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**Relationships Among Iron, Aluminum, Carbon, and Sulfate in a Variety of Forest Soils**

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# Relationships Among Iron, Aluminum, Carbon, and Sulfate in a Variety of Forest Soils<sup>1</sup>

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## ABSTRACT

Among several soil properties tested, percent Fe, (i.e., Fe by citrate-dithionite minus oxalate extraction) was the single parameter most closely related to  $\text{SO}_4^{2-}$  adsorption properties in a variety of forest soils. There were exceptions to this general relationship, however, and a combination of percent C, citrate-dithionite, and oxalate extractions for both Fe and Al appear most promising in predicting sulfate adsorption. Percent clay, pH, and pyrophosphate-extractable Fe + Al were either insignificantly or inconsistently related to  $\text{SO}_4^{2-}$  adsorption. Because organic matter had a decidedly negative influence upon  $\text{SO}_4^{2-}$  adsorption, surface soils and B horizons of Spodosols (and highly podzolized soils) had relatively poor  $\text{SO}_4^{2-}$  adsorption properties, even when their dithionite-extractable Fe values were high. Organic matter also reduced Fe crystallinity (i.e., increased  $\text{Fe}_o/\text{Fe}_d$ , or the ratio of oxalate to dithionite Fe), and the results of this study suggest that crystalline rather than amorphous, inorganic Fe (i.e., oxalate minus pyrophosphate Fe) is most highly correlated with adsorbed, water-insoluble  $\text{SO}_4^{2-}$ .

**Additional Index Words:** Spodosol, Ultisol, oxalate, pyrophosphate, dithionite, adsorbed  $\text{SO}_4^{2-}$ , soluble  $\text{SO}_4^{2-}$ .

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CRITERIA used for assessing soil sensitivity to cation leaching by acid rain usually include cation exchange capacity (CEC), base saturation, pH, and carbonate content (Wiklander, 1974, 1980a; McFee et al., 1976; McFee, 1980; Klopatek et al., 1980; Cowell et al., 1981). Although these criteria are very important in themselves,  $\text{SO}_4^{2-}$  adsorption properties should also be included in assessments of soil sensitivity. Due to charge balance considerations,  $\text{SO}_4^{2-}$  adsorption can prevent the transport of cations (including  $\text{H}^+$  and  $\text{Al}^{3+}$ ) from soils to surface waters (Johnson, 1980; Seip, 1980). Specifically, cations cannot leach from soils without an equivalent concentration of anions in solution; therefore, the entire process of soil leaching is very much dependent on the inputs or internal production of mobile anions (Johnson and Cole, 1980). In nonadsorbing soils, the introduction of  $\text{H}_2\text{SO}_4$  from the atmosphere must result in accelerated cation leaching (Cronan et al., 1977) and, in acid soils, this can result in an increase in  $\text{H}^+$  and  $\text{Al}^{3+}$  leaching (Seip, 1980; Abrahamsen and Stuanes, 1980). On the other hand, adsorption of  $\text{SO}_4^{2-}$  to soils prevents leaching by  $\text{H}_2\text{SO}_4$  (Johnson and Cole, 1977; Johnson et al., 1979; Singh et al., 1980) and may cause displacement of the zero point of charge to a lower pH value, effecting an increase in CEC (Rajan, 1978; Couto et al., 1979; Wiklander, 1980b).

Unfortunately,  $\text{SO}_4^{2-}$  adsorption capacity is not as routinely measured in soils as are CEC, base saturation, pH,

and carbonate content. Thus, efforts to map soil  $\text{SO}_4^{2-}$  adsorption are hampered by a lack of regional soils information. Sulfate adsorption is known to occur mainly on free Fe and Al oxide surfaces, however (and to a minor extent on kaolinite clays; Chao et al., 1962; Harward and Riesenauer, 1966; Rajan, 1978; Parfitt and Smart, 1978). Recent studies suggest that organic matter is an important factor, also, in that it appears to exert a negative influence on  $\text{SO}_4^{2-}$  adsorption (Couto et al., 1979; Johnson et al., 1979, 1980; Singh, 1980).

The purpose of this study was to investigate the relationships among soil  $\text{SO}_4^{2-}$  content,  $\text{SO}_4^{2-}$  adsorption properties, C, and commonly measured Fe and Al fractions in a variety of forest soils. This study expands upon the data base previously described (Johnson et al., 1980) to include additional soils (Spodosols and heavily podzolized Inceptisols) and additional extraction procedures for Fe and Al (oxalate and pyrophosphate in addition to citrate-dithionite extractions). Our overall goal was to determine if  $\text{SO}_4^{2-}$  content and adsorption patterns are consistent with the USDA soil classification system (USDA/SCS, 1975) and well-known soil-forming processes.

## METHODS

Soil samples were supplied by various investigators from sites across the United States and one site in Costa Rica (Table 1). The soil samples were those used in the study by Johnson et al. (1980) with the addition of samples from the Chesuncook, Maine, and Findley Lake sites. The Chesuncook, Telos, and Becket soils are classified as Spodosols according to Rourke et al. (1978) and Hoyle (1973). Singer and Ugolini (1974) report that the Findley Lake soils, while closely resembling Spodosols, do not fit the criterion that the pyrophosphate-extractable Al plus Fe-to-clay ratio be  $> 0.2$ . Thus, the Findley Lake soils fall under the Cryanepit Great Group (Inceptisols). These soils do fit the Canadian classification for an ortho ferro humic Podzol, however (Singer and Ugolini, 1974), and Ugolini et al. (1977) state that they prefer to refer to these soils as Podzols rather than Inceptisols. According to the pyrophosphate Fe plus Al-to-clay ratio criterion, none of the soils tested here fit the chemical criteria for spodic horizons. Presumably Rourke et al. (1978) and Hoyle (1973) used field criteria (USDA-SCS, 1975) for classifying the Becket, Chesuncook, and Telos soils as Spodosols, and we will accept their classification in this paper.

All soil samples were air-dried and passed through a 2-mm sieve prior to analysis. Sulfate content and  $\text{SO}_4^{2-}$  adsorption were determined according to the methods described by Johnson et al. (1980) except that a mechanical extractor (Concept Engineering Corp., Lincoln, NE 68502) rather than Buchner funnels were used for extraction and adsorption procedures. Extraction time was set at 1 h. Initial  $\text{SO}_4^{2-}$  content was determined by sequential extractions of triplicate 10 g of soil with 0.2 L of  $\text{H}_2\text{O}$  (soluble  $\text{SO}_4^{2-}$ ) followed by 0.05 L of 0.016M  $\text{NaH}_2\text{PO}_4$  (adsorbed  $\text{SO}_4^{2-}$ ). Total  $\text{SO}_4^{2-}$  was defined as the sum of  $\text{SO}_4^{2-}$  extracted by  $\text{H}_2\text{O}$  and  $\text{NaH}_2\text{PO}_4$ .

