CHAPTER 49

REGIONAL PATTERNS OF SOIL SULFATE ACCUMULATION: RELEVANCE TO ECOSYSTEM SULFUR BUDGETS*

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ABSTRACT

Analyses of soils from Walker Branch, Camp Branch, and Cross Creek, Tennessee; Coweeta, North Carolina; and Hubbard Brook, New Hampshire, support the hypothesis that watershed sulfur accumulation is due to inorganic sulfate adsorption in soils. Analyses of soils from lysimeter study sites at La Selva, Costa Rica, and Thompson site, Washington, produced similar results. In laboratory adsorption studies, only soils from Coweeta retained substantial (50 to 100%) additional amounts of sulfate in insoluble forms.

Soil adsorbed sulfate content and sulfate adsorption capacity were positively correlated with free iron content but negatively correlated with organic matter content. Organic matter apparently blocks adsorption sites, preventing sulfate adsorption in iron-rich A horizons and Spodosol B2ir horizons. This blockage may account for the accumulation of adsorbed sulfate in B horizons in temperate and tropical soils and the susceptibility of New England Spodosols to leaching by H$_2$SO$_4$.

INTRODUCTION

Ecologists and foresters have been concerned about the effects of acid rain on terrestrial ecosystems for over a decade. In particular, suggestions of reduced forest growth in southern Sweden due to accelerated calcium leaching from soils sparked several research efforts to determine the effects of acid rain on soil leaching (Tamm, 1976; Johnson et al., 1972; Cole and Johnson, 1977; Cronan et al., 1978). There is some evidence that atmospheric sulfuric acid inputs are contributing significantly to increased soil leaching rates in the northeastern United States (Johnson et al., 1972;

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Cronan et al., 1978) and Scandinavia (Malmer, 1976). Tamm (1976) cites evidence suggesting that forest nitrogen cycling processes are disrupted by atmospheric H₂SO₄ additions as well.

Reuss (1976), however, argues that the effects of acid rain on soil nutrient status must be assessed within the perspective of numerous natural acidifying processes within the soil (e.g., carbonic acid production, nitrification, sulfur oxidation, H⁺ release from plant roots). In several cases the H⁺ production by these mechanisms far exceeds H⁺ input via acid rain (Cole and Johnson, 1977; Johnson et al., 1977; Andersson et al., 1979; Sollins et al., 1979).

The anionic components of acid rain, usually sulfate and nitrate, often constitute more significant additions to the ecosystem than H⁺. Ecologists have recently begun to turn their attention to the effects of atmospheric sulfur inputs on the cycling of both sulfur (Likens et al., 1977; Shriner and Henderson, 1978) and nitrogen (Turner et al., 1979) in forest ecosystems. The fate of sulfate is of interest not only in itself but also in terms of the effects of acid rain on cation leaching from soils. Unless sulfate is mobile in the soil, inputs of sulfuric acid will have no effect on cation leaching. Due to charge balance considerations, cations cannot leach without associated anions, in this case, sulfate. This fact has been amply demonstrated in both laboratory (Wiklander, 1976) and field (Johnson and Cole, 1977) studies of the effects of sulfate mobility on soil leaching processes.

Input-output budgets for sulfate in various forest ecosystems indicate that some ecosystems accumulate S (Heinrichs and Mayer, 1977; Shriner and Henderson, 1978; Swank and Douglass, 1977), whereas other ecosystems either show a net loss or maintain a balance of S inputs and outputs (Likens et al., 1977; Cole and Johnson, 1977). A likely mechanism of ecosystem sulfur accumulation is sulfate adsorption in subsoil horizons. Sulfate adsorption is known to occur on sesquioxide (and, to a lesser extent, kaolinite) surfaces (Chao et al., 1964; Harward and Reisenauer, 1966). Sulfate adsorption is strongly pH-dependent, however, with little adsorption occurring above pH 6–7 (Harward and Reisenauer, 1966).

