

DIVISION S-7—FOREST & RANGE SOILS

Sulfate Adsorption in Forest Soils of the Great Lakes Region

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ABSTRACT

Sulfate adsorption by forest soils modifies the impact of pollutant deposition on cation leaching processes. We examined relationships among SO_4^{2-} 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_4^{2-} adsorption indices, to examine within- and among-site variability in SO_4^{2-} adsorption potential, and to investigate the effects of seasonal changes in soil solution chemistry on SO_4^{2-} 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_4^{2-} releasing subsurface horizons, seriously limiting the applicability of the published regression equations. We developed improved regression equations using the sum of initial extractable SO_4^{2-} and additional SO_4^{2-} adsorbed under laboratory conditions as the dependent variable. Sulfate retention indices predicted by the improved equations were independent of existing levels of extractable SO_4^{2-} and past history of atmospheric SO_4^{2-} deposition. Examination of within- and among-site variability in SO_4^{2-} adsorption potentials suggested that soils need to be grouped tightly on a taxonomic basis for modelling purposes. Seasonal variation in soil solution SO_4^{2-} concentrations and fluxes was consistent with an annual cycle of SO_4^{2-} retention and release. Although seasonal patterns in SO_4^{2-} concentrations and fluxes appeared to be controlled by hydrologic and S-cycling processes, the magnitude of SO_4^{2-} fluxes was primarily related to atmospheric SO_4^{2-} deposition rates.

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SULFATE ADSORPTION modifies the effects of elevated pollutant (H^+ , SO_4^{2-}) deposition on cation leaching processes in forest ecosystems. For this reason, quantifiable soil SO_4^{2-} adsorption characteristics are necessary components of models used to estimate pollutant impacts on sensitive ecosystems (Holdren et al., 1993). Knowledge of SO_4^{2-} adsorption characteristics of forest soils also may be important for predicting ecosystem response either to decreases in atmospheric SO_4^{2-} deposition (Driscoll et al., 1989; Harrison et al., 1989) or to alteration in S mineralization rates related to regional climate change. One problem encountered in assessing pollutant deposition impacts was that only limited soil SO_4^{2-} adsorption data existed (Johnson and Todd, 1983). However, existing soil characterization data may be used to estimate the SO_4^{2-} retention abilities of soils across large geographic regions if SO_4^{2-} adsorption characteristics can be predicted from other previously measured soil properties.

Various studies have examined the SO_4^{2-} adsorption characteristics of forest soils in both the United States (Johnson and Todd, 1983; Fuller et al., 1985; Harrison et al., 1989) and Canada (Neary et al., 1987; Courchesne and Hendershot, 1989). Although experimental conditions significantly affect observed SO_4^{2-} adsorption characteristics (Hodges and Johnson, 1987; Comfort et al., 1991; Schnabel and Potter, 1991), there is no standardized methodology for determining the SO_4^{2-} adsorption

Abbreviations: Fe_d , dithionite-citrate extractable Fe; Al_d , dithionite-citrate extractable Al; Fe_o , ammonium oxalate extractable Fe; Al_o , ammonium oxalate extractable Al. **, ***Significant at the 0.01 and 0.001 probability levels, respectively.

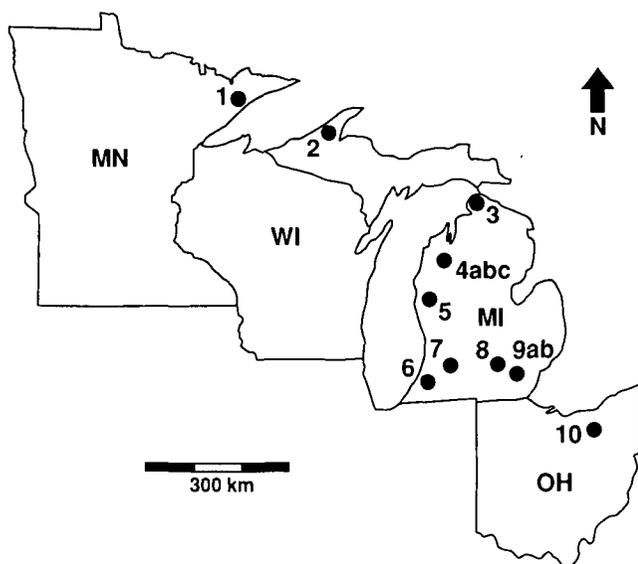


Fig. 1. Forest ecosystem research sites in the Great Lakes region.

