

## THE EFFECT OF pH ON SULFATE ADSORPTION BY A FOREST SOIL

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**Acidic deposition and forest clear-cutting are disturbances that have resulted in increased acidification of northeastern forest ecosystems. This study was conducted to evaluate whether acidification processes can significantly affect adsorption processes that are important in regulating sulfate transport and cycling in a Spodosol at the Hubbard Brook Experimental Forest, New Hampshire. The results of adsorption experiments demonstrated that small changes in solution pH have a large effect on sulfate adsorption characteristics of mineral soil at Hubbard Brook. The ability of the soil to remove sulfate from solution increased as the pH of the solution was decreased, with a maximum removal occurring at about pH 4.0. Through the use of initial mass isotherms, we determined that sulfate removal depended upon (1) the ability of the soil to partition sulfate between the soil and solution phases and (2) the amount of reactive native sulfate that is present in the soil. Our analysis demonstrated that both these soil properties depend strongly upon solution pH.**

In recent years interest has expanded in the processes that regulate the transport of sulfate through soils (e.g., Johnson and Cole 1980; Johnson et al. 1982). Sulfate is the predominant anion in precipitation in the eastern United States and, as sulfuric acid, is the major contributor to the total acidity of precipitation (Galloway et al. 1976). Henrikson (1979) hypothesized that atmospheric deposition of sulfur is a major factor contributing to surface water acidification. Understanding the fate of sulfur in terrestrial ecosystems is essential for an evaluation of the factors that control nutrient leaching and

the acidity of streamwater (Seip 1980; Christopher and Wright 1981; Singh et al. 1980; Lee and Weber 1982).

At the Hubbard Brook Experimental Forest (HBEF), New Hampshire, researchers have been studying a number of anthropogenic perturbations that affect sulfur cycling in forest ecosystems. Two perturbations of particular interest are clear-cutting and acidic deposition. Atmospheric deposition of acidic substances has substantially increased the loading of both sulfate and hydrogen ion to the forested ecosystem (Cogbill and Likens 1974). Clear-cutting and herbicide treatments of forest ecosystems in both experimental and commercial cutting operations have resulted in alterations of the sulfur cycle at HBEF and other locations in the White Mountains of New Hampshire (Likens et al. 1970). By enhancing nitrification, these treatments induced increased production of hydrogen ion within the soil, which resulted in the acidification of streamwater (Likens et al. 1969).

Adsorption reactions within the soil profile can regulate concentrations of aqueous sulfate in forest ecosystems (Johnson and Cole 1980). A soil's ability to remove sulfate from solution depends upon its inherent adsorption properties, the degree to which the soil has previously adsorbed sulfate, and the concentrations of sulfate in incoming solutions relative to concentrations in which the soil has previously equilibrated (Johnson and Todd 1984). The master variable that governs the extent of adsorption reactions in a particular soil is pH (Schindler 1981), and the adsorption of sulfate by soils is strongly influenced by solution pH (Chao et al. 1964; Parfitt 1978). Thus we hypothesize that acidification of the soil due to either acidic deposition or forest clear-cutting may have a significant impact on the cycling of sulfur within the ecosystem by affecting adsorption reactions important in regulating sulfate transport and cycling within the soil profile.

To test this hypothesis, we have initiated a series of studies to evaluate the importance of adsorption and acidification processes in the regulation of sulfur cycling at HBEF. We present here the results of research designed to

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evaluate the relationship between sulfate adsorption and the solution pH in soil at HBEF.

#### MATERIALS AND METHODS

We conducted adsorption experiments using soil collected from a site adjacent to watershed 6 at HBEF. The soil at HBEF is a well-drained spodosol (Typic Fragiorthod) of the Beckett series (Likens et al. 1977). In our experiments, we used composite samples of B-horizon soil, which had been collected from the Bhs2 and Bhs3 layers.

