SULFATE MOBILITY IN AN OUTWASH SOIL IN WESTERN WASHINGTON

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ABSTRACT

The effect of acidic precipitation on cation leaching in a second-growth Douglas-fir ecosystem at the Thompson Research Center is reviewed. Sulfate mobility and soil pH buffering power were tested by applications of heavy doses of sulfuric acid to the study plot. Sulfate at high concentrations proved to be immobilized, presumably by adsorption to soil sesquioxide surfaces. Soil sulfate adsorption was determined at varying sulfate concentrations, and two mechanisms of adsorption are implied by the shapes of the adsorption isotherms.

INTRODUCTION

In a paper given at the American Geophysical Union Annual meeting last April, we reported that acid rainfall and associated sulfate ions accounted for approximately 25% of the yearly cation removal from the Thompson site (Cole and Johnson, 1974). It appeared that sulfate was mobile in the Everett soil whereas hydrogen ions immediately exchanged with metal cations resulting in the transport of sulfate salts out of the system. However, continued sulfate output during periods of zero input suggested that the system had some buffering capacity with respect to sulfate.

Two approaches were taken to determine and characterize the sulfate and pH buffering power of the soil system: (1) the lysimeter study plot was leached with aliquots of sulfuric acid ranging in concentration from 10 to 1000 times higher than that occurring at Cedar River at present, and (2) a series of soil sulfate adsorption studies was conducted in the laboratory.

METHODS

Successive aliquots of 10^{-3}, 10^{-2}, and 10^{-1} N H_2SO_4 followed by distilled water were applied to the soil over the forest floor, A- and B-horizon lysimeter plates such that the forest floor received 1.6 cm and the A and B received 3.2 cm of solution each time for a total of eight leachings. The first two applications were designed to simulate heavier acid loads that the system might experience in the future, and the last application was designed to potentially exhaust the exchangeable cation capital of the soil to 50 cm depth (30000 eq/ha). Incoming precipitation was shielded from the plot during these applications. Solution samples were taken daily following each application and analyzed for pH, specific conductance, HCO_3^-, SO_4^{2-}, Na^+, Ca^{2+}, Mg^{2+}, K^+, and Mn^{2+}. Bicarbonate was done by titration to pH 4.5, sulfate was done on a Technicon Autoanalyzer 11 (method 226-72W), and the cations were done by atomic absorption (I. L. Spectrophotometer 353).

For three months following these applications, solutions from the plot were collected and analyzed, allowing naturally occuring precipitation to fall on it. At the end of this period, soils in the study plot and the surrounding area were sampled and extracted for sulfate by shaking 20 grams of air-dried soil with 100 ml 0.02 N K_2HPO_4 for 30 minutes, a slight modification of the method given by Ensminger (1954).

Soil sulfate adsorption was determined by shaking six replicates of 5 g air dried samples with 25 ml solution for 24 hours. Initial solution sulfate concentration ranged from zero (distilled water) to 10 meq/l.

RESULTS

Figure 1 shows the sulfate concentrations and pH of solutions taken following acid application. All points were shifted to the left so that the lag due to soil moisture storage is approximately accounted for.

It is immediately obvious that acid deposition had a very small effect on sulfate levels in the B-horizon solution, raising them from 0.06 to 0.17 meq/l only after the 10^{-1} N (100 meq/l) application. B-horizon pH apparently began to drop with the 10^{-3} N application. Forest floor and A-horizon leachates showed dramatic increases in sulfate concentrations beginning after the 10^{-3} N acid application. Forest floor and A-horizon solution pH dropped similarly to B-horizon solution pH, but remained at the low levels for longer periods. Forest floor pH appeared to be climbing rapidly back to normal levels toward the end of the study period following a low of 3.83, A-horizon pH rose slowly from a low of 4.31 to 4.64, and B-horizon pH began to drop erratically as

