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Factors affecting sulfate adsorption, organic sulfur formation, and mobilization in forest and grassland spodosols

Abstract Forest and grassland soils that contained varying amounts of Fe and Al were collected from England and Wales. Fractionation of free Fe and Al was accomplished to determine which components affected sulfate adsorption. Organic Fe and Al were the dominant fractions in most soil horizons and high amounts of these organically bound metals and, to some extent, crystalline Fe oxide were associated with high sulfate adsorption potentials. These adsorption potentials reflected naturally occurring amounts of adsorbed sulfate and ester sulfate. Overall, the C content exhibited a positive relationship with sulfate adsorption potentials. Soils with a high C content also exhibited high rates of organic S formation. The rate of organic S mobilization was greater in soils with higher amounts of soluble sulfate. Organic S was the largest pool and, typically, sulfonate S was the most abundant constituent of the organic pool.

Key words Sulfate adsorption · Organic S formation · Organic S mobilization

Introduction

The negative effect of the anionic component of acidic precipitation, such as sulfate, on cation leaching in soils is dependent on the mobility of these incoming anions. Cations cannot be leached from the soil profile without an associated anion. Therefore, the interest in sulfate is to determine its fate in soil in terms of its mobility or its retention capabilities. One mechanism of sulfate retention is anion adsorption. The dominant mechanism of sulfate adsorption is believed to be by specific adsorption, sometimes known as ligand exchange, in which sulfate becomes associated with a metal oxide, primarily Fe and Al and to some extent kaolinite, displacing another anion (usually OH^- or H_2O; Hingston et al. 1967; Parfitt and Smart 1978; Rajan 1979).

It has been demonstrated that sulfate adsorption in soils can immobilize sulfate and thus decrease cation leaching (Johnson and Cole 1977; Abrahamsen and Stuanes 1980). Some forest soils have sulfate adsorption capabilities and have accumulated adsorbed sulfate in subsurface soils (Johnson and Cole 1977; Johnson 1980). Although research on sulfate adsorption has been focused on forest soils, there is evidence that grassland soils are also capable of adsorbing sulfate (Coughenour et al. 1980). Due to its importance in S accumulation, factors which affect sulfate adsorption have been investigated. Several researchers have demonstrated that sulfate adsorption increases which decreasing soil pH (Patil et al. 1989). Organic matter, however, was shown to have a negative influence on sulfate adsorption (Couto et al. 1979; Johnson and Todd 1983); it was proposed that organic matter blocked adsorption sites. Other studies indicated that organic matter has a positive effect on sulfate adsorption (Haque and Walmsley 1974; Patil et al. 1989; Stanko and Fitzgerald 1990). Because sulfate adsorbs to Fe and Al oxides, several investigators determined the amount and nature of these oxides, and how they influence sulfate adsorption capacities (Singh 1984; Johnson and Todd 1983; Fuller et al. 1985; MacDonald and Hart 1990). In general, soils that contain higher quantities of Fe and Al oxides will have greater adsorption capacities.

Another mechanism that reduces sulfate mobility is organic S formation. Unlike sulfate adsorption, organic S formation is a biotic process and has been shown to be time-, temperature- and moisture-dependent (Fitzgerald et al. 1983; Stanko-Golden and Fitzgerald 1991). Organic

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S formation appears to be dominant in litter and upper soil horizons, apparently due to abundant soil moisture and sources of C, although this process does occur at lower soil depths (Swank et al. 1984; Watwood et al. 1988). While organic S formation has the potential to accumulate sulfate, organic S mobilization has the capability to release sulfate. The term mobilization was defined by Strickland and coworkers (1984) as the depolymerization of a large organic matrix by preformed enzymes into smaller organic moieties. These smaller organic components are capable of undergoing mineralization to release sulfate (Strickland et al. 1986), which is then subject to the same fates as atmospherically derived sulfate. Although mobilization may serve to prevent S accumulation, in all of the soils investigated, mobilization rates have not exceeded organic S formation rates (Strickland et al. 1984; Watwood et al. 1988; Stanko and Fitzgerald 1990).