Accumulations of adsorbed sulfate in acid subsoils have been noted throughout the world (Williams and Steinbergs, 1964; Ensminger, 1954; Neller, 1959), particularly in sesquioxide-rich tropical subsoils (Hesse, 1957; Hasan et al., 1970). Johnson et al. (1979b) noted that soil sesquioxide content, sulfate content, and sulfate adsorption capacity were much greater in soils from a tropical sulfur-accumulating forest ecosystem than in soils from a temperate non-sulfur-accumulating ecosystem.

Soil sulfate content is a function of adsorption properties and sulfate input integrated over time. Thus, while soil properties (e.g., sesquioxide and clay content) may favor sulfate adsorption, the degree of soil sulfate saturation will influence the net annual accumulation of sulfate at any point in time. In order to properly characterize soil sulfate adsorption capacity and its influence on ecosystem sulfur budgets, we must determine basic soil properties relevant to sulfate adsorption, e.g., sulfate content and the capacity of the soil for further sulfate accumulations.

The purpose of the following study was to characterize soils from a variety of ecosystems in the above manner and to relate these soil characteristics to measured ecosystem sulfate budgets.

**STUDY SITES**

Soils selected for characterization were obtained from the seven locations listed in Table 1. The sites chosen represent a variety of forest and soil types as well as geologic bases. Additionally, data on soils, vegetation, climate, and sulfur inputs
Table 1. Summary site descriptions for watershed study areas

<table>
<thead>
<tr>
<th>Location</th>
<th>Elevation range (m)</th>
<th>Precipitation (cm)</th>
<th>Forest type</th>
<th>Dominant species</th>
<th>Basal area (m²/ha)</th>
<th>Parent material</th>
<th>Soil series</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walker Branch, Tenn.*</td>
<td>265–360</td>
<td>151</td>
<td>Mixed hardwood</td>
<td><em>Quercus, Carya, Pinus</em></td>
<td>21</td>
<td>Dolomitic limestone</td>
<td>Claiborne</td>
<td>Fine-loamy, siliceous, mesic, typic paleudult</td>
</tr>
<tr>
<td>Camp Branch, Tenn.*</td>
<td>598–518</td>
<td>144</td>
<td>Mixed hardwood</td>
<td><em>Quercus, carya</em></td>
<td>20</td>
<td>Pennsylvanian sandstone</td>
<td>Hartsell</td>
<td>Fine-loamy, siliceous, thermic, typic paleudult, Coarse loamy, mixed, mesic, fluvaquentic dystrochrept</td>
</tr>
<tr>
<td>Cross Creek, Tenn.*</td>
<td>574–495</td>
<td>155</td>
<td>Mixed hardwood</td>
<td><em>Quercus, Carya</em></td>
<td>22</td>
<td>Pennsylvanian sandstone</td>
<td>Hartsell</td>
<td>Fine-loamy, mixed mesic, aquic hapludult</td>
</tr>
<tr>
<td>Coweeta, N.C.*</td>
<td>720–1740</td>
<td>180</td>
<td>Mixed hardwood</td>
<td><em>Quercus, Carya, Acer</em></td>
<td>25</td>
<td>Gneiss, schist, sandstone</td>
<td>Porters</td>
<td>Fine-loamy, mixed mesic, humic hapludult</td>
</tr>
<tr>
<td>Hubbard Brook, N.H.*</td>
<td>500–800</td>
<td>120</td>
<td>Northern hardwood</td>
<td><em>Acer, Fagus, Betula</em></td>
<td>24</td>
<td>Gneiss, schist</td>
<td>Becket</td>
<td>Coarse-loamy, mixed, frigid, typic fragiorthods</td>
</tr>
<tr>
<td>Thompson, Wash.*</td>
<td>210</td>
<td>136</td>
<td>Douglas fir plantation</td>
<td><em>Pseudotsuga</em></td>
<td>37</td>
<td>Glacial outwash</td>
<td>Everett</td>
<td>Loamy-skeletal, mixed, mesic dystric xerochrept</td>
</tr>
<tr>
<td>La Selva, Costa Rica†</td>
<td>40</td>
<td>430</td>
<td>Tropical rain forest</td>
<td><em>Pentaclethera, Grias, Palmae</em></td>
<td></td>
<td>Alluvium</td>
<td>La Selva</td>
<td>Typic hydredext</td>
</tr>
</tbody>
</table>

and losses were available for each site. In the interest of brevity, pertinent information relating to each site has been summarized in Table 1. Readers are directed to the indicated references for more specific descriptions of individual sites.