The number of analyses required to obtain  $\text{SO}_4^{2-}$  adsorption isotherms on all 54 soil samples was prohibitive, and thus adsorption of  $\text{SO}_4^{2-}$  from 0.05 L of 2.34 mmol  $\text{Na}_2\text{SO}_4$  was used as an index of a soil's ability to adsorb sulfate. Adsorption isotherms were available for the Everett, La Selva, and Fullerton soils from previous research (Johnson and Cole, 1977; Johnson et al., 1979; Johnson and Henderson, 1979), and these results showed that a good separation in soil  $\text{SO}_4^{2-}$  adsorption prop-

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Table 1—Location, forest type, and initial soil classification for each study site.

Location	Forest type	Parent material	Classification	Series	Soil texture	Sample locations	Cooperator in this study
Walker Branch, Tenn.	Mixed hardwood	Dolomitic limestone	Typic Paleudult	Fullerton Claiborne	Cherty silt loam	Ridgetop Cove	D. W. Johnson
Camp Branch, Tenn.	Mixed hardwood	Pennsylvanian sandstone	Typic Halpludult	Lily	Fine loam	Hilltop	J. M. Kelly (Tennessee Valley Authority, Muscle Shoals, Ala.)
			Fluvaquentic Dystrochrept	Philo	Coarse loam	Near stream channel	
Cross Creek, Tenn.	Mixed hardwood	Pennsylvanian sandstone	Typic Hapludult	Lily	Fine loam	Hilltop	J. M. Kelly
			Aquic Hapludult	Cotaco	Fine loam	Near stream channel	
Coweeta, N.C.	Mixed hardwood	Gneiss, schist, sandstone	Humic Hapludult	Porters	Fine loam	Steep slopes, higher elevation. Watersheds 36 and 27	W. T. Swank (U.S. Forest Service, Otto, N.C.)
			Typic Hapludult	Saluda	Loam	Steep slopes, lower elevation. Watersheds 6 and 18	W. T. Swank
Hubbard Brook, N.H.	Northern hardwood	Gneiss, schist	Typic Fragiorthod	Becket	Stony sandy loam	Lower elevation slopes	J. W. Hornbeck (U.S. Forest Service, Durham, N.H.)
Thompson, Wash.	Douglas fir	Glacial outwash	Dystric Xerochrept	Everett	Gravelly sandy loam	Glacial outwash terrace	D. W. Cole (University of Washington, Seattle)
La Selva, Costa Rica	Mixed palms <i>Grias, pentaclethera</i>	Alluvium	Typic Hydrandept	La Selva	Clay loam	Near river channels	S. P. Gessel (University of Washington, Seattle)
Findley Lake, † Wash.	Subalpine fir, mountain hemlock	Volcanic ash	Cryandept†	--	Clay loam	Moraine site, 180-year-old forest and hillside, 23-year-old forest	C. C. Grier (University of Washington, Seattle)
Chesuncook, Mass.	Spruce-fir	Glacial till	Typic Fragiorthod	Chesuncook	Coarse loam	Upland till sites	J. W. Hornbeck
			Aquic Fragiorthod	Telos	Coarse loam	Lower elevation till sites	

† Ugolini et al. (1977) prefer to refer to the Findley Lake soil as a podzol because, although it does not meet the strict criteria for a Spodosol, it does have the morphology and chemistry of one, and similar soils are called podzols in the Canadian classification system.

erties was exhibited at solution  $\text{SO}_4^{2-}$  concentrations near 2.0  $\text{mmol}\cdot\text{L}^{-1}$ . Thus, we chose input solutions at 2.34  $\text{mmol}$  to provide indices of  $\text{SO}_4^{2-}$  adsorption among these soils. Total  $\text{SO}_4^{2-}$  after  $\text{Na}_2\text{SO}_4$  treatment was defined as total initial  $\text{SO}_4^{2-}$  content plus disappearance of  $\text{SO}_4^{2-}$  from solution during  $\text{Na}_2\text{SO}_4$  leaching of previously untreated soils (triplicate 10-g samples treated with 0.05 L of 2.34  $\text{mmol}$  of  $\text{Na}_2\text{SO}_4$ ). Following  $\text{Na}_2\text{SO}_4$  treatment, columns were leached with 0.2 L of  $\text{H}_2\text{O}$  to remove soluble  $\text{SO}_4^{2-}$  (including interstitial sulfate) and with  $\text{NaH}_2\text{PO}_4$  to determine adsorbed  $\text{SO}_4^{2-}$ ,  $\text{SO}_4^{2-}$  extraction, and adsorption procedures are shown schematically in Fig. 1.

Sulfate in water and  $\text{Na}_2\text{SO}_4$  leachings was determined colorimetrically on a Technicon Autoanalyzer (Technical Industrial Systems, Tarrytown, NY 10591). Due to phosphate interferences on the Autoanalyzer,  $\text{SO}_4^{2-}$  in  $\text{NaH}_2\text{PO}_4$  leachates was determined by the barium chloranilate procedure of Bertolacini and Barney (1957).

Free Fe and Al fractions were determined by separate (not sequential) extractions with (i) 0.1M  $\text{Na}_4\text{P}_2\text{O}_7$ , (ii) 0.2M ammonium oxalate adjusted to pH 2, and (iii) the dithionite-citrate-bicarbonate reagent according to standard soil survey methods (USDA, 1972). It is generally believed that extraction (i) removes organically bound Fe ( $\text{Fe}_p$ ), extraction (ii) removes organically bound plus inorganic amorphous Fe ( $\text{Fe}_o$ ), and extraction (iii) removes organically bound, inorganic amorphous, and crystalline Fe ( $\text{Fe}_d$ ) (Blume and Schwertmann, 1969; McKeague et al., 1971). Crystalline Fe ( $\text{Fe}_c$ ) is designated as  $\text{Fe}_d - \text{Fe}_o$  and amorphous inorganic Fe ( $\text{Fe}_a$ ) is designated as  $\text{Fe}_o - \text{Fe}_p$ . The same general scheme can be applied to Al, but the extractions are less specific and include more overlap (McKeague et al., 1971). Percent carbon was determined by combustion in a LECO furnace, pH in a 1:1 water-to-soil ratio, and percent clay by the hydrometer method. Statistical analyses were performed using the Statistical Analysis System, 1979 Edition (Barr et al., 1979).