Stock solutions of sodium sulfate were used to make experimental solutions that had initial concentrations ( $C_i$ ) of either 0, 42, 104, or 146  $\mu\text{mol}(\text{e}^-) \cdot \text{L}^{-1} \text{SO}_4^{2-}$ . Either nitric acid or sodium hydroxide was added to the initial experimental solutions to adjust the pH. We chose nitric acid for two reasons. First, disturbances such as clear-cutting induce nitrification in the soils at Hubbard Brook, and this research was part of a larger study to evaluate the effects of disturbance on sulfur cycling at HBEF. Second, nitrate is a nonspecifically adsorbed anion and therefore should not compete with sulfate for adsorption sites. For each trial, we added 100 ml of an experimental solution to 10 g of sieved (2-mm), air-dry soil. The suspension was equilibrated for 24 h on a rotary shaker table at 20°C. Particulate matter was removed from the final solution by centrifugation (15 min at 4950  $g$ 's). After equilibration, solution pH was measured potentiometrically using a glass electrode, and sulfate was determined by ion chromatography (Tabatabai and Dick 1983).

Our evaluation of the sulfate adsorption experiments was facilitated by the use of the initial mass isotherm. The development of this isotherm and detailed definitions of the parameters used have been described in Nodvin et al. (1986).

#### RESULTS AND DISCUSSION

##### *Factors affecting sulfate release and removal from soil*

In our experiments, the amount of sulfate removed from or released to the solution by the soil with respect to the soil mass ( $RE$ ) was a function of the solution pH and of the amount of sulfate added to the soil-water system ( $X_i$ ) (Fig. 1). When no acid or base was added, the solution pH was 4.8. Maximum sulfate retention occurred at ca. pH 4.0. For each pH, there was

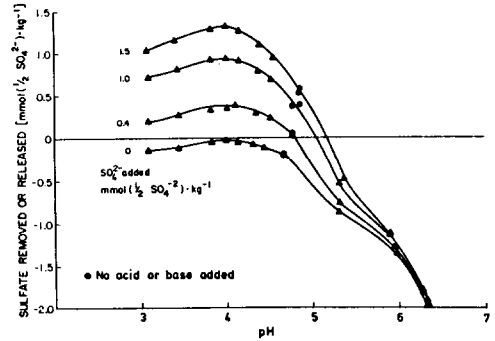


FIG. 1. Sulfate removal or release in response to initial sulfate added and equilibrium pH. (Positive values indicate net removal, and negative values indicate net release.)

a level of  $X_i$  in which no net removal of sulfate occurred; at added concentrations below this level, there were net releases of the anion from the soil. The pattern of sulfate removal/release with variations in solution pH was similar for all concentrations of added sulfate (Fig. 1). The results of other sulfate adsorption studies have demonstrated similar pH-dependent responses and retention maxima near pH 4.0 (see Couto et al. 1979; Gebhart and Coleman 1974; Harward and Reisenhauer 1966; and Chao et al. 1963, 1964).

It is well established that the amount of sulfate that can be removed from solution by soil is not constant but dependent upon the concentration of sulfate in solution (see Couto et al. 1979; Harward and Reisenhauer 1966; Chao et al. 1962; Lichtenwalner et al. 1923). In our study we also found that, at each pH,  $RE$  was a statistically linear function of  $X_i$  (Fig. 2, Table 1).

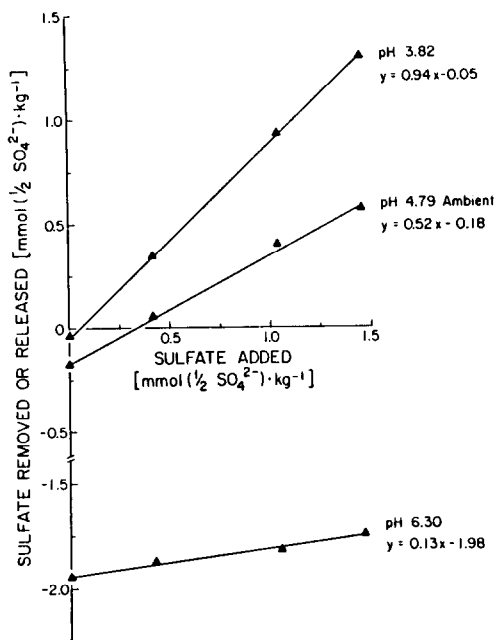
##### *The partitioning of sulfate in a forest soil*

We have used the term *initial mass* (IM) isotherm to describe plots of  $RE$  on  $X_i$ . The use of the IM isotherm variable definitions is given in Nodvin et al. (1986). At all pH values IM plots for sulfate were statistically linear (Fig. 2). Changes in solution pH affected both the slope and intercept of this linear relationship (Table 1). Note that sulfate concentrations used in our experiments were in the range of those found in natural waters at HBEF (Likens et al. 1977) and that these concentrations are low (0 to 146  $\mu\text{mol}(\text{e}^-) \cdot \text{L}^{-1}$ ) relative to levels used in previous sulfate adsorption studies. The range of sulfate concentrations used will affect the goodness of