potential of a soil. A common thread uniting recent studies has been the attempt to statistically relate either indices of SO_4^{2-} adsorption (Johnson and Todd, 1983; Harrison et al., 1989; MacDonald and Hart, 1990) or adsorption isotherm parameters (Comfort et al., 1992) to other soil properties. Although these studies demonstrated that SO_4^{2-} adsorption characteristics of soils could be predicted by other soil properties, only Comfort et al. (1992) specifically tested the validity of the relationships presented. Shaffer and Stevens (1991) discussed the problems encountered when aggregating SO_4^{2-} 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_4^{2-} adsorption characteristics among similar soils.

Static, laboratory measures of the ability of a soil to adsorb SO_4^{2-} 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_4^{2-} 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_4^{2-} retention in forest ecosystems through soil acidification and alteration in soil solution chemistry. The dynamic nature of SO_4^{2-} 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_4^{2-} 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 relat-

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

Site	Family	Series
1	coarse-loamy, mixed, frigid Alfic Haplorthod	Sarona
2	coarse-loamy, mixed, frigid Alfic Fragiorthod	Wakefield
	sandy, mixed, frigid Typic Haplorthod	Kalkaska
3	sandy, mixed, frigid Alfic Haplorthod	Keweenaw
	coarse-loamy over clayey, mixed, frigid Alfic Haplorthod	Superior
3	sandy, mixed, frigid Typic Haplorthod	Kalkaska
4a	sandy, mixed, frigid Alfic Haplorthod	Blue Lake
4b	sandy, mixed, frigid Typic Haplorthod	Kalkaska
4c	sandy, mixed, frigid Alfic Haplorthod	Blue Lake
5	sandy, mixed, frigid Entic Haplorthod	Rubicon
5	sandy, mixed, mesic Typic Haplorthod	Kalkaska†
6	coarse-loamy, mixed, mesic Typic Hapludalf	Oshtemo
7	sandy, mixed, mesic Psammentic Hapludalf	Spinks
8	coarse-loamy, mixed, mesic Typic Hapludalf	Oshtemo
8	mixed, mesic Typic Udipsamment	Oakville
8	sandy, mixed, mesic Psammentic Hapludalf	Spinks
9a	coarse-loamy, mixed, mesic Typic Hapludalf	Oshtemo
9b	fine-loamy, mixed, mesic Typic Hapludalf	Miami
10	fine, illitic, mesic Aquic Hapludalf	Ellsworth

† 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).

ing SO_4^{2-} adsorption potentials to soil properties proposed by MacDonald and Hart (1990), (ii) examine variability in soil SO_4^{2-} adsorption potentials within and among sites, and (iii) investigate the effects of seasonal changes in soil solution chemistry on SO_4^{2-} 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_4^{2-} 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 4c, 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 Fragiorthods or Haplorthods; soils at Sites 6 to 10 were Udipsamments or Hapludalfs (Table 1).

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/H₂O and 1:2 soil/0.01 M CaCl₂); texture (hydrometer); H₂O and PO₄³⁻ [0.008 M Ca(H₂PO₄)₂ · H₂O] extractable SO₄²⁻; NH₄Cl exchangeable Ca²⁺, Mg²⁺, and K⁺; KCl exchangeable Al³⁺; NH₄F-HCl extractable P, and Fe_d and Al_d. To provide data for mesic zone prediction equations, samples from Sites 6 to 10 also were analyzed for organic C (H₂SO₄-K₂Cr₂O₇ oxidation) and Fe_o and Al_o. Cations were determined by atomic absorption spectrophotometry, SO₄²⁻ by ion chromatography, organic C by titration with FeSO₄, 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-

mented by the Soil Conservation Service (1982), Page et al. (1982), and Klute (1986).

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 1990 and 1992. 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). Soil solution SO₄²⁻ fluxes were estimated for each fall (July–December) and spring (January–June) season between July 1988 and June 1990 using volume-weighted mean seasonal soil solution concentrations and monthly leaching losses calculated for each sampling depth using the Thornthwaite water balance equation (Mather, 1978). Seasonal breakpoints coincide with greatly decreased soil water movement caused by increased evapotranspiration in late spring (June) and snowpack establishment at the northern sites in late fall (December).