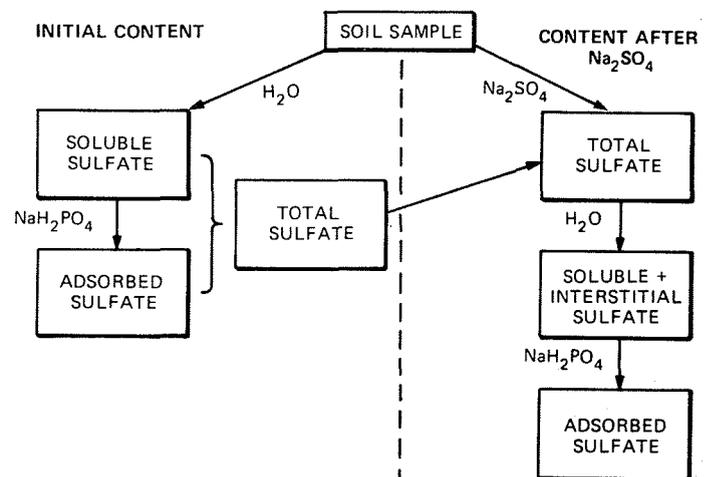


Fig. 1—Schematic diagram of  $\text{SO}_4^{2-}$  extraction and adsorption procedures.

## RESULTS

### Spodosols and Cryandepts

The Spodosols and the Findley Lake Cryandepts all had similar patterns in Fe, Al, and organic matter: increases from A2 to B horizons followed by decreases in C horizons (where present) (Fig. 2 and 3). Oxalate-extractable Fe and Al ( $\text{Fe}_o$  and  $\text{Al}_o$ ) accounted for 50 to 90% of dithionite-extractable Fe Al ( $\text{Fe}_d$  and  $\text{Al}_d$ ); thus,  $\text{Fe}_c$  and  $\text{Al}_c$  values were generally low (the latter being zero in many cases). Pyrophosphate-extractable Fe and Al ( $\text{Fe}_p$  and  $\text{Al}_p$ ) accounted for 20 to 70% of dithionite-

extractable values, depending upon C content (as expected). Amorphous inorganic Fe and Al ( $Fe_a$  and  $Al_a$ ) were significant (35 to 67%) portions of dithionite-extractable Fe and Al.

Initial contents of soluble and adsorbed  $SO_4^{2-}$  were very low in the Becket and Findley Lake soils. The Becket and Telos soils contained no adsorbed  $SO_4^{2-}$  (although the Telos contained considerable soluble  $SO_4^{2-}$ ) and the

Findley Lake soils (from both the 23- and 180-year-old forests) contained very small amounts ( $< 15 \text{ mg} \cdot \text{kg}^{-1}$ ) of adsorbed  $SO_4^{2-}$  (Fig. 2 and 3). Only the Chesuncook soils contained an appreciable amount ( $35 \text{ mg} \cdot \text{kg}^{-1}$ ) of adsorbed  $SO_4^{2-}$  (as well as soluble  $SO_4^{2-}$ ) in the  $B_{21}/B_{22}$  horizon, corresponding to a large accumulation of Fe (Fig. 3).

Upon treatment with  $Na_2SO_4$ , some soils actually re-

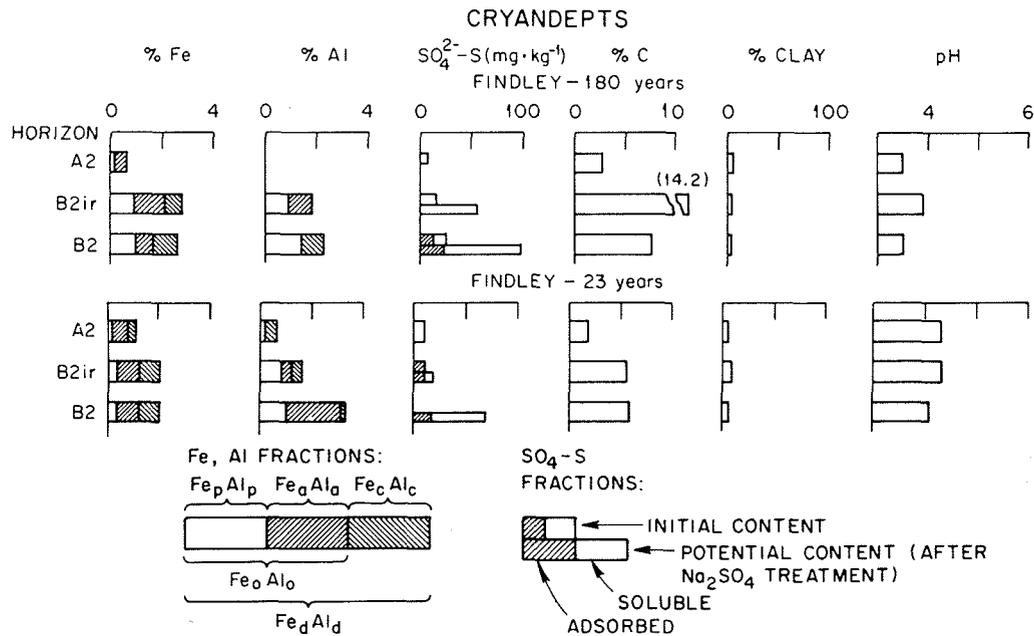


Fig. 2—Iron and Al fractions,  $SO_4^{2-}$ -S fractions and adsorption, percent C, percent clay, and pH in forested Cryandepts from Findley Lake, WA (180- and 23-year-old stands).