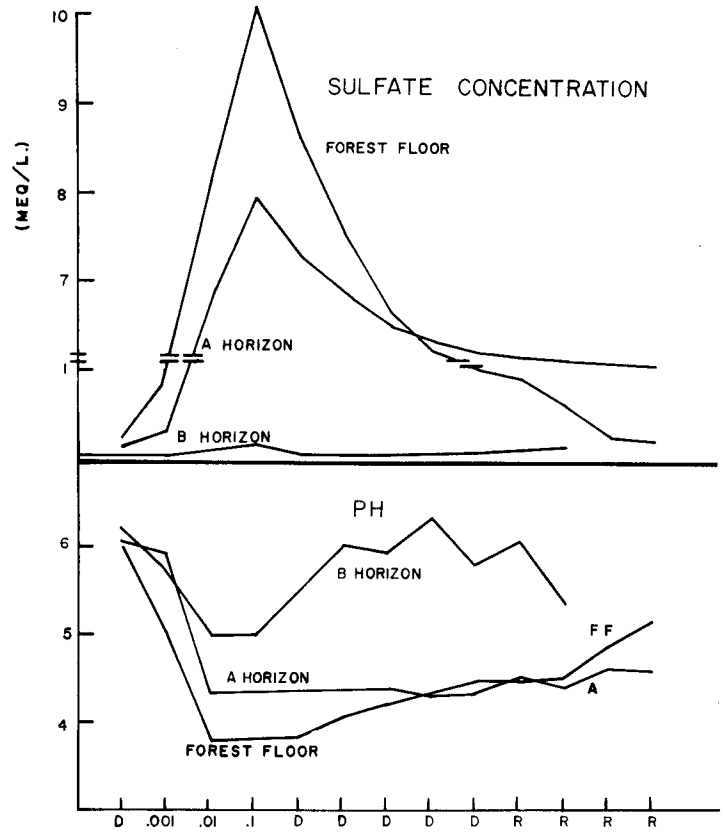

Figure 1. Soil solution pH and sulfate concentration after acid leaching. Normality of applied acid is indicated, D = distilled water leaching, R = natural rainfall leaching.

sulfate concentration rose slightly to 0.095 meq/l. In all cases, the pH drop occurred with the 10^{-3} N acid application and reached a minimum with the 10^{-2} N application.

Table 1 gives the figures for total input, output, and storage for H^+, SO_4^{2-}, and total cations for the various horizons. It is obvious from these data that the hydronium ion is far less mobile in this soil than the sulfate ion, even though pH drops were dramatic. The total H^+ loading should have been sufficient to exhaust all exchangeable cations within this soil section. It is quite conceivable that the higher acid concentrations mineralized some litter, though this was not physically apparent.

The total of H^+, Ca^{2+}, Na^+, K^+, Mg^{2+}, and Mn^{2+} removal was lower than that of SO_4^{2-} probably because of the removal of other cations such as NH_4^+ and Al^{3+} not accounted for. About two-thirds of the calculated total supply of Na^+, Ca^{2+}, and K^+ was removed from the forest floor and

Table 1. H^+, SO_4^{2-}, and total cation budgets after acid leaching from lysimeter data., (eq/ha).

Horizon	Input			Output			Storage		
	H^+	SO_4^{2-}	TC[2]	H^+	SO_4^{2-}	TC	H^+	SO_4^{2-}	TC
Forest floor	17760	17760	0	0.2	16000	10000	17760	1760	-10000
Forest floor +A	35520	35520	0	0.2	15000	11200	35520	20000	-11200
B (50 cm)	0.2	15000	11200	0.0	200	200	0.2	14800	11000

[1]Background concentration factors subtracted

[2]Ca^{2+}, Mg^{2+}, Mn^{2+}, Na^+, and K^+ only. TC = total cations

A-horizon yet virtually none of this cation capital was removed past 50 cm in the B-horizon.

Table 2 gives the results of the sulfate extractions done on the

Table 2. Soil pH and sulfate content of acid-treated (AT) plot and Cedar River (CR) soil (Everett series).

Horizon and depth (cm)	pH		Soil sulfate				Storage in AT soil	
			AT		CR			
	AT	CR	meq/100g	eq/ha	meq/100g	eq/ha	meq/100g	eq/ha
A(4-12)	4.57	5.10	0.74	6,200	0.26	2,200	0.48	4,000
B(12-30)	5.01	5.18	0.78	19,600	0.26	6,500	0.52	13,100
B(30-50)	5.40	5.38	0.86	30,500	0.13	4,500	0.73	26,000
B(12-50)	5.45	5.48	0.80	56,300	0.18	11,000	0.62	45,300
TOTAL				62,500		13,200		49,300

acid treated plot (AT) and the surrounding soil (CR). Most of the sulfate now retained in the Everett soil is held in the A-horizon and the upper 22 cm of the B-horizon, yet acid application resulted in the greatest storage in the lower 20 cm of the B-horizon. This implies that the bulk of the as yet unfilled sulfate adsorption capacity lies in the lower B-horizon. Estimated total sulfate storage from this data is higher than that calculated from lysimeter data, but the relative magnitudes of storage between horizons is clear nonetheless. Acid treatment resulted in pH lowering in the A and upper B-horizon, where net sulfate storage was least, implying that soil hydrogen ion and sulfate ion buffering power are related with respect to sulfuric acid input.