The main objective of the present study was to collect several soils from England and Wales that might be expected to contain differing amounts and forms of free Fe and Al oxides. The Fe and Al was differentiated into crystalline, inorganic amorphous, and organically bound fractions to determine which fraction had the greatest effect on sulfate adsorption potentials. Amounts of naturally occurring adsorbed sulfate and adsorbed ester S were also assayed to determine what relationship these S pools might have with Fe and Al and with sulfate adsorption potentials. Other factors known to influence sulfate adsorption were also determined in an effort to establish their relationship to this process. Organic S formation and organic S mobilization potentials were determined, as well as soil variables that influence these processes.

Materials and methods

Site description and sampling

Soil samples from one pit for each horizon were collected in the fall of 1987. Samples were taken from Dartmoor in Southwest England and in the Plynlimon region of Wales. The Dartmoor soils were from an acid grassland used for extensive grazing and a sitka spruce (*Picea sitchensis*) forested area. These samples belonged to the Moretonhamstead series which are described as coarse, well drained, loamy typical brown podzolic soils (Findlay et al. 1984). The samples collected from Wales consisted of a grassland and a forest soil, which have been classified as ferric podzols and are from the Hafren series. The grassland samples were taken from pasture land that had been ploughed, reseeded, and limed in 1976. The forest samples were collected from a mature stand of (48-year-old) sitka spruce. Past management included thinning in 1978. These soils were also limed from 1975 to 1981 (Chappell 1990). The samples were stored field-moist in air-tight bags at about 5 °C for no more than 2 weeks until assayed. Root material was removed before analysis.

Soil properties

Samples were assayed in triplicate for free Fe and Al using the method of McKeague et al. (1971). This procedure uses extraction with

0.1 M pyrophosphate to remove organically bound Fe and Al. It is believed that treatment with 0.2 M ammonium oxalate will remove organically bound plus inorganic amorphous Fe and Al. Extraction with a dithionite–citrate–bicarbonate reagent was done and is known to remove organically bound, inorganic amorphous, plus crystalline Fe and Al. Crystalline Fe and Al was determined from the difference between (organically bound, amorphous, plus crystalline) and (organically, bound plus inorganic amorphous) Fe and Al, while inorganic amorphous Fe and Al was determined as the difference between (organically bound plus inorganic amorphous) and organically bound Fe and Al. All fractions were measured by absorption spectrophotometry. The C content was determined by combustion in a Leco Total Carbon Analyzer. Soil pH was determined in a 1:2 soil:water suspension.

A diagram of the different S pools is shown in Fig. 1. Total S was determined by hypobromite oxidation (Tabatabai and Bremner 1970) followed by hydriodic acid reduction. Hydriodic acid-reducible S, which consists of ester sulfate and inorganic sulfate, was determined by direct reduction with hydriodic acid (Freney 1961). C-bonded S was calculated as the difference between total S and hydriodic acid reducible S. This C bonded S pool was further differentiated by measuring the amount of amino acid S by Raney Ni reduction (Freney et al. 1970). The remaining S, which is resistant to reduction by both hydriodic acid and Raney Ni, is considered to be sulfonate S. Results of previous research demonstrated that several authentic alkyl sulfonates were resistant to hydriodic acid and Raney Ni reduction (Fitzgerald and Franklin 1982).

Soluble S was recovered by washing soil samples with 20-ml aliquots of deionized distilled water. The residues were then washed twice with 20-ml aliquots of 0.02 M Na$_2$HPO$_4$ to remove adsorbed S. All extracts were filtered sequentially through a 0.45-μm and a 0.20-μm membrane filter. These extracts containing soluble and adsorbed S were subjected to hydriodic acid reduction and anion chromatography (Dick and Tabatabai 1979) to determine ester S and sulfate. Insoluble ester S was calculated as the difference between hydriodic acid-reducible S and the combined values of soluble S and adsorbed S. All samples were assayed in triplicate.