Equality of variance between within-site and within-series estimates of SO₄²⁻ adsorption potentials for major soil horizons was tested using an *F* test (Steel and Torrie, 1980). Seasonal soil solution SO₄²⁻ concentration data were analyzed using a two-way analysis of variance with site and sampling depth as factors and season treated as a repeated measure (fall 1988, spring 1989, fall 1989, spring 1990). Concentration data were ln-transformed to improve normality and homogeneity of variance.

Sulfate adsorption indices, $y = \ln[(\text{mg SO}_4^{2-} - S \text{ kg}^{-1}) + 2]$, were predicted for subsurface soil horizons using regression equations proposed by MacDonald and Hart (1990). Equation [1] applies to frigid zone Spodosols, whereas Eq. [2] and [3] apply to mesic zone Entisols and Alfisols. We predicted indices for 114 samples from frigid zone soils (Sites 1–5) and 104 samples from mesic zone soils (Sites 6–10).

$$y = -1.0843 + 0.5897[\ln(\text{Al}_d)] \\ - 0.1647(\text{pH in CaCl}_2) \quad [1]$$

$$y = 0.4896 + 0.2138[\ln(\text{exchangeable Al} + 1)] \\ - 0.2997(\text{pH in CaCl}_2) \\ - 0.2341[\ln(\text{extractable P})] + 0.4115[\ln(\text{Fe}_o)] \quad [2]$$

$$y = 5.8998 + 0.2051[\ln(\text{exchangeable Al} + 1)] \\ - 0.2208[\ln(\text{organic C})] + 0.4886[\ln(\Sigma\text{bases} + 1)] \\ - 0.6196(\text{pH in H}_2\text{O}) \quad [3]$$

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 $\ln[(\text{mg SO}_4^{2-} - S \text{ kg}^{-1}) + 1]$ 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 serves only to obscure relationships between SO₄²⁻ adsorption and other physical and chemical soil properties.

RESULTS AND DISCUSSION

Validity of Adsorption Prediction Equations

Sulfate adsorption potentials in subsurface horizons of Spodosols (Sites 1–5) were significantly predicted by the regressed indices from Eq. [1] ($r^2 = 0.59^{***}$). Examination of residuals revealed two samples with greatly overpredicted SO₄²⁻ adsorption indices. These outliers were Bt and C horizon samples characterized by high silt plus clay content (>75%) combined with high base saturation (>99.9%). None of the other Spodosol soil horizons sampled had this combination of properties. The influence of these two outliers on the relationship between observed and predicted values is demonstrated by the increase in r^2 to 0.75^{***} upon their removal. No other patterns were noted in the residuals that suggested a systematic lack of fit, even though certain soil horizons from Sites 1 and 2 exceeded the range of chemical properties in the original data set.

Sulfate adsorption potentials in subsurface horizons of the mesic zone Udipsamments and Hapludalfs (Sites

Table 2. Improved regression equations for SO_4^{2-} retention in subsurface horizons of forest soils in the Great Lakes region.

Predictor variable†	Parameter estimate	Standard error	R^2	SE‡	df§
Frigid zone Fragiorthods and Haplorthods					
Constant	-0.0378	0.3747			
$\ln(\text{Al}_d)$	0.6326***	0.0323			
pH in CaCl_2	-0.4206***	0.0469	0.78***	0.456	223
Mesic zone Udipsammets and Hapludalfs					
<i>Regression A</i>					
Constant	0.7597	0.5205			
$\ln(\text{Fe}_d)$	0.5401***	0.0550			
pH in CaCl_2	-0.6489***	0.0318	0.77***	0.471	160
<i>Regression B</i>					
Constant	4.7906	0.2066			
$\ln(\text{clay})$	0.3329***	0.0430			
pH in CaCl_2	-0.6406***	0.0346	0.74***	0.509	160

*** Significant at $P < 0.001$.

† Dependent variable = $\ln[(\text{mg SO}_4\text{-S kg}^{-1}) + 1]$; Al_d and Fe_d in mg kg^{-1} ; clay in percent.