TABLE 1

Adsorption parameters from initial mass isotherms<sup>a</sup>

| Equilibrium pH    | <i>m</i>   | - <i>b</i> | RSP  | <i>r</i> <sup>2</sup> |
|-------------------|--|------------|------|-----------------------|
|                   | mmol (1/2 SO <sub>4</sub> <sup>2-</sup> ) · kg <sup>-1</sup> |            |      |                       |
| 3.08              | 0.81   | 0.13       | 0.70 | 1.00                  |
| 3.43              | 0.88   | 0.11       | 0.86 | 1.00                  |
| 3.82              | 0.94   | 0.05       | 0.79 | 1.00                  |
| 4.00              | 0.93   | 0.03       | 0.43 | 1.00                  |
| 4.14              | 0.90   | 0.02       | 0.24 | 1.00                  |
| 4.36              | 0.80   | 0.06       | 0.30 | 1.00                  |
| 4.51              | 0.72   | 0.08       | 0.30 | 1.00                  |
| 4.76 <sup>b</sup> | 0.51   | 0.20       | 0.41 | 0.99                  |
| 4.79 <sup>b</sup> | 0.52   | 0.18       | 0.37 | 1.00                  |
| 5.31              | 0.28   | 0.87       | 1.22 | 0.98                  |
| 5.92              | 0.16   | 1.35       | 1.61 | 0.94                  |
| 6.30              | 0.13   | 1.98       | 2.29 | 0.98                  |

<sup>a</sup> *n* = 4.<sup>b</sup> No acid or base added.FIG. 2. Linear relationship between sulfate removal or release (*RE*) and sulfate added (*X<sub>i</sub>*) at several equilibrium pH levels.

fit of a set of adsorption data to a particular isotherm. For example, Chao et al. (1962) found that below initial sulfate concentrations (*C<sub>i</sub>*) of 1560 μmol(e<sup>-</sup>) · L<sup>-1</sup>, the amount removed increased linearly with increasing *C<sub>i</sub>*, though at higher concentrations this relationship deviated from linearity. Below an equilibrium concentration (*C<sub>f</sub>*) of 940 μmol(e<sup>-</sup>) · L<sup>-1</sup>, their data con-

formed to a Langmuir-type equation, whereas above this concentration, their data were in good agreement with the Freundlich equation. We found that neither of these isotherms satisfactorily described our results, but that linear IM isotherms provided the best fit for the data within the range of sulfate concentrations used (Nodvin et al. 1986).

Application of the IM isotherm to the results of our experiments allowed us: (1) to describe the response of *RE* to changes in both *X<sub>i</sub>* and pH and (2) to formulate hypotheses of mechanisms regulating the concentration of sulfate in forest soils. Because IM plots were linear, we were able to use regression analysis to determine the slope (*m*) and intercept (-*b*) of each IM isotherm

$$RE = mX_i - b \quad (1)$$

for each pH value (Table 1). We then used these data to evaluate the change in either the slope (*m*) or intercept (*b*) in response to variations in solution pH (Figs. 3 and 4). This evaluation

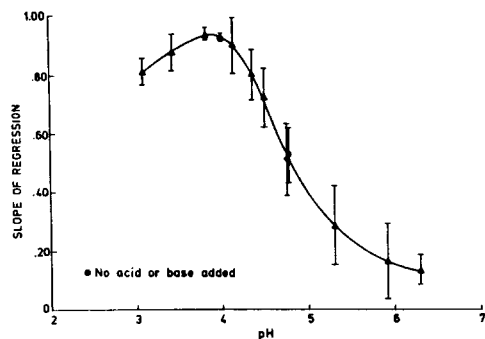


FIG. 3. Slope of IM isotherm at various equilibrium pH values. Error bars are 95% CI.