**METHODS**

Soil samples were air-dried and passed through a 2-mm sieve prior to analysis. Free iron and aluminum were determined by the citrate-buffer-dithionite method of Jackson (1973). Total carbon was determined by combustion in a LECO automated furnace. Percent clay data were available for all but the Cross Creek and Camp Branch soils, and determinations of clay in the latter were conducted by the hydrometer method (Day, 1965).

Initial soil sulfate content was determined by sequential leachings with H₂O and NaH₂PO₄. Triplicate 10-g samples from each horizon were placed in Buchner funnels lined with Whatman No. 50 filter paper and leached with 200 ml of distilled H₂O followed by 50 ml of NaH₂PO₄ containing 500 ppm P (Ensminger, 1954). Sulfate removed by water extraction was designated as initial soluble sulfate, and that removed by NaH₂PO₄ was designated as initial insoluble sulfate. Sulfate adsorption and desorption were determined by leaching another set of three samples with 50 ml of Na₂SO₄ containing 75 ppm S followed by H₂O and NaH₂PO₄ extractions. The loss of sulfate from the Na₂SO₄ leachate was termed total sulfate adsorption, and a significant (α = 0.05, t test) change in insoluble sulfate (relative to initial insoluble sulfate content) was termed insoluble sulfate adsorption. Sulfate removed from the latter samples by NaH₂PO₄ leaching was termed potential insoluble sulfate content. Figure 1 shows a flow diagram for the extractions.

Sulfate in water and Na₂SO₄ leachings was determined colorimetrically on a Technicon Autoanalyzer. Due to phosphate interferences on the Autoanalyzer, sulfate in NaH₂PO₄ leachates was determined by the barium chloranilate procedure of Bertolacini and Barney (1957).

Fig. 1. Flow diagram for soil sulfate extraction and adsorption procedures.
Correlations between sulfate content (soluble and insoluble), sulfate adsorption (total and insoluble), free iron and aluminum, organic matter, and clay content were performed by the CORR procedure of the SAS data analysis system (Barr et al., 1976).

RESULTS

All soils tested except the Becket series contained insoluble sulfate in subsurface horizons (Fig. 2 and 3). The Philo and Hartsells series contained very small amounts of insoluble sulfate relative to other soils.

Fig. 2. Sulfate content of soils from Coweeta, N.C.; La Selva, Costa Rica; and Thompson site, Wash., before and after leaching with Na₂SO₄ containing 75 ppm S.
Total sulfate adsorption was significant in all subsoils except those from the Hartsells and Clairborne series, but insoluble sulfate adsorption was significant only in the Cotaco, Becket, Porters, Saluda, and Everett series subsoils. The Porters and Saluda series had much greater capacities for insoluble sulfate adsorption (15–70 ppm) than the Cotaco, Becket, and Everett series (5–13 ppm). Samples from the Cross Creek, Hartsells C horizon, and the Cotaco B horizon experienced an unexplainable net decrease in insoluble sulfate following Na$_2$SO$_4$ and H$_2$O leachings.

Surface soils contained little or no insoluble sulfate and generally had lower total sulfate adsorption capacities than subsoils did (Fig. 2 and 3). Surface horizons of the Claiborne and Hartsells series actually desorbed significant amounts of sulfate during Na$_2$SO$_4$ leachings (Fig. 2). It should be noted, however, that an "aging effect", or increasing adsorption of sulfate with time of soil-solution contact, has been observed in samples from the Fullerton A horizon (Johnson and Henderson, 1979). Aging effects were not measured in this study, but they could have an effect on sulfate retention in the field for any of the soils tested. This is an area deserving of further investigation.
DISCUSSION