‡ Standard error of the estimate (ln 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_4^{2-} release under laboratory conditions and overprediction of SO_4^{2-} adsorption. These outliers were samples from fine-textured Bt2, 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 $\text{mg SO}_4^{2-}\text{-S kg}^{-1}$ during laboratory equilibrations. Desorption from these horizons at Site 10 was associated with high ambient solution SO_4^{2-} concentrations (>0.4 mmol L^{-1}) resulting from high rates of atmospheric SO_4^{2-} deposition (MacDonald et al., 1993). The occurrence of SO_4^{2-} 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_4^{2-} concentrations >0.3 mmol L^{-1} .

Development of Improved Adsorption Prediction Equations

Improved regression equations, where the dependent variable was the \ln -transformed SO_4^{2-} 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_4^{2-} because it accounted for native adsorbed and soluble SO_4^{2-} in the soil as well as additional amounts of SO_4^{2-} that could be adsorbed. The R^2 values and standard errors of the esti-

Table 3. Range, mean, and standard deviation of soil properties used in developing regression equations for SO_4^{2-} retention in subsurface horizons† of forest soils in the Great Lakes region.

Property	Range	Mean	SD
Frigid zone soils (n = 226)			
$\text{SO}_4^{2-}\text{-S retained, mg kg}^{-1}$	0.0-65.6	11.2	10.9
$\text{Al}_d, \text{mg kg}^{-1}$	93-20426	1332	2207
pH in CaCl_2	4.01-7.98	4.83	0.72
Mesic zone soils (n = 163)			
$\text{SO}_4^{2-}\text{-S retained, mg kg}^{-1}$	0.0-74.2	13.2	13.5
$\text{Fe}_d, \text{mg kg}^{-1}$	1840-26192	8007	5614
clay, %	1.3-43.6	11.1	10.9
pH in CaCl_2	3.59-7.92	5.03	1.17

† Frigid zone A, AE, E, and mesic zone A horizons were not included in regression equation development because these horizons were inactive in SO_4^{2-} adsorption. All subsurface horizons to a depth of 150 cm were included.

mate were similar for both frigid and mesic zone regressions (Table 2). No major outliers were detected, and residuals from all three equations were normally distributed. Two equations are presented for mesic zone soils, Regression A representing a stronger statistical relationship and Regression B driven by a more readily available predictor variable (percentage clay). Sulfate retention indices were positively correlated with Al_d , Fe_d , and clay and negatively correlated with pH, all factors previously related to SO_4^{2-} adsorption in the literature (Johnson and Todd, 1983; Fuller et al., 1985; Nodvin et al., 1986; MacDonald and Hart, 1990; Comfort et al., 1992).

Sulfate retention indices predicted using the improved regression equations have the advantage of being independent of ambient levels of extractable SO_4^{2-} and extrinsic factors affecting adsorption potentials such as differences in atmospheric SO_4^{2-} deposition rates. Knowledge of current extractable SO_4^{2-} concentrations is not required to use these prediction equations because this property was incorporated into the dependent variable. These equations also encompass a greater range in soil properties than equations previously published for Michigan (Table 3). Predicted indices could be used to make relative comparisons of SO_4^{2-} retention ability among forest soils as part of a regional assessment of soil sensitivity to pollutant deposition. However, the predicted indices have only limited use in the study of dynamic processes. Predicting SO_4^{2-} adsorption isotherm constants from soil properties would be more useful for regional ecosystem modelling applications, as demonstrated by Comfort et al. (1992).

Data from frigid zone A, AE, E, and mesic zone A horizons were excluded from equation development; any attempt to predict retention indices for surface soils from these equations would yield erroneous results. Similarly, attempts to predict retention indices for subsurface soils with properties outside the range of those presented in Table 3 would yield uncertain results. Prediction of SO_4^{2-} retention indices is appropriate only for subsurface soil horizons to a depth of 150 cm, because this was the common lower limit of sampling of soils used to develop the prediction equations. Use of these equations to predict retention indices for soil taxonomic groups not included in equation development is unwarranted, as is their uncritical use for soils outside of the Great Lakes region.

Table 4. Sites and soil horizons with significantly different within-site and within-series estimates of variance for SO_4^{2-} adsorption potential of major soil horizons.

Site	Horizon	Within-site variance (n = 3)	Within-series variance† (n = 6)	F‡
2	Bt/BC	43.5	0.6-4.4	72.5**
	2C	3.4	0.4	8.5*
6	2C	9.1	0.4-0.8	22.8**
	Bt/E' and Bt	21.9	0.8-49.0	27.4**
7	E' and Bt/Bt	15.8	0.8-49.0	19.8**
	2C	3.7	0.4-0.8	9.2*
8	E' and Bt	6.8	0.8	8.5*
9b	Bt1	0.2	28.1	140.5*

*, ** Significant at $P < 0.05$ and 0.01 (two-tailed test).