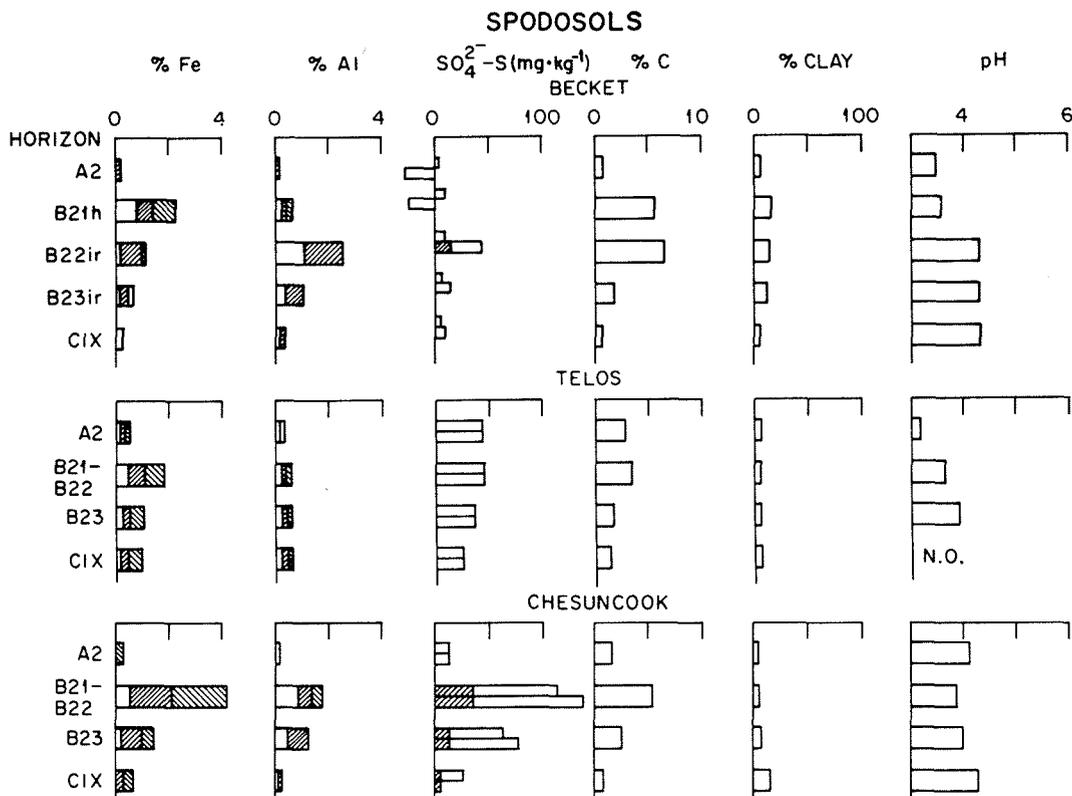


Fig. 3—Iron and Al fractions,  $SO_4^{2-}$ -S fractions adsorption, percent C, percent clay, and pH in forested Spodosols from Hubbard Brook, N.H. (Becket and Chesuncook, Me. (Telos and Chesuncook). See Fig. 2 for legend.

leased  $\text{SO}_4^{2-}$  (Becket A2, B21h; Chesuncook C1X; Findley, 180 yr, A2), others accumulated only soluble  $\text{SO}_4^{2-}$  (Becket B23ir; Chesuncook B21-B22, B23; Findley, 180 yr, B2ir, B2; Findley, 23 yr, B2ir, B2), others accumulated adsorbed  $\text{SO}_4^{2-}$  (Becket B22ir, Findley, 180 yr, B2; Findley, 23 yr, B2), and others showed no change at all (Telos, all horizons; Chesuncook, A2; Findley, 23 yr, A2). Horizons accumulating  $\text{SO}_4^{2-}$  in soluble or adsorbed forms were generally higher in Fe and Al than those not accumulating or losing  $\text{SO}_4^{2-}$  after  $\text{Na}_2\text{SO}_4$  treatment.

Percent clay was low (< 20%) in all soils tested and generally showed little relationship to Fe, Al, or  $\text{SO}_4^{2-}$  content (Fig. 2 and 3). Soil pHs (1:1 soil to water) were low in all cases, especially in A2 horizons where values < pH 3.5 were measured in the Becket, Telos, and Findley, 180 yr soils (Fig. 2 and 3). No consistent relationship between pH and Fe, Al,  $\text{SO}_4^{2-}$ , or percent C was noted, however.

### Ultisols

Patterns of Fe and Al in Ultisols were similar to those observed in the Spodosols and Cryandeps (increases from A to B horizons), but patterns of carbon were the reverse (decreases from A to B horizons, Fig. 4 and 5). Although the patterns of Fe and Al distribution in Ultisols were similar to those in the Spodosols and Cryandeps, the forms of Fe and Al were quite different. Whereas amorphous forms predominated Fe and Al fractions in the Spodosols and Cryandeps (Fig. 2 and 3), crystalline forms

(i.e., dithionite minus oxalate) predominated in the Ultisols (especially for Fe). Given the nature of Ultisols and the length of time involved in their development, this is as expected.

Sulfate distribution in the Ultisols exhibited a typical pattern wherein water-soluble  $\text{SO}_4^{2-}$  predominated in A horizons, and adsorbed  $\text{SO}_4^{2-}$  concentrations increased with depth and usually predominated in B and C horizons (Fig. 4 and 5). The pattern in adsorbed  $\text{SO}_4^{2-}$  correlated with patterns in  $\text{Fe}_d$  and  $\text{Al}_d$  within horizons of a given soil series but not as well among soil series. For example, the C horizons of the Lily series from both Camp Branch and Cross Creek Watersheds (TN) had much lower adsorbed  $\text{SO}_4^{2-}$  concentrations (10 to 15  $\text{mg}\cdot\text{kg}^{-1}$ ) than the Claiborne B (Walker Branch, Tenn.) and Saluda C (Coweeta, N.C.) horizons (25 to 70  $\text{mg}\cdot\text{kg}^{-1}$ ) even though their  $\text{Fe}_d$  and  $\text{Al}_d$  concentrations were similar (Fig. 4 and 5).

Following treatment with  $\text{Na}_2\text{SO}_4$ , most A horizons underwent little or no change [exceptions being the gains in soluble  $\text{SO}_4^{2-}$  in the Cotaco (Cross Creek, Tenn.) and Saluda, Watershed 18 (Coweeta, N.C.) soils]. Most subsurface horizons gained soluble  $\text{SO}_4^{2-}$  [exceptions being Claiborne (Walker Branch, Tenn.) and Lily (Camp Branch and Cross Creek, Tenn.) soils], but only Porters and Saluda soils from Coweeta, N.C., gained adsorbed  $\text{SO}_4^{2-}$  (Fig. 4 and 5).