Relationships to Ecosystem Sulfur Budgets

The relationship between watershed sulfur budgets and soil sulfate accumulations can be assessed by expressing the latter in units of kilograms per hectare. We did not analyze a sufficient number of samples to get accurate quantitative data for soil sulfate accumulation in each watershed, but the values in Table 2 provide some perspective for selected soil series within the various watersheds. The fact that the soil (Becket) from the one non-sulfur-accumulating watershed (Hubbard Brook) contained no insoluble sulfate is consistent with our hypothesis that soil sulfate adsorption accounts for watershed sulfur retention. It is also noteworthy that the Saluda soil on watershed 6 at Coweeta, which was treated with sulfate-containing fertilizer in 1959 (Swank and Douglass, 1977), contained over three times as much

Table 2. Sulfur budgets and soil sulfate content at various research sites

<table>
<thead>
<tr>
<th>Site and soil</th>
<th>Annual sulfate sulfur accumulation* (kg ha⁻¹ year⁻¹)</th>
<th>Soil sulfate sulfur content*(kg/ha)</th>
<th>Depth to parent material (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Watershed Studies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Walker Branch, Tenn.</td>
<td>6.6</td>
<td>250</td>
<td>450</td>
</tr>
<tr>
<td>Fullerton</td>
<td></td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Claiborne</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coweeta, N.C.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saluda-WS 6</td>
<td>8.7</td>
<td>150</td>
<td>500</td>
</tr>
<tr>
<td>Saluda-WS 18</td>
<td>9.3</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>Porters-WS 36</td>
<td>6.2</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Porters-WS 27</td>
<td>6.6</td>
<td>350</td>
<td>400</td>
</tr>
<tr>
<td>Hubbard Brook, N.H.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Becket</td>
<td>-4.9</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Cross Creek, Tenn.</td>
<td>6.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hartsells</td>
<td></td>
<td>150</td>
<td>20</td>
</tr>
<tr>
<td>Cotaco</td>
<td></td>
<td>250</td>
<td>350</td>
</tr>
<tr>
<td>Camp Branch, Tenn.</td>
<td>8.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hartsells</td>
<td></td>
<td>180</td>
<td>130</td>
</tr>
<tr>
<td>Philo</td>
<td></td>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>Lysimeter studies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thompson, Wash.</td>
<td>-2.7</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>Everett</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La Selva, Costa Rica</td>
<td>11.0</td>
<td>100</td>
<td>900</td>
</tr>
<tr>
<td>La Selva</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Input via bulk precipitation minus output in streamwater or soil solution.
*Approximate values for top meter of soil.
insoluble sulfate as the unfertilized Saluda soil on watershed 18. Laboratory adsorption tests indicated that both the Saluda and Porters series soils from Coweeta had large capacities to adsorb additional sulfate into insoluble forms (Fig. 2). These findings suggest that the watersheds at Coweeta can continue to adsorb atmospherically deposited sulfate for longer periods of time than the other sulfur-accumulating watersheds at Walker Branch, Cross Creek, and Camp Branch.

The heterogeneity among soils from a given watershed could have an effect on ecosystem sulfur budgets also; for instance, the Fullerton soil on Walker Branch has accumulated more sulfate than the Claiborne soil (Table 2). Similarly, the Cotaco soil has accumulated more sulfate than the Hartsells soil on the Cross Creek watershed. Thus, it is probable that sulfate accumulations indicated by watershed-level input-output budgets occur primarily within specific soil series (e.g., Fullerton, Cotaco).

Another important consideration in the watershed studies is soil depth. The soil sulfate contents in Table 2 were calculated for a 1-m soil depth, whereas in some cases the soil mantle is many meters thick. At Walker Branch, for example, there is an estimated accumulation of over 2700 kg/ha of sulfate sulfur in the top 30 m in the Fullerton soil (Johnson and Henderson, 1979).