† Estimates of within-series variance (s^2) 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 s^2 /smaller s^2 with appropriate numerator and denominator degrees of freedom.

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_d and Fe_d and, to a lesser extent, pH measured in CaCl_2 , 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 SO_4^{2-} 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 SO_4^{2-} retention characteristics within groups of taxonomically related soils.

Variation in Adsorption Within and Among Sites

The variance of SO_4^{2-} 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 SO_4^{2-} 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 SO_4^{2-} 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 SO_4^{2-} .

Sulfate adsorption potentials were highest in Bt horizons of mesic zone Hapludalfs (Fig. 3a-3f). In Udipsamments 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 SO_4^{2-} adsorption characteristics of forest soils in the Great Lakes region. The magnitude of SO_4^{2-} 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, SO_4^{2-} retention characteristics of soils should be predictable within a soil taxonomic framework. Such predictions need to take into consideration the past history of SO_4^{2-} 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 SO_4^{2-} 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 SO_4^{2-} 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 SO_4^{2-} 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 SO_4^{2-} in surface soils during the summer, and the autumnal flux of SO_4^{2-} leached from foliar litter. Soil solution SO_4^{2-} 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 SO_4^{2-} concentrations tended to decrease from lower E to lower B horizons, whereas in the spring, SO_4^{2-} concentrations increased with depth in the soil profile. Similar seasonal fluctuations in soil solution SO_4^{2-} concentrations were reported for northern hardwood forests at the Turkey Lakes Watershed, Ontario, Canada (Foster, 1985; Foster et al., 1992).

Estimated SO_4^{2-} fluxes, incorporating variation in both SO_4^{2-} concentrations and hydrologic fluxes, display seasonal differences in SO_4^{2-} release and retention more clearly. During the fall, lower B horizon SO_4^{2-} fluxes were less than E horizon SO_4^{2-} fluxes (Fig. 4c), which