Most Ultisols tested showed the expected accumulations of clay in their B horizons (Fig. 4 and 5). By the strict definition of a Ultisol, however, neither of the Por-

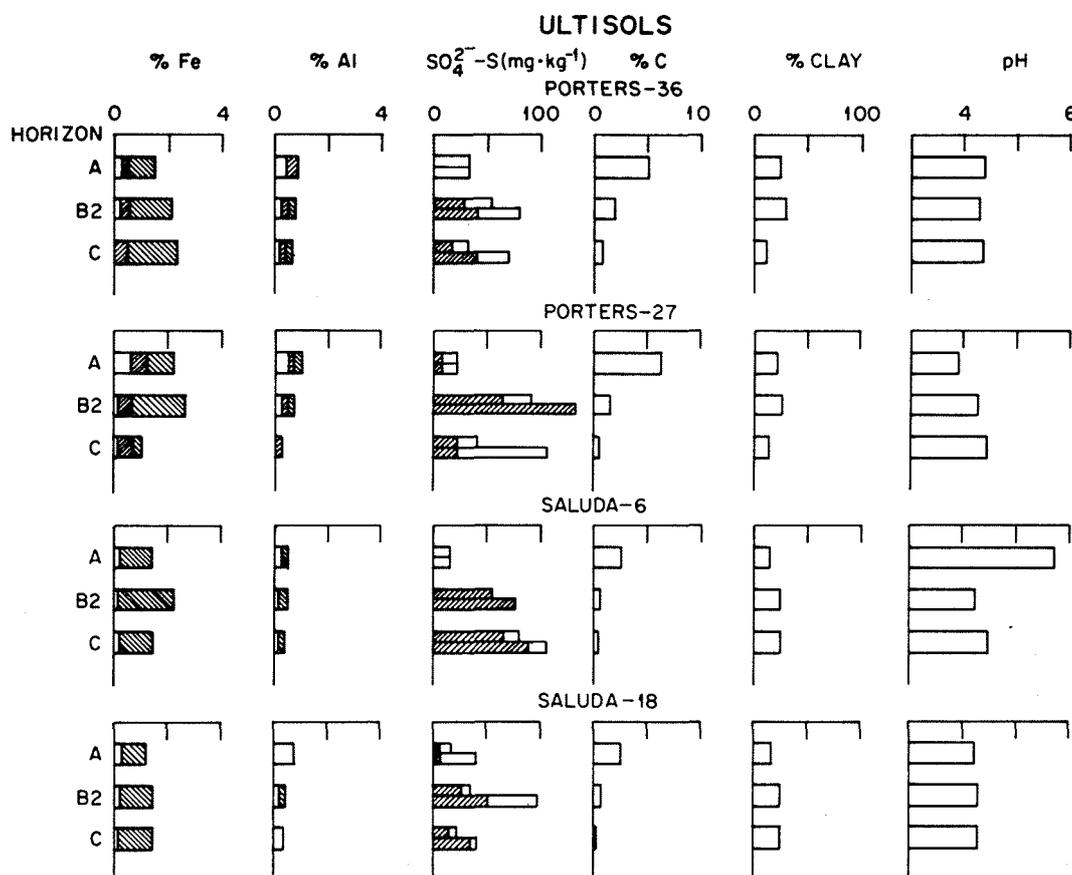


Fig. 4—Iron and Al fractions,  $\text{SO}_4^{2-}\text{-S}$  fractions and adsorption, percent C, percent clay, and pH in four forested Ultisols from watersheds 36, 27, 6, and 18 at Coweeta, N.C. See Fig. 2 for legend.

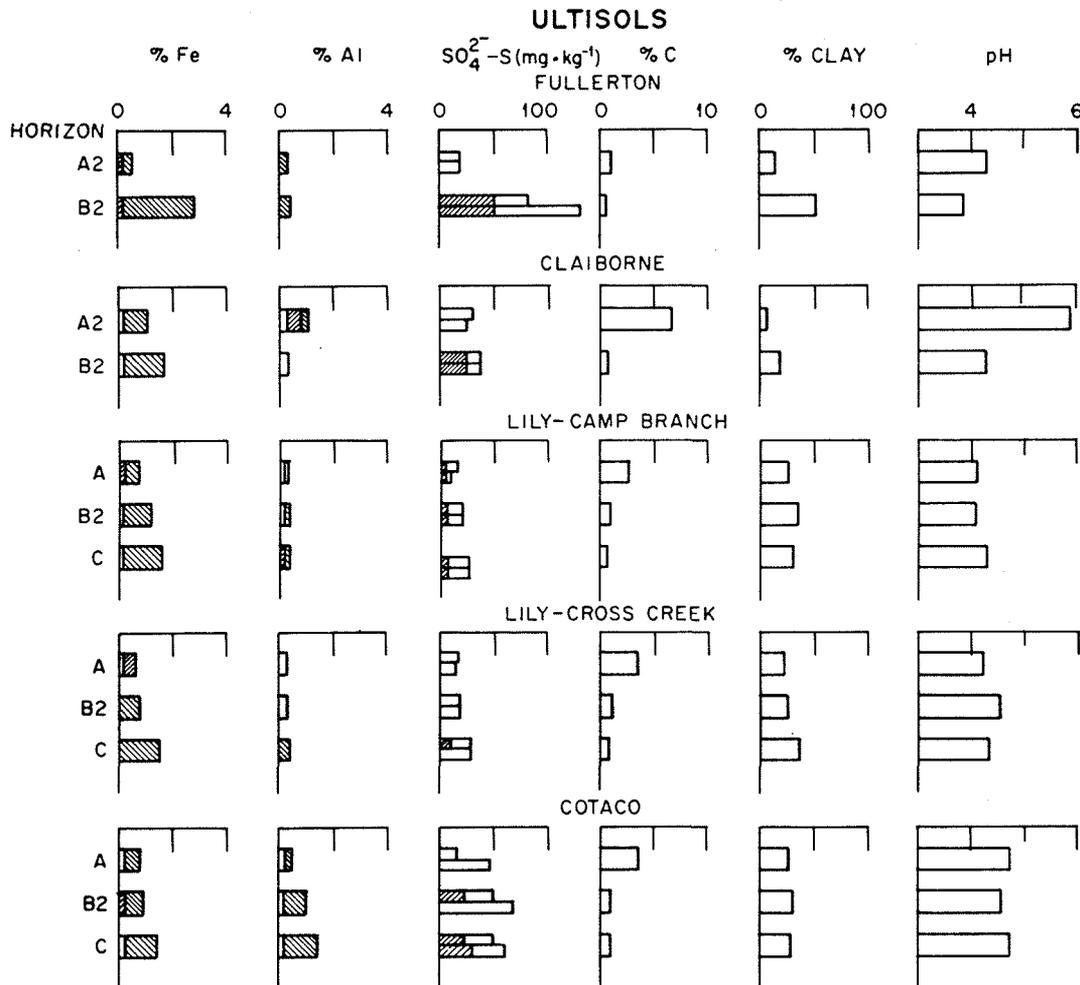


Fig. 5—Iron and Al fractions, SO<sub>4</sub><sup>2-</sup>-S fractions and adsorption, percent C, percent clay, and pH in Ultisols from Walker Branch Watershed, Tenn. (Fullerton and Claiborne), Camp Branch Watershed, Tenn. (Lily), and Cross Creek Watershed, Tenn. (Lily and Cotaco). See Fig. 2 for legend.

ters (Coweeta, N.C.) soils qualify. Specifically, the difference in percent clay in A and B horizons was not sufficient to qualify for an argillic horizon (percent clay in the B horizon must be > 1.2 times the percent clay in the A horizon if the percent clay in the A horizon is between 15 and 40%; USDA-SCS, 1975). Thus, the Porters soils, like the Findley Lake soils, strictly fall under the classification of Inceptisols. For the purposes of this study, however, and because the criteria were nearly met (percent clay in the B horizon equalled 1.1 times percent clay in the A horizon in both cases), both Porters soils will be considered under the category of Ultisols.