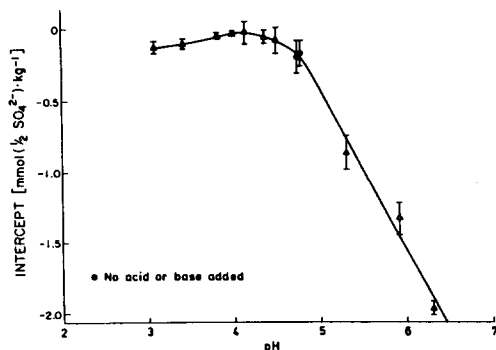


FIG. 4. Intercept of IM isotherm at various equilibrium pH values. Error bars are 95% CI.

facilitated a description of sulfate adsorption in the Beckett soil. The relationships in Figs. 3 and 4 can be used as an empirical model to estimate the amount of sulfate that would be removed or released for any pH and  $X_i$  value within the range of those which we tested.

We also found that the linear IM isotherms were consistent with a simple partitioning of reactive sulfate between soil and solution phases given the range of sulfate concentrations used (see Nodvin et al. 1986). Briefly, there appear to be two sources of reactive sulfate in the soil-water system: (1) a reactive soil pool of sulfate (RSP), which is derived from the soil; and (2) the sulfate that is added to the system via the solution ( $X_i$ ). A simple partitioning of sulfate during an adsorption experiment will produce a linear IM isotherm in which  $m$  is the fraction of the total reactive sulfate that remains adsorbed on the soil and  $b$  is the amount of RSP released when  $X_i$  is zero. The reactive soil pool therefore can be easily estimated

$$\text{RSP} = b/(1 - m) \quad (2)$$

and regression statistics can be used to determine error limits for RSP (see Nodvin et al. 1985). The value of RSP should be equivalent to reactive sulfate as determined by isotopic exchange. Hasan et al. (1970) found that the estimates of the labile sulfate pool, as determined by isotopic exchange, were comparable to their measurements using an extrapolation approach similar to our method of estimating RSP.

The amount of sulfate removed from solution by the soil in our experiments depended upon two properties of the soil: (1) the ability of the soil to partition the anion between the soil and solution phases, and (2) the amount of reactive sulfate present in the soil. The partitioning of sulfate, as expressed by the parameter  $m$ , was strongly affected by solution pH (Fig. 3). Variations in solution pH also had a significant effect on the size of the soil pool (Table 1); in particular, RSP was greatly increased with increases in pH (Fig. 5). A minimum value of RSP occurred at pH 4.1. Because RSP was not constant, we conclude that there are at least two sources of sulfate in the soil: (1) a reactive pool (RSP), which readily exchanges with sulfate in solution; and (2) a less reactive source, which may become labile due to changes in properties of the soil solution.

Anions can be bound to soil by either specific

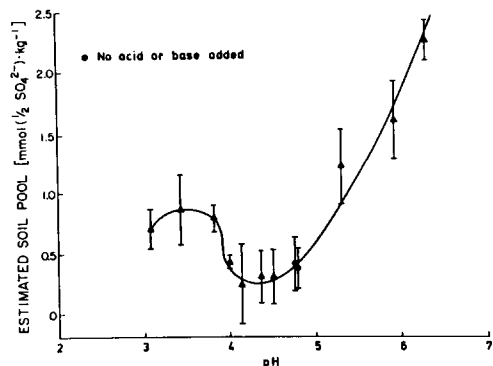


FIG. 5. Estimated soil pool at various equilibrium pH values. Error bars are 95% CI.

or nonspecific adsorption reactions (Hingston et al. 1967). Specific adsorption is believed to occur as a process of hydroxyl exchange (also called *ligand exchange*) (Parfitt and Smart 1978). The data suggest that as the pH of our soil-water systems increased, hydroxyl ions displaced sulfate from coordination sites on amorphous oxides (e.g., Al or Fe) thus increasing the reactive sulfate pool.

A second process may also have affected the size of the soil pool in our experiments. A significant proportion of sulfur in soil is present in the form of sulfate esters (Freney 1961; Williams and Steinbergs 1959). In Beckett B horizon soil from the Adirondack Mountains, New York, the dominant form of sulfur is organic (93%), with carbon-bonded sulfur and ester sulfate being 74 and 18% of total S, respectively (David et al. 1982). Freney et al. (1969) found that organic sulfur in soil extracts was converted to inorganic sulfate under highly alkaline conditions (see also Spencer and Freney 1960 and Williams and Steinbergs 1959). Organic sulfate can also be hydrolyzed to sulfate in heated acid (Johnson et al. 1982). Thus, adjustment of the pH in our soil-water systems may also have affected the size of RSP by inducing the release of sulfate from soil organic compounds.