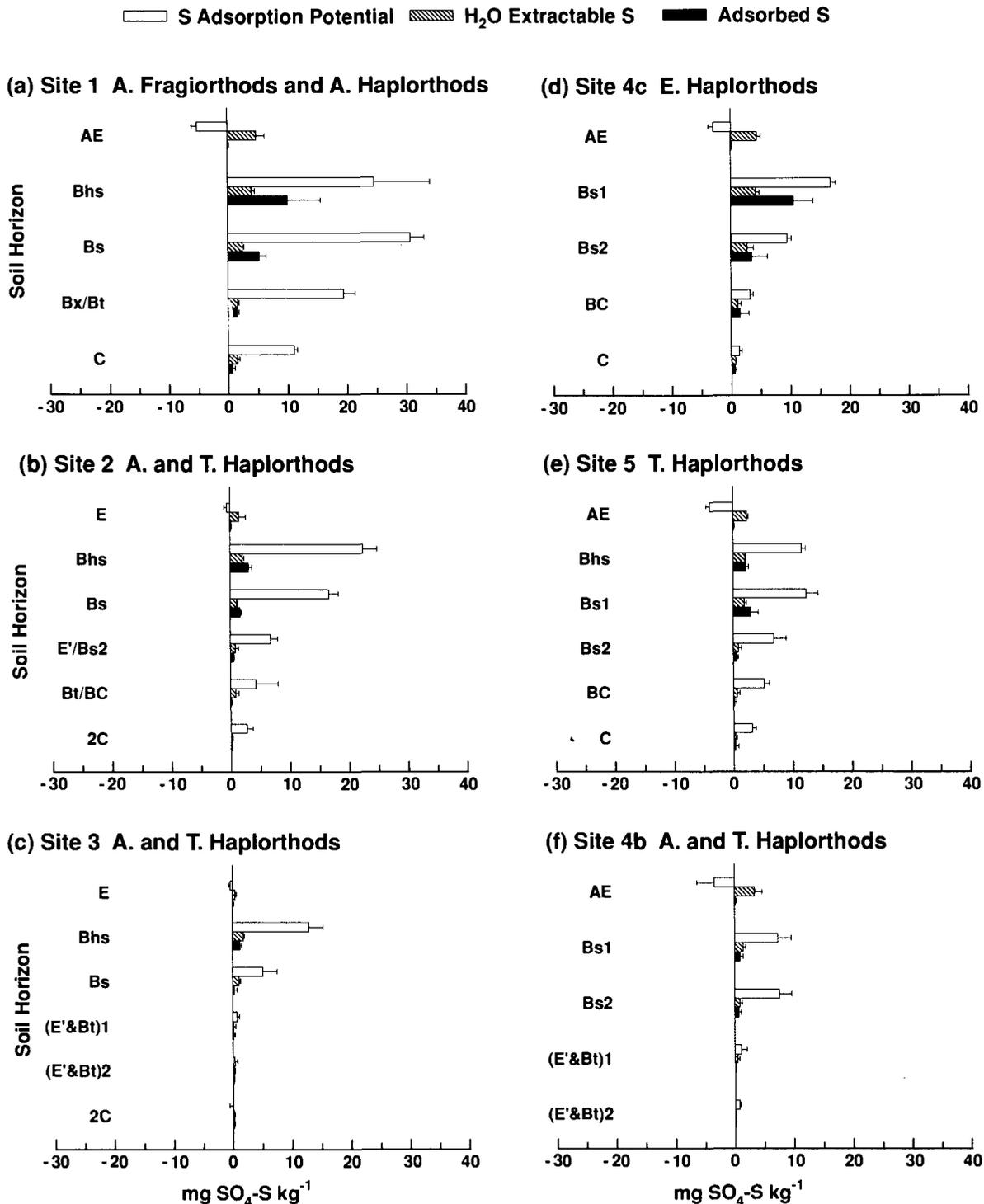


Fig. 2. Sulfate adsorption potential, water-extractable SO₄²⁻-S, and adsorbed SO₄²⁻-S in frigid zone forest soils of the Great Lakes region. Bars represent mean + standard error for major soil horizons present at each site to a depth of 150 cm. (a) to (c), trend of decreasing spodic expression and decreasing acidity in Orthods; (d) to (f), trend of decreasing acidity in Haplorthods. A. = Alicic, E. = Entic, T. = Typic.

is consistent with adsorption or retention in B horizons. During the spring, lower B horizon SO₄²⁻ fluxes were greater than E horizon SO₄²⁻ fluxes at Sites 3 to 10 (Fig. 4d), which is consistent with SO₄²⁻ desorption or release from B horizons. Sites 1 and 2, which have low rates of atmospheric SO₄²⁻ deposition and soils with high adsorption potentials, retained small amounts of SO₄²⁻ in both spring and fall.

Both spring and fall SO₄²⁻ 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 SO₄²⁻ deposition. Net SO₄²⁻ flux in the fall of 1990 also was positively correlated ($r = 0.77^{**}$) with total SO₄²⁻ deposition. Net spring SO₄²⁻ fluxes were negatively correlated ($r = -0.79^{**}$ to -0.81^{**}) with total SO₄²⁻ deposition. Additional varia-