With two exceptions, all horizons of all Ultisols had pH < 5 (Fig. 4 and 5). The two exceptions were the A horizon of the Saluda, watershed 6 (Coweeta, N.C.) and Claiborne (Walker Branch, Tenn.) soils. In the former case, a heavy liming in 1959 is undoubtedly responsible (Swank and Douglass, 1977), and in the latter case its receiving slope position (cove sites) probably accounts for the high base status (i.e., base-rich deciduous litter).

#### Inceptisols

Amounts and fractions of Fe and Al varied considerably among the remaining Inceptisols (Fig. 6). The Everett (Wash.) soil had large amounts of Al<sub>o</sub>, and in fact, Al<sub>o</sub> exceeded Al<sub>d</sub> by a factor of 2 or more in both hori-

zons. The LaSelva (Costa Rica) soil had large accumulations of Fe (mostly as Fe<sub>c</sub>) in both horizons tested. The Philo soil had a large accumulation of Fe (mostly as Fe<sub>c</sub>) in the C horizon, and in general its profile was similar to the Ultisols which surround it on Camp Branch Watershed, Tenn.

These three Inceptisols varied considerably in SO<sub>4</sub><sup>2-</sup> content, although the pattern of increasing adsorbed SO<sub>4</sub><sup>2-</sup> with depth was consistent. All horizons of all three soils accumulated soluble SO<sub>4</sub><sup>2-</sup>, but little or no additional adsorbed SO<sub>4</sub><sup>2-</sup> was accumulated following Na<sub>2</sub>SO<sub>4</sub> treatment.

These three Inceptisols showed similar patterns of percent carbon (decreases with depth) but different patterns of percent clay. The Everett and LaSelva soils had vastly different clay contents but decreases with depth in both cases. The Philo soil had an increase in percent clay with depth and a sharp increase in Fe in the C horizon. The pHs ranged from 3.7 (Philo A horizon) to 4.7 (Everett B horizon) and showed no relationship to Fe, Al, SO<sub>4</sub><sup>2-</sup>, percent C, or percent clay.

#### Correlations Among Soil Properties

Of the various Fe and Al fractions tested, only Fe<sub>d</sub> and Fe<sub>c</sub> were significantly ( $p < 0.05$ ) correlated with SO<sub>4</sub><sup>2-</sup> (Table 2). The Fe<sub>d</sub> was significantly correlated to both

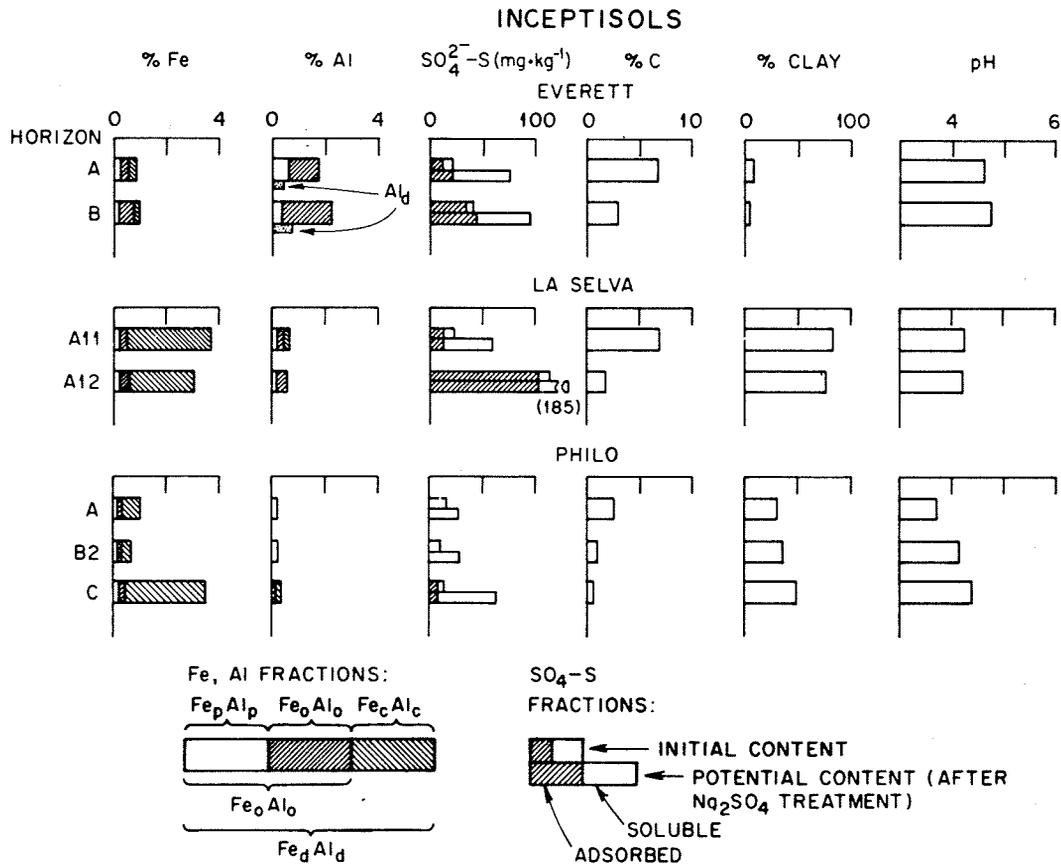


Fig. 6—Iron and Al fractions, SO<sub>4</sub>-S fractions and adsorption, percent C, percent clay, and pH in Inceptisols from LaSelva, Costa Rica (LaSelva), Thompson Site, Wash. (Everett), and Camp Branch, Tenn. (Philo).

total and adsorbed SO<sub>4</sub><sup>2-</sup> content, before and after Na<sub>2</sub>SO<sub>4</sub> treatment, but Fe<sub>c</sub> was most highly correlated with adsorbed SO<sub>4</sub><sup>2-</sup> (Table 2). Restricting correlations to B horizons resulted in greater *r*-values, especially for Fe<sub>c</sub> vs. adsorbed SO<sub>4</sub><sup>2-</sup>.