Figure 2 shows the results of the sulfate adsorption study. Sul-

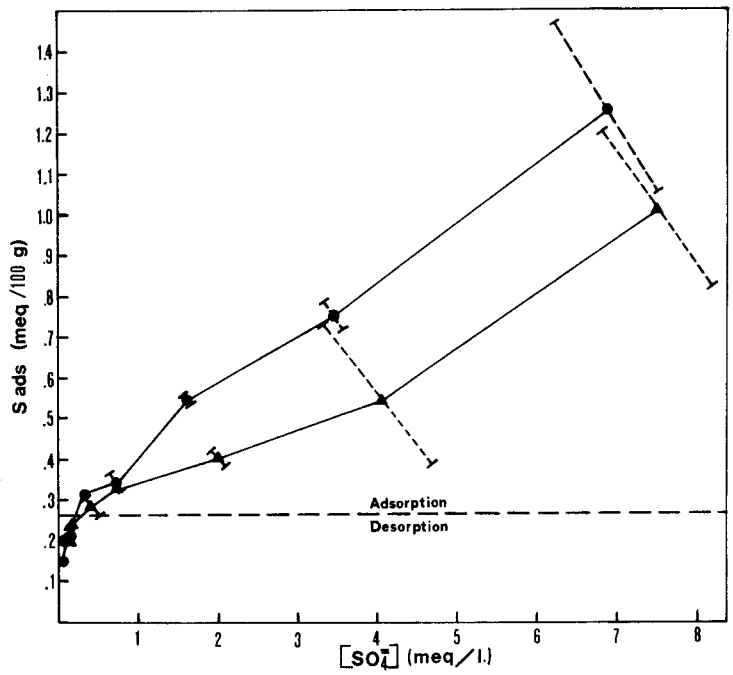

Figure 2. Sulfate adsorption (Sads) on the Everett soil vs equilibrium sulfate concentration [$SO_4^=$]. ▲——▲ = A-horizon, ●——● = B-horizon. Error bars indicate 95% confidence intervals in solution sulfate concentration and calculated sulfate adsorption.

fate adsorbed on soil colloids (Sads) is plotted against equilibrium sulfate concentration in solution. Sulfate adsorbed is calculated from initial minus final solution sulfate concentrations, using 0.26 meq/100g as an initial value for adsorbed sulfate (Table 2). (Soil from the upper 22 cm of the B-horizon was used.) Error bars represent 95% confidence intervals.

B-horizon sulfate adsorption is greater than A-horizon adsorption at a given solution sulfate concentration, but no maximum adsorption value is indicated for either horizon from these data points. The lower portions of both adsorption-desorption isotherms seem to asymptotically approach maxima, but beyond roughly 0.7 meq/l the slopes of the isotherms increase drastically, implying no maximum adsorption value to at least 7.5 meq/l.

Figure 3 shows plots of $[SO_4^{=}]/Sads$ vs $[SO_4^{=}]$ for the lower

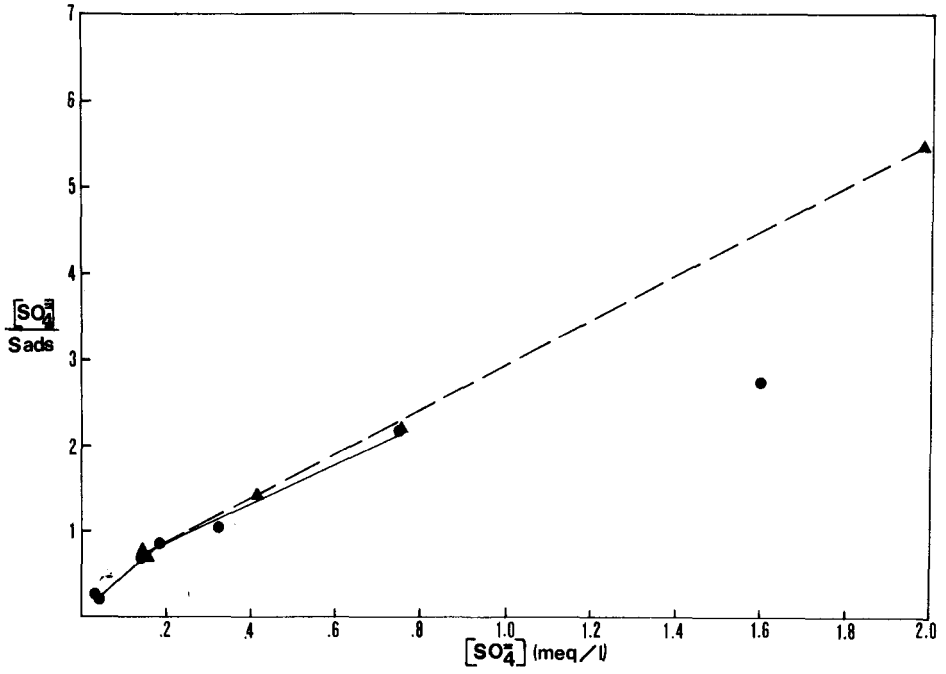

Figure 3. Test of fit to the Langmuir equation. ●——● = A-horizon, ▲——▲ = B-horizon.