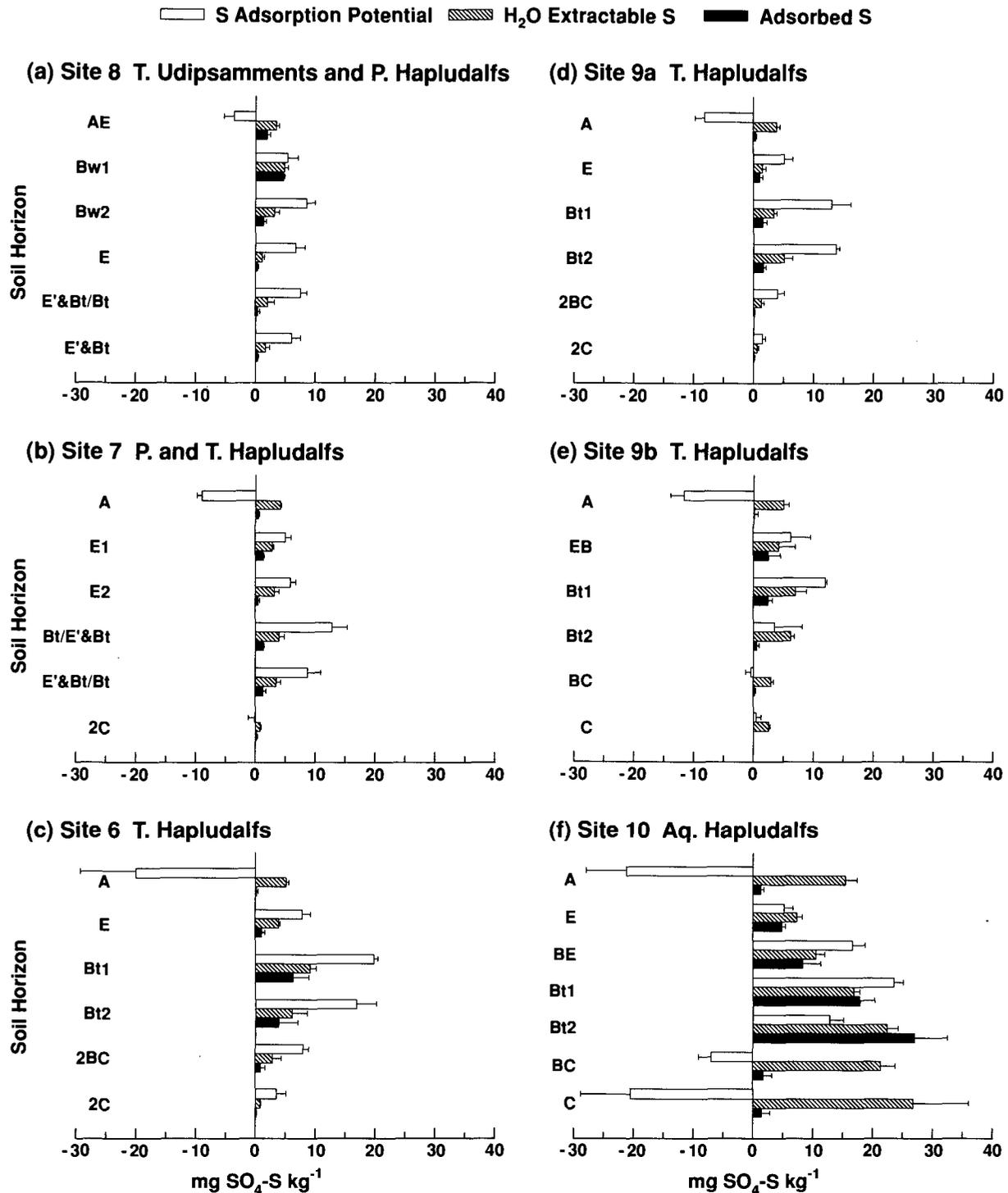


Fig. 3. Sulfate adsorption potential, water-extractable SO_4^{2-} -S, and adsorbed SO_4^{2-} -S in mesic zone forest soils of the Great Lakes region. Bars represent mean + standard error for major soil horizons present at each site to a depth of 150 cm. (a) to (c), trend of increasing clay content in Udipsamments and Hapludalfs with acidic C horizons; (d) to (f), trend of increasing clay content in Hapludalfs with shallow calcareous C horizons. Aq. = Aquic, P. = Psammentic, T. = Typic.

tion in net spring SO_4^{2-} fluxes was explained by either B horizon SO_4^{2-} adsorption potential ($R = 0.82^{**}$) or SO_4^{2-} retention index ($R = 0.83^{**}$ to 0.88^{**}). These relationships are consistent with the magnitude of seasonal SO_4^{2-} fluxes in these forest ecosystems being driven by rates of atmospheric 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 SO_4^{2-} . On an ecosystem level, annual input-output balances (MacDonald et al., 1992) suggested that SO_4^{2-} outputs below B horizons equalled or exceeded atmospheric SO_4^{2-} inputs, supporting the contention that adsorption does not represent a significant net sink for SO_4^{2-} in forest ecosystems that