No Al fraction was significantly correlated with any SO<sub>4</sub> fraction and adding Al<sub>d</sub> to Fe<sub>d</sub> or Al<sub>c</sub> to Fe<sub>c</sub> reduced the *r*-values obtained using Fe alone (Table 2). There was a slight but nonsignificant negative correlation between C and SO<sub>4</sub><sup>2-</sup>. Multiple regressions using Fe<sub>d</sub> or Fe<sub>c</sub> plus percent C or percent clay did not yield significantly better *r*-values than using Fe<sub>d</sub> or Fe<sub>c</sub> alone.

Percent clay was significantly correlated only with adsorbed SO<sub>4</sub><sup>2-</sup>, and, again, *r*-values were greater among B horizons than among all soils. pH was not significantly correlated with any SO<sub>4</sub><sup>2-</sup> fraction (Table 2).

## DISCUSSION

Parfitt and Smart (1978) noted greater SO<sub>4</sub><sup>2-</sup> adsorption on amorphous Fe oxides than on more highly crystallized forms such as hematite, and thus the correlation between adsorbed SO<sub>4</sub><sup>2-</sup> and Fe<sub>c</sub> is somewhat surprising. Fe<sub>c</sub> is a good measure of nonamorphous Fe oxides (McKeague et al., 1971; Blume and Schwertmann, 1969; Kodama and Schnitzer, 1977), but Fe<sub>c</sub> may include crystalline forms with varying SO<sub>4</sub><sup>2-</sup> adsorption properties (e.g., goethite adsorbs more SO<sub>4</sub><sup>2-</sup> than hematite; Parfitt and Smart, 1978).

Nonetheless, other studies have shown that amorphous Fe and Al oxides adsorb considerable amounts of SO<sub>4</sub><sup>2-</sup> (Rajan, 1978, 1979; Parfitt and Smart, 1978; Singh, 1980), and thus one would expect good correlations between Fe<sub>d</sub> or Al<sub>d</sub> and SO<sub>4</sub><sup>2-</sup>. In the case of Al, the ex-

Table 2—Correlation coefficients (*r*) for SO<sub>4</sub><sup>2-</sup> (total and adsorbed, before and after treatment with 75 ppm S as Na<sub>2</sub>SO<sub>4</sub>) vs. selected Fe and Al fractions, percent carbon (C), pH, and percent clay in various forest soils.

	Initial content				Content after Na <sub>2</sub> SO <sub>4</sub>			
	Total		Adsorbed		Total		Adsorbed	
	All soils	B horizons	All soils	B horizons	All soils	B horizons	All soils	B horizons
Fe <sub>d</sub>	0.51*	0.63**	0.49*	0.53*	0.61**	0.63**	0.45*	0.49*
Fe <sub>c</sub>	0.51*	0.74**	0.58**	0.79**	0.56*	0.69**	0.53*	0.73**
(Fe + Al) <sub>d</sub>	0.37	0.29	0.33	0.17	0.54*	0.48*	0.32	0.21
(Fe + Al) <sub>c</sub>	0.46*	0.59**	0.49*	0.57**	0.43*	0.51*	0.43*	0.51*
C	-0.19	-0.29	-0.28	-0.33	-0.07	-0.11	-0.26	-0.29
pH	-0.26	-0.16	-0.17	0.08	-0.13	-0.11	-0.20	0.12
Clay	0.33	0.39	0.45*	0.67**	0.27	0.44*	0.29	0.45*

\* Significant at the 5% level.

\*\* Significant at the 1% level.

tractions for various forms are less specific than for Fe (McKeague et al., 1971). This was particularly evident in the Everett soil where  $Al_o$  exceeded  $Al_d$  by two- to threefold, leading to the artificial conclusion that  $Al_c$  was negative (Fig. 5). The Everett soil was one of the two cases in which total Al exceeded total Fe, (the other being the Becket B22ir) and it would indeed appear that amorphous Al (rather than  $Fe_c$  which was very low), lent this soil its  $SO_4^{2-}$  adsorption properties.

As noted previously (Couto et al., 1979; Johnson et al., 1979, 1980; Singh, 1980), organic matter appeared to have a negative effect on  $SO_4^{2-}$  adsorption even though correlation coefficients did not reflect this. Spodosols, highly podzolized soils, and several surface soils (La Selva, Porters, Saluda) rich in both percent C and  $Fe_d$  or  $Fe_c$  had much lower  $SO_4^{2-}$  contents and adsorption properties than subsoils with comparable amounts of  $Fe_d$  or  $Fe_c$  but lower percent C. This is especially striking in the LaSelva soil where  $SO_4^{2-}$  is much lower in the surface horizon than in the subsurface horizon, yet the opposite is true for both  $Fe_d$  and  $Fe_c$  (Fig. 5). Organic matter does not account for the lack of  $SO_4^{2-}$  in the Fe-rich Philo C horizon, however, (Fig. 5) and reasons for this particular exception to the general pattern are unknown.

Organic matter is known to interfere with Fe and Al crystallization processes also (Schwertmann, 1966; Kodama and Schnitzer, 1977, 1980). The negative influence of organic matter on Fe and Al crystallinity in these soils can be seen by the positive correlations between percent C and  $Fe_o/Fe_d$  or  $Al_o/Al_d$ , especially among B horizons (Table 3). The latter are referred to as "activity ratios" (Blume and Schwertmann, 1969) and reflect the fraction of total free Fe or Al that is amorphous in nature. A negative influence of organic matter on Fe/Al crystallinity is also suggested by the significant correlations between percent C and inorganic, amorphous Fe and Al ( $Fe_a$  and  $Al_a$ ). The significant correlations between percent C and  $Fe_p$  and  $Al_p$  are to be expected, and the significant correlations between  $Fe_o$  and  $Al_o$  are not surprising because the oxalate extraction removes organically bound as well as inorganic amorphous Fe and Al. Reasons for the significant correlation between  $Al_d$  and percent C are not known.

The soils from Coweeta, N.C., and Findley Lake, 180-yr stand, accumulated additional adsorbed  $SO_4^{2-}$  after  $Na_2SO_4$  treatment, and  $SO_4^{2-}$  budgets for these sites indicate accumulations under field conditions, also (i.e., outputs < inputs; Swank and Douglass, 1977; Johnson,

1975). However, many of the soils from  $SO_4^{2-}$  accumulating sites did not accumulate additional adsorbed  $SO_4^{2-}$  upon treatment with  $Na_2SO_4$ . This does not imply that such soils are incapable of doing so. The Walker Branch, Camp Branch, Cross Creek, and LaSelva sites show a net  $SO_4^{2-}$  accumulation (Shriner and Henderson, 1978; Kelly, 1979; Johnson et al., 1979) even though soils from these sites (with the exception of the Cotaco C horizon) do not accumulate additional adsorbed sulfate under laboratory conditions. For instance, the Fullerton soil is known to be capable of accumulating considerable amounts of adsorbed  $SO_4^{2-}$  under field conditions (Johnson et al., 1981) even though it fails to do so under a variety of laboratory conditions (Fig. 5; see also Johnson and Henderson, 1979). Differences between laboratory and field tests may be due to soil-solution contact time, wetting and drying cycles, differing concentrations of ions (especially  $H^+$ ), or a variety of other factors. Thus, these laboratory adsorption studies probably provide only minimal indices of actual  $SO_4^{2-}$  adsorption properties in the field.