portions of the isotherms. A straight line indicates a fit to the langmuir equation,

$$\frac{Sads}{max\ Sads} = \frac{b[SO_4^{=}]}{1+b[SO_4^{=}]}$$

where b is a constant and max Sads is the maximum adsorption capacity.

The entire low level portion of A-horizon isotherm fits this equation, and parts of the B-horizon isotherm do.

DISCUSSION

Both the acid leaching experiment and the soil sulfate adsorption studies clearly show that sulfate has limited mobility in the Everett soil. Total sulfate adsorption has been shown to be proportional to the

sesquioxide content of the soil (Chao, et al., 1964; Barrow, et al., 1969). This apparently does not hold true for the Everett soil, however, in that the A-horizon contains 1.4% Fe and 0.23% Al, the upper 17 cm of the B-horizon contains 1.02% Fe and 0.06% Al,and the lower 20 cm of the B-horizon contains 0.93% Fe and 0.118% Al (as free oxides) (Schlichte, 1968).

Sulfate adsorption has been shown to be strongly pH dependent, greater amounts being adsorbed at low pH values (Gebhardt and Coleman, 1974; Harward and Reisenauer, 1966; Chao et al., 1965). This is presumably due to (1) the protonation of hydroxy surfaces, giving them a more positive charge, and (2) the reduction of the concentration of competing OH^- ions. The reduction of A-horizon and upper B-horizon pH during the acid leaching experiment undoubtedly enhanced sulfate adsorption, and greater quantities of sulfate may have remained mobile if neutral sulfate salts rather than acid had been applied.

Various mechanisms of sulfate adsorption have been proposed: Gebhardt and Coleman (1974) suggest that HSO_4^- is adsorbed rather than $SO_4^=$ on the basis of the similarity between sulfate and chloride adsorption isotherms for tropical soils. Aside from the sulfur species adsorbed, two basic mechanisms of adsorption have been proposed; (1) OH^- displacement on sequioxide surfaces (Chao, et al., 1965; Chang, et al., 1963; Gebhardt and Coleman, 1974), and (2) -O- displacement from within sequioxide structures, or "anion penetration" (Chao, et al., 1962; Harward and Reisenauer, 1966). The first mechanism would result in readily exchangeable sulfate, the second in more strongly bound, less available sulfate.

The sulfate adsorption isotherms for the Everett soil indicate that at least two mechanisms or sites of adsorption are at work, in that the low concentration portions of both curves are distinct from the high concentration portions. The low concentration portions, which roughly conform to the Langmuir isotherm, may represent mostly OH^- displacement, whereas the roughly linear high concentration portions may reflect a greater degree anion penetration. Presumably some OH^- adsorption and some anion penetration occurs at any given sulfate concentration.

CONCLUSIONS

Sulfate mobility is limited in the Everett soil, as in others (Harward and Reisenauer, 1966; Bornemisza and Lianos, 1967; Chao, et al., 1962), by the capacity of the soil to adsorb sulfate. Such adsorption probably consists of at least two mechanisms, resulting in both tightly and loosely bound sulfate. Full recovery of high-level adsorbed sulfate can apparently be obtained by extraction with a more highly adsorbed anion such as phosphate, and nearly full recovery of

low-level adsorbed sulfate is indicated by the distilled water extractions (Figure 2).

In considering the possible effects of acidic precipitation on cation removal from a given ecosystem, the mobility of sulfate in the given soil must be considered, or there exists a distinct possibility of overestimating the net transfer of cations due to acid deposition. The data presented here and in a previous paper (Cole and Johnson, 1974) has shown that the ecosystem studied has the ability to buffer and moderate cation losses due to heavy loads of sulfuric acid over short periods, and certain other ecosystems may possess this capacity as well. The long-term effects of sulfuric acid deposition may be another matter; if the soil's ability to adsorb sulfate (and thus prevent increased cation loss) is reached or a new equilibrium level is attained, acid deposition may result in equivalent sulfate salt losses. The fact remains, however, that sulfate, especially in acid form, interacts strongly with soils that have appreciable sesquioxide contents, and the characteristics of this interaction must be known and employed in evaluating and modeling cation losses due to sulfuric acid deposition.

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