 cm were negatively correlated ($r = -0.38^{**}$, $n = 78$), which is also consistent with effects of nitrification. Results of our study suggest that a strong link between SO$_4^{2-}$ adsorption and nitrification may be limited to specific forest ecosystems with soils that nitrify readily or to periods following disturbances as severe as clearcutting that induce high rates of nitrification and soil acidification. Although the short period of our study limits this conclusion, monitoring of soil solutions at Sites 2 to 5 for 5 yr (1988–1993) has revealed no consistent relationships among soil solution NO$_3^-$, SO$_4^{2-}$, and pH.

**CONCLUSIONS**

The applicability of previously published SO$_4^{2-}$ adsorption prediction equations was seriously limited by over-prediction of adsorption in certain SO$_4^{2-}$ releasing horizons. Improved regression equations were developed using the sum of native extractable SO$_4^{2-}$ and additional SO$_4^{2-}$ adsorbed under laboratory conditions as the dependent variable. This SO$_4^{2-}$ retention index accounted for current SO$_4^{2-}$ concentrations in the soil, included additional amounts of SO$_4^{2-}$ that could be adsorbed, and was independent of atmospheric SO$_4^{2-}$ deposition rates.

Comparison of within-site estimates of variance in
SO$\text{\textsubscript{4}}^{-}$ adsorption potentials with previously determined within-series variance estimates suggested that much of the variation in SO$\text{\textsubscript{4}}^{-}$ adsorption potential among similar soils arises at local, not regional, scales. Variation in SO$\text{\textsubscript{4}}^{-}$ adsorption potential among sites was related to soil morphological, physical, and chemical characteristics, suggesting that SO$\text{\textsubscript{4}}^{-}$ retention ability should be predictable within a soil taxonomic framework. The need to maximize similarity in soil properties while aggregating SO$\text{\textsubscript{4}}^{-}$ retention data for modelling purposes requires that such data be combined at the lowest soil taxonomic level possible.

Soil solution SO$\text{\textsubscript{4}}^{-}$ concentration data and flux estimates were consistent with an annual cycle of SO$\text{\textsubscript{4}}^{-}$ retention and release, adsorption predominating in the fall and desorption predominating in the spring. Seasonal patterns in soil solution SO$\text{\textsubscript{4}}^{-}$ concentrations and fluxes were consistent with changes in soil water content, S mineralization, and litterfall but did not appear to be strongly related to nitrification at the majority of sites studied. The magnitude of net seasonal SO$\text{\textsubscript{4}}^{-}$ fluxes was primarily related to atmospheric SO$\text{\textsubscript{4}}^{-}$ deposition rates, and secondarily to soil SO$\text{\textsubscript{4}}^{-}$ retention ability.

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