S processing

After incubation with 7.5 nmol Na$_2$^{35}SO$_4$ (ca. 1.7 × 10^{10} Bq mmol^{-1}, ICN) for 48 h at 20 °C, samples (1 g wet weight, not sieved) were washed with deionized distilled water followed by centrifugation. The supernatants containing soluble S were pooled. The resulting soil was then washed sequentially with 1 M Na$_2$SO$_4$, NaH$_2$PO$_4$, LiCl, and deionized distilled water followed by centrifugation to remove adsorbed ^{35}S. Organically bound ^{35}S was released by treatment with 6 M HCl at 121 °C for 12 h and 2 M NaOH for 12 h at room temperature (ca. 25 °C). The radioactivity
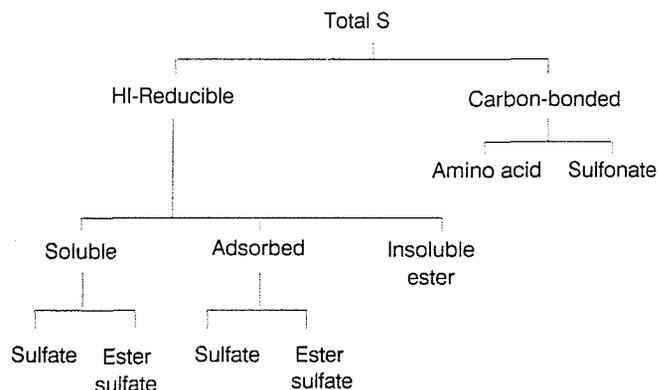

Fig. 1 Differentiation of sulfur pools (*HI*, hydriodic acid)

in the fractions containing soluble, adsorbed, and organic ^{35}S was measured separately by liquid scintillation. Total ^{35}S recoveries were >92% and all samples were assayed in triplicate.

Organic S mobilization rates were determined by incubating soils (1 g wet weight, not sieved) with 7.5 nmol $Na_2{}^{35}SO_4$ at 20°C for 24 h to allow organic S formation to occur (Strickland and Fitzgerald (1984). After incubation, the samples were washed with 1 M Na_2HPO_4 and deionized distilled water to remove ^{35}S that had not been incorporated into organic matter. The microbial populations removed by the phosphate wash were re-established by adding the appropriate soil: water mixture to the samples, which were then re-incubated at 20°C for 24 h. Following this second incubation, the samples were washed sequentially (followed by centrifugation) with 1 M Na_2SO_4, NaH_2PO_4, LiCl, and deionized distilled water to remove any ^{35}S that had been mobilized. The remaining residue containing insoluble organic [35]S (e.g., organic S that had not been mobilized) was released by acid (6 M HCl at 121°C for 12 h) and base extraction (2 M NaOH at room temperature for 12 h). Mobilized S was expressed as a percentage of the ^{35}S incorporated into organic matter in the initial incubation. The radioactivity of each fraction was assayed by liquid scintillation. Total ^{35}S recoveries were >93% and all samples were assayed in triplicate.

Results

Soils collected from the Dartmoor grassland had similar amounts of dithionite-citrate-bicarbonate extractable Fe, pyrophosphate (organically bound) extractable Fe, and crystalline Fe in the A1 and A2 horizons, with correspondingly similar sulfate adsorption potentials (Fig. 2). The B horizon, however, had smaller amounts of dithionite—citrate—bicarbonate extractable Fe and pyrophosphate extractable Fe, with a lower sulfate adsorption potential. Most of the Al was pyrophosphate (organically bound) extractable in all horizons. Adsorbed sulfate, ester