Lysimeter studies of elemental budgets have distinct advantages over watershed studies in that only one soil series and one soil depth are considered at a time. This was the case for the tropical-temperate sulfur comparison reported on previously (Johnson et al., 1979b). Soils from these two sites were reanalyzed for the purposes of this study, since procedures differed somewhat. The La Selva soil (tropical) had a very large accumulation of insoluble sulfate, and the sulfur budget showed a large net annual accumulation (Table 2). No statistically significant additional accumulation of insoluble sulfate was noted following laboratory Na\(_2\)SO\(_4\) additions, however. The Everett soil had a lower accumulation of insoluble sulfate, and the sulfur budget indicated a slight net annual loss. Apparently a steady-state condition had been reached in the Everett soil at the current (1974) sulfate input levels (~ 4 kg of S per hectare per year), which were considerably lower than those at any of the other sites (inputs range from 12 to 18 kg of S per hectare per year). Since sulfate adsorption is concentration-dependent (Harward and Reisenauer, 1966), further accumulations could occur in the Everett soil at higher input levels. According to laboratory adsorption tests the Everett soil has a moderate capacity to accumulate additional insoluble sulfate (Fig. 2). Field studies involving the application of H\(_2\)SO\(_4\) and municipal wastewater have also shown that the Everett soil can accumulate additional sulfate (Johnson and Cole, 1977; Johnson et al., 1979a).

Factors Affecting Sulfate Content and Adsorption

Factors potentially influencing retention of sulfate in various soil series include free iron and aluminum oxide content (Chao et al., 1964), clay content (Neller, 1959), and organic matter content (Haque and Walmsley, 1973). Regression analysis of these soil properties indicated that free iron was most closely correlated with initial sulfate content (both soluble and insoluble), sulfate adsorption from Na\(_2\)SO\(_4\) solutions (both total and insoluble), and potential insoluble sulfate content (Table 3). Clay content was significantly correlated with both initial and potential insoluble sulfate content but was not significantly correlated with soluble sulfate content or total sulfate adsorption. Free Al content was not significantly correlated with any soil sulfate parameter. It should be noted, however, that the citrate-dithionite method may not remove all free Al oxides in soils (Jackson, 1973).
Table 3. Correlation coefficients (R) between soil sulfate, free iron, free aluminum, carbon, and clay content

<table>
<thead>
<tr>
<th></th>
<th>Soil sulfate</th>
<th>Initial content</th>
<th>Adsorption*</th>
<th>Potential content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Soluble</td>
<td>Insoluble</td>
<td>Total</td>
<td>Adsorption</td>
</tr>
<tr>
<td>Percent Fe</td>
<td>0.28°</td>
<td>0.50°</td>
<td>0.55°</td>
<td>0.40°</td>
</tr>
<tr>
<td>Percent Al</td>
<td>0.19</td>
<td>-0.06</td>
<td>-0.0001</td>
<td>0.20</td>
</tr>
<tr>
<td>Percent carbon</td>
<td>0.29*</td>
<td>-0.31*</td>
<td>-0.21</td>
<td>-0.01</td>
</tr>
<tr>
<td>Percent clay</td>
<td>0.05</td>
<td>0.43°</td>
<td>0.42°</td>
<td>0.21</td>
</tr>
</tbody>
</table>

*After leaching with 75 ppm S as Na₂SO₄.
°90% significance.
°99% significance.
°95% significance.

Some interesting relationships were found between soil sulfate and percent carbon. The initial content of soluble sulfate was positively correlated with percent carbon, but both the initial and the potential content of insoluble sulfate were negatively correlated with percent carbon (Table 3). Organic matter may be a source of soluble sulfates (e.g., by breakdown of ester sulfates, e.g., Tabatabai and Bremner, 1972), but it may also block sulfate adsorption sites on sesquioxide surfaces (Johnson et al., 1979b; Couto et al., 1979).

Although there were significant correlations between adsorbed sulfate, iron oxide, and clay content, there were notable exceptions in cases where organic matter, sesquioxides, and clay accumulated together. In the Porters and La Selva soils, organic-matter-rich surface horizons contained very little insoluble sulfate despite high sesquioxide and clay contents (Figs. 2 and 5). The Becket soil had a slight accumulation of clay and large accumulations of both sesquioxides and organic matter in B horizons, as is typical of a Spodosol (Fig. 4). Again, there was no insoluble sulfate associated with the sesquioxide and organic matter accumulation (Fig. 3).