The retention of reactive sulfate, as expressed by the slope ( $m$ ) of the IM isotherm, was strongly pH-dependent (Fig. 3). Retention of sulfate increased from 52% at the ambient solution pH of 4.8 to a maximum of 94% at pH 3.8. Minimum retention of 13% occurred at pH 6.3. As we have stated, a number of studies have also observed sharp increases in sulfate retention as solution pH decreases, with maximum

retention occurring around pH values of 4.0. The surface charge of amorphous aluminum and iron sesquioxides is pH-dependent. If the pH of a soil is lowered, the net positive surface charge of sesquioxides in the soil will be increased, and it is this process that is believed to facilitate increased anion adsorption (see Johnson and Cole 1980). Chao et al. (1964) concluded that the decreased adsorption of sulfate below pH 4.0 was attributable to the dissolution of aluminum oxides. Thus, although the net surface charge of sesquioxides may be high, the dissolution of these materials below pH 4.0 may effectively reduce the positive charge per surface area of the bulk soil. An alternative mechanism may be important in decreasing sulfate retention at low pH values: the formation of aqueous aluminosulfate complexes that, at low pH, can successfully compete with solid-phase sesquioxides for sulfate anions.

#### *Plant-available sulfur*

The main sources of sulfur available for plant uptake are believed to be adsorbed and soluble (Metson 1979). However, sulfate that is strongly adsorbed by the soil is relatively unavailable to plants (Barrow 1969). Many methods have been used to estimate how much sulfur in soils is available to microorganisms and plants. Sulfate that is extractable using water or a solution containing an indifferent electrolyte appears to provide a better index of readily available sulfur than the amount of sulfate that can be extracted with a specifically adsorbed anion (Elkins and Ensminger 1971). For example, Kowalenko and Lowe (1975) found that microbial activity (as measured by carbon dioxide evolution and nitrogen mineralization) was best correlated with sulfate extracted with a calcium chloride solution, compared with extraction in either sodium acetate, orthophosphate, or sodium bicarbonate solutions. Elkins and Ensminger (1971) found that adding  $\text{CaCO}_3$  to a soil decreased sulfate retention by the soil and increased plant uptake of sulfur. Calcium carbonate addition also increased water-extractable sulfate, but did not significantly affect the amount of sulfate that was extractable using sodium acetate. Considering these results and correlations with the sulfur contents of plants used in their study, they concluded that water-extractable sulfate was a better measure of plant availability than sulfate extractable with acetate.

We view the RSP value as determined from the IM isotherm (Eq. (2)) as a measure of labile and therefore available soil sulfate. In the determination of RSP, the soil is subjected to less harsh treatment than in many extraction procedures. Many extractants can alter pH of the soil solution, and, as we have shown, this pH change can affect both sulfate partitioning and the size of the soil pool. The IM approach and the RSP value thus provide an estimate of plant-available sulfur under ambient soil conditions and can be used to experimentally evaluate how changes in the soil chemical environment will affect sulfur availability.

#### CONCLUSIONS

The results of our study demonstrate that a small change in solution pH can have a large effect on the sulfate-adsorption characteristics of mineral soil at HBEF. Thus, these results support the hypothesis that acidification of the soil due to either acidic deposition or forest clear-cutting may have a significant impact on sulfur cycling and sulfate loss from watersheds in the White Mountains of New Hampshire.

We observed that maximum removal of sulfate from solution occurred at a solution pH of about 4.0. Sulfate removal or release followed the IM isotherm over the pH range 3.1 to 6.3. Changes in solution pH affected both the slope and intercept of the IM isotherm, and therefore the response curves of these two parameters could be used to empirically relate solution pH values and sulfate concentrations to sulfate retention and transport.

Sulfate removal or release by the soil depended upon the magnitude of the partition coefficient and the size of the reactive soil pool of sulfate, both of which were affected by solution pH. Alteration of the soil pH may increase RSP through hydroxyl exchange of specifically adsorbed sulfate, hydrolysis of organic sulfate esters, or both. Our interpretation of sulfate adsorption has been facilitated through the use of the IM isotherm. This adsorption isotherm has enabled us to: (1) empirically describe sulfate adsorption, and (2) suggest processes that regulate concentrations of aqueous sulfate in HBEF soil solutions. Finally, the reactive soil pool as determined by the IM isotherm should serve as a useful index of biologically available sulfate in soils.

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