Fig. 2 Fe and Al fractions, sulfate adsorption potentials, adsorbed sulfate, adsorbed ester sulfate, C, and pH of Dartmoor grassland soils. All values are expressed per gram dry weight. □, Dithionite—citrate—bicarbonate extractable (organic, inorganic, amorphous, crystalline oxide); ⊠, ammonium oxalate extractable (organic, inorganic amorphous); ⊠, sodium pyrophosphate extractable (organic); ▨, inorganic amorphous (ammonium oxalate extractable—sodium pyrophosphate extractable); ▧, crystalline oxides (dithionite—citrate—bicarbonate extractable—ammonium oxalate extractable)
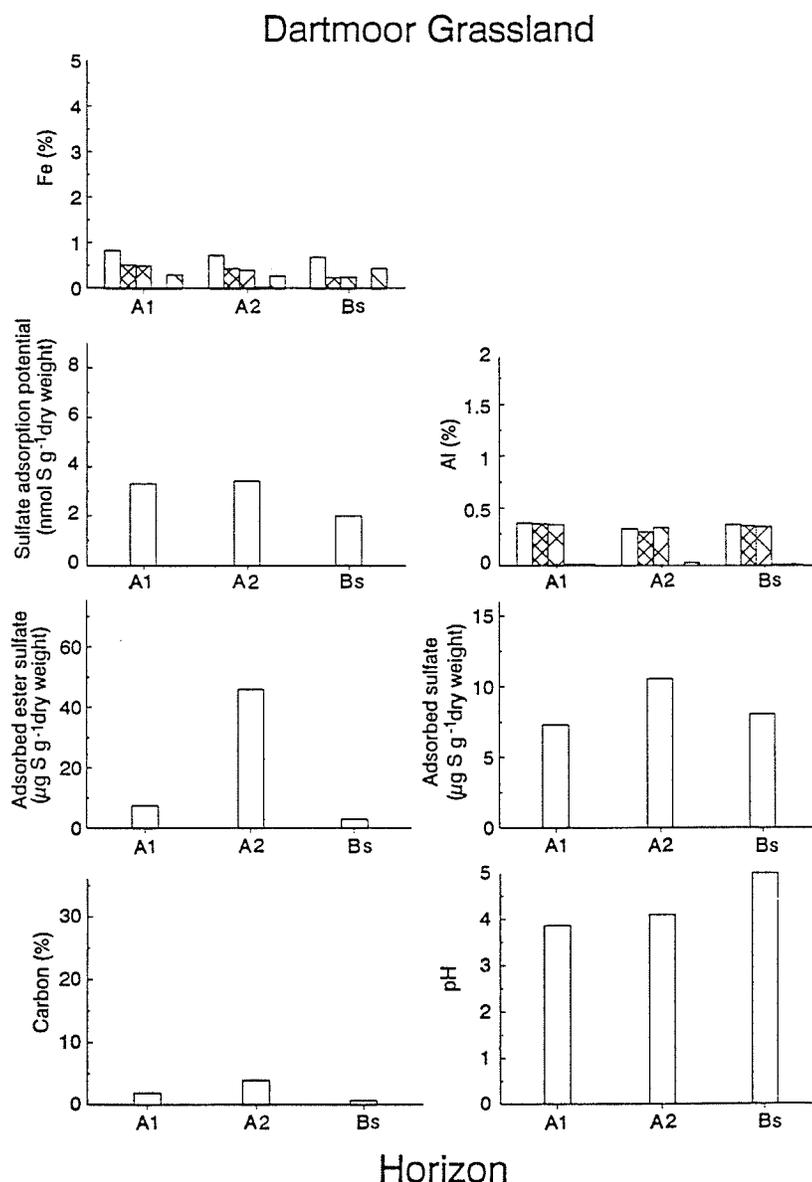
sulfate, and the C content were greatest in the A2 horizon and soil pH increased as depth increased (Fig. 2).

Samples of the A horizon soil collected from the Dartmoor forest exhibited similar levels and distribution patterns of Fe and Al compared to the Dartmoor grassland A horizons, but had a lower sulfate adsorption potential (Fig. 3). The B horizon had substantial amounts of dithionite−citrate−bicarbonate extractable Fe and Al which was mainly organically bound. These high amounts of Fe and Al corresponded to a high sulfate adsorption (8.4 nmol S g^{-1} soil dry weight 48 $^{-1}$) and large amounts of adsorbed sulfate and adsorbed ester sulfate (15.1 and 54.8 µg S, respectively). The C content and soil pH were similar in both horizons (Fig. 3).

The A horizon soil from the Plynlimon grassland (Fig. 4) had a high sulfate adsorption potential (7.9 nmol

S) with a low soil pH and a high C content (35.7%). The adsorbed ester sulfate pool in this horizon was also high (72.9 µg S). The B2 horizon had a high rate of sulfate adsorption (8.6 nmol S g^{-1} dry weight 48 h^{-1}) which corresponded to large amounts of dithionite−citrate−bicarbonate extractable Fe (4.4%). Crystalline Fe was no more important than organically bound Fe in this soil horizon. Organically bound Al was the largest Al fraction and was fairly low (0.5%) compared to Fe levels. Both C content and soil pH were low in this horizon. The C horizon exhibited a low adsorption potential with correspondingly low amounts of Fe and Al, and soil pH and C were low as well (Fig. 4). The only soil horizon collected from the Plynlimon forest (A horizon) exhibited a moderate rate of sulfate adsorption (5.0 nmol S g^{-1} dry weight 48 h^{-1}) which corresponded to a moderate amount of dithionite−citrate−bicarbonate extractable Fe (1.5%), consist-

Fig. 3 Fe and Al fractions, sulfate adsorption potentials, adsorbed sulfate, adsorbed ester sulfate, C, and pH of Dartmoor forest soils. For descriptions of Fe and Al fractions, see Fig. 2