In all other soils analyzed in this study, there was a pattern of decreasing percent carbon but increasing insoluble sulfate, sesquioxide, and clay content with depth. Profiles for the Fullerton and Hartsells (Cross Creek) series illustrate this general pattern for high- and low-sesquioxide soils, respectively (Figs. 3 and 4). Excluding the Porters A horizon, La Selva A 11 horizon, and Becket soils, data from regression analysis improved the correlation coefficients of free iron vs insoluble sulfate content (from 0.55 to 0.61), insoluble sulfate adsorption (from 0.27 to 0.38), and potential insoluble sulfate content (from 0.41 to 0.52).

Results of this study support previous speculations concerning the blocking effect of organic matter on soil sulfate adsorption sites (Johnson et al., 1979b; Couto et al., 1979). We are currently testing this hypothesis by measuring soil sulfate adsorption properties with and without organic matter removal. If this hypothesis proves correct, it will help account for the observation that only subsoils with low quantities of organic matter accumulate substantial quantities of sulfate, even where surface soils have appreciable clay and sesquioxide contents. It also has implications in terms of the susceptibility of Spodosols to H₂SO₄ leaching. Although large accumulations of sesquioxides are common in Spodosol subsoils, such accumulations are usually associated with organic matter in the form of the fulvic acids, which transport iron and aluminum to lower horizons (Kononova, 1966).
Fig. 4. Percent clay, free iron and aluminum, and carbon in the Becket, Fullerton, and Hartsells soil series from Hubbard Brook, N.H., and Walker Branch and Cross Creek, Tenn., respectively.

Fig. 5. Percent clay, free iron and aluminum, and carbon in the Porters and La Selva soil series from Coweeta, N.C., and La Selva, Costa Rica, respectively.
Thus, despite their high sesquioxide contents, Spodosols would be very susceptible to leaching by atmospheric H$_2$SO$_4$. This does in fact seem to be the case in view of studies by Johnson et al. (1972), Likens et al. (1977), and Cronan et al. (1978) on acid rain effects on nutrient leaching from Spodosols in New England. Further research on this subject is needed.

**CONCLUSIONS**

Laboratory studies indicated that of the sulfur-accumulating ecosystems examined, soils from La Selva, Walker Branch, Cross Creek, and Camp Branch may be near saturation with respect to sulfate accumulation, whereas soils from Coweeta have considerable additional sulfate adsorption capacity remaining. Potential sulfate content (sulfate content plus laboratory adsorption) was greatest at La Selva and Coweeta, intermediate at Walker Branch, and lowest at Cross Creek and Camp Branch.

Of the two non-sulfur-accumulating ecosystems studied, only soils from the Thompson site contained insoluble sulfate. A steady-state condition had apparently been reached with regard to the relatively low atmospheric sulfate inputs at this site (4 kg ha$^{-1}$ year$^{-1}$ vs 12-18 kg ha$^{-1}$ year$^{-1}$ at all other sites), but both laboratory and field experiments have demonstrated that further soil sulfate accumulations could occur at greater input levels due to concentration-dependent increases in sulfate adsorption.

Despite large free iron and aluminum accumulations in subsurface horizons, soil from Hubbard Brook (a Spodosol) contained no insoluble sulfate, and only minor amounts (5-15 ppm) of sulfate were adsorbed in laboratory tests. The high organic matter accumulations in the Hubbard Brook subsoils and surface soils from other sites appear to block sulfate adsorption sites. Thus, while the well-documented relationship between sulfate adsorption and sesquioxide content does hold true for these soils in general, there are important exceptions in cases where both organic matter and sesquioxides are high. Organic matter blockage of sulfate adsorption sites has important implications with respect to sulfur budgets and the susceptibility of surface soils and Spodosols to leaching by atmospheric H$_2$SO$_4$.