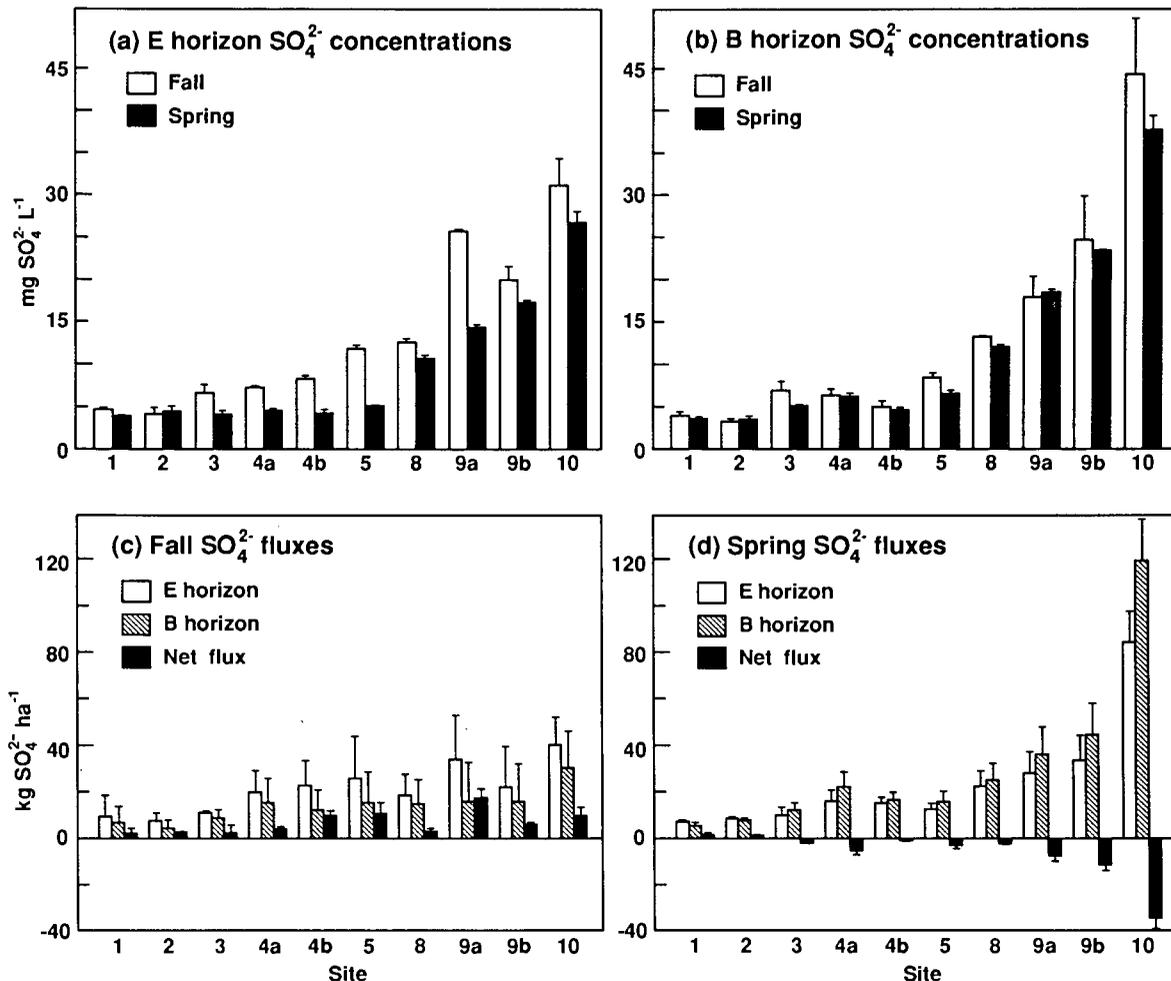


Fig. 4. Mean seasonal soil solution SO_4^{2-} concentrations and fluxes in forest soils of the Great Lakes region. Bars represent mean + standard error for 2 yr of data.

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_4^{2-} adsorption potentials with previously determined within-series variance estimates suggested that much of the variation in SO_4^{2-} adsorption potential among similar soils arises at local, not regional, scales. Variation in SO_4^{2-} adsorption potential among sites was related to soil morphological, physical, and chemical characteristics, suggesting that SO_4^{2-} retention ability should be predictable within a soil taxonomic framework. The need to maximize similarity in soil properties while aggregating SO_4^{2-} retention data for modelling purposes requires that such data be combined at the lowest soil taxonomic level possible.

Soil solution SO_4^{2-} concentration data and flux estimates were consistent with an annual cycle of SO_4^{2-} retention and release, adsorption predominating in the fall and desorption predominating in the spring. Seasonal patterns in soil solution SO_4^{2-} 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_4^{2-} fluxes was primarily related to atmospheric SO_4^{2-} deposition rates, and secondarily to soil SO_4^{2-} retention ability.

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