It is safe to say, however, that soils with no initial adsorbed  $SO_4^{2-}$  content have not accumulated any under field conditions. Thus, one would hypothesize that ecosystems with Becket and Telos soils have a balanced  $SO_4^{2-}$  budget, assuming the samples tested here are representative. (It should be noted that previous tests on another Becket sample indicated no adsorbed  $SO_4^{2-}$  as well; Johnson et al., 1980). This appears to be the case for the Becket because the Hubbard Brook Watershed shows no  $SO_4^{2-}$  retention (Likens et al., 1977). Budgets for the Telos are not yet available, but current watershed studies on Chesuncook and Telos soils will soon provide some tests of these hypotheses (j. W. Hornbeck, U.S. Forest Service, Durham, N.H., personal communication).

On the other hand, the presence of adsorbed  $SO_4^{2-}$  or the ability of a soil to accumulate additional adsorbed  $SO_4^{2-}$  is not a guarantee that the ecosystem is accumulating  $SO_4^{2-}$ . Sulfate adsorption is concentration-dependent (Chao et al., 1962), and once a soil accumulates sufficient  $SO_4^{2-}$  to come into equilibrium with input concentration, a steady state will be achieved in which input equals output. Such a soil will once again begin to accumulate  $SO_4^{2-}$  if input concentrations increase, however. For example, Johnson and Cole (1977) and Stednick (1982) report that the Everett soil can accumulate  $SO_4^{2-}$  under conditions where inputs exceed the value of  $4.1 \text{ kg ha}^{-1} \text{ year}^{-1}$  reported by Cole and Johnson (1977). Hopefully, the  $Na_2SO_4$  treatments give a relative index of these various soils' capacities to accumulate additional  $SO_4^{2-}$ . Thus, one would hypothesize that the Porters and Saluda soils from Coweeta, N.C., have the greatest capacity, the Findley Lake, Becket, Cotaco, and Everett soils have intermediate capacities, and the remaining soils (Telos, Chesuncook, Fullerton, Claiborne, Lily LaSelva, and Philo) have the least capacities to accumulate additional adsorbed  $SO_4^{2-}$ .

## CONCLUSIONS

Of the various soil properties tested, percent C and Fe + Al by both citrate-dithionite and oxalate extractions offer the most promise in terms of predicted  $SO_4^{2-}$  adsorption. Specifically,  $Fe_c$  (dithionite minus oxalate-ex-

Table 3—Correlation coefficients ( $r$ ) for Fe and Al fractions vs. percent C in various forest soils.

	All soils	B horizons
$Fe_d$	0.20	0.34
$Al_d$	0.52*	0.77**
$Fe_o$	0.66**	0.86**
$Al_o$	0.57*	0.66**
$Fe_p$	0.69**	0.81**
$Al_p$	0.68**	0.78**
$Fe_c$	-0.17	-0.29
$Al_c$	-0.16	-0.002
$Fe_a$	0.52*	0.76**
$Al_a$	0.37*	0.41*
$Fe_o/Fe_d$	0.50*	0.65**
$Al_o/Al_d$	0.35*	0.19

\* Significant at the 5% level.

\*\* Significant at the 1% level.

tractable Fe) was most closely correlated with both total and adsorbed  $\text{SO}_4^{2-}$ . Percent clay, pH, and pyrophosphate-extractable Fe + Al were either insignificantly or inconsistently correlated to total and adsorbed  $\text{SO}_4^{2-}$ . The citrate-dithionite extraction alone was less useful in predicting  $\text{SO}_4^{2-}$  adsorption because of important interactions among Fe, Al, and organic matter. Organic matter seems to have a decidedly negative influence on sulfate adsorption in surface soils and in the Fe- and Al-rich B horizons of Spodosols and highly podzolized soils.

These results corroborate the often-noted phenomenon that surface soils adsorb little  $\text{SO}_4^{2-}$  (Williams and Steinbergs, 1964; Singh, 1980; Hesse, 1957; Johnson and Henderson, 1979) due to their high organic matter and in many cases low Fe + Al as well. Surface soils frequently have a large pool of water-soluble  $\text{SO}_4^{2-}$ , however (as noted previously by Hesse, 1957; Johnson et al., 1980) perhaps because of S mineralization from organic matter (Johnson et al., 1982).

Subsoils of Ultisols generally adsorb more  $\text{SO}_4^{2-}$  than subsoils of Spodosols and highly podzolized soils even when dithionite-extractable Fe + Al values are similar. This appears to be due to the negative influence of organic matter and to the less crystalline nature of Fe + Al in Spodosol B horizons. In contrast to previous studies with various pure Fe oxides, which indicate that amorphous Fe adsorbs more  $\text{SO}_4^{2-}$  than crystalline Fe, the results of this study indicate that the presence of crystalline Fe oxides ( $\text{Fe}_c$ , as measured by dithionite minus oxalate extractions) usually lends soils the greatest  $\text{SO}_4^{2-}$  adsorption capacity. This may be due to the lack of specificity of extractant solutions for crystalline Fe. Further research on the exact nature of  $\text{Fe}_c$  in soils and its relationship to adsorbed  $\text{SO}_4^{2-}$  is needed.

Soil  $\text{SO}_4^{2-}$  adsorption capacity can be broadly related to certain Fe fractions, percent C, and perhaps soil classification. A given soil's capacity to adsorb  $\text{SO}_4^{2-}$  in addition to what it initially contains is dependent on its inherent  $\text{SO}_4^{2-}$  adsorption properties, the degree to which that soil has previously adsorbed  $\text{SO}_4^{2-}$ , and the concentration of  $\text{SO}_4^{2-}$  in incoming solutions relative to concentrations with which the soil has previously equilibrated. Thus, the capacities of the soils tested here to adsorb *additional*  $\text{SO}_4^{2-}$  varied widely within classifications and were undoubtedly related to the history of  $\text{SO}_4^{2-}$  input (as reflected by initial  $\text{SO}_4$  content) as well as percent C and dithionite and oxalate-extractable Fe and Al content.

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