**REFERENCES**


DISCUSSION

Ron McLean, Domtar Research: In a lot of the postulations about the effects of acid precipitation in North America we've extrapolated a lot of the results from the Hubbard Brook studies. It seems to me, looking at your data, that you're suggesting that perhaps Hubbard Brook, as far as soil is concerned, is not a typical situation to look at.

D. W. Johnson: Oh, not at all; I'd say it's a very typical spodosol profile, and, in fact, I'm anxious to do more spodosol profiles, and I fully expect them to behave the same way. It's not typical of an ultisol; I think this brings out the importance of knowing what kind of soil you're dealing with. The ultisol we have at Walker Branch is completely different from the Hubbard Brook soil, and its behavior with regard to leaching is totally different. Hubbard Brook happens to be the only spodosol I've done to date, and I'd like to do more to find out how representative it is. I suspect, though, it is representative.

Bill Graustein, Yale University: How does the capacity of soil to absorb sulfate vary with the pH of the solution that carries sulfate?

D. W. Johnson: Well, the sulfate absorption goes up with the pH, as I'm sure you know. I didn't include pH in this study because pH among the soils didn't vary more than a unit, on the grades between 4 and 5, so that the correlations between that and sulfate absorption were not significant, but I know that it is significant over a wide range of pH's. Also, if you apply your sulfate as an acid rather than as a salt, you get much greater absorption in the acid form than you will in the neutral salt form.

Chris Cronan, Dartmouth: I was reminded of a paper that Rich Barton from UPM published on a test for spodosol character, and as I recall he uses phosphate adsorption in different mineral profiles to test for adsorption characteristics and in the B2 horizon gets a great increase in phosphate adsorption. Now we already know
that phosphate and sulfate have some different affinities for aluminum and iron oxides and hydroxides, but nevertheless he seems to find a significant increase in phosphate adsorption where you have got that alluvial horizon and where you're not seeing sulfate adsorption.

D. W. Johnson: Well, I kind of whizzed through that quickly, but if you notice there was a higher sulfate adsorption associated with the B2 AR. It was not permanent. It did not adsorb into the insoluble form. After the sodium sulfate treatment I got adsorption in three cases. The trouble is that very little of it was obtained in a permanent form, so I think you have to look at adsorption and desorption in these things, because so what, if it adsorbs and comes back off again. There's another effect I did not include which probably is important and that's aging. If you allow soil to sit in contact for a long time with these solutions, you get further adsorption with time. That's not included in this study, and it could be an important factor too.

Bill McFee, Purdue: I wonder if you'd comment. Is nitrate likely to behave like sulfate, and secondly, at the very end you talked about the need for considering other acid inputs, organic matter, decay, root exudates, and so forth. I wish you'd comment on the availability of good estimates of those.

D. W. Johnson: First of all, I don't think nitrate is going to behave at all like sulfate. It is totally different, nonadsorbing, much more biologically active, and deficient in most of the regions of the world; I expect that nitrate would probably be immobilized biologically but not chemically. And the second part, the estimates of internal hydrogen ion production are few and far between. I only know of, well, I know of one complete one from Sweden by Andersson, who did an estimate of the hydrogen ion production through various sources including root exudation and carbonic acid and organic acid production, and in his site, which, I don't know if it was subjected to acid rain or not, but the atmospheric input was 10% of that produced within the system, but the estimates are hard to get. I agree with that.

Carl Schofield, Cornell: Did the differences you see in sulfate adsorption capacity in the soil show any relationship to stream discharge sulfate concentration relationships in different areas?

D. W. Johnson: Yes, they do. Grey Henderson did some studies on the sulfate concentration during discharge at Walker Branch and found that the sulfate concentration increased as the hydrograph increased—the stream flow increased—and what we thought happened in this case was that the water table would rise into that A horizon, where we have a substantial pool of soluble sulfate, during these periods of high flow and then pick up that soluble sulfate pool, and then during, as the storm receded, well, it would go back down to the B2 horizon, and the sulfate there is insoluble, and it would not escape. I'm sure that—I wouldn't be surprised if that's a common effect among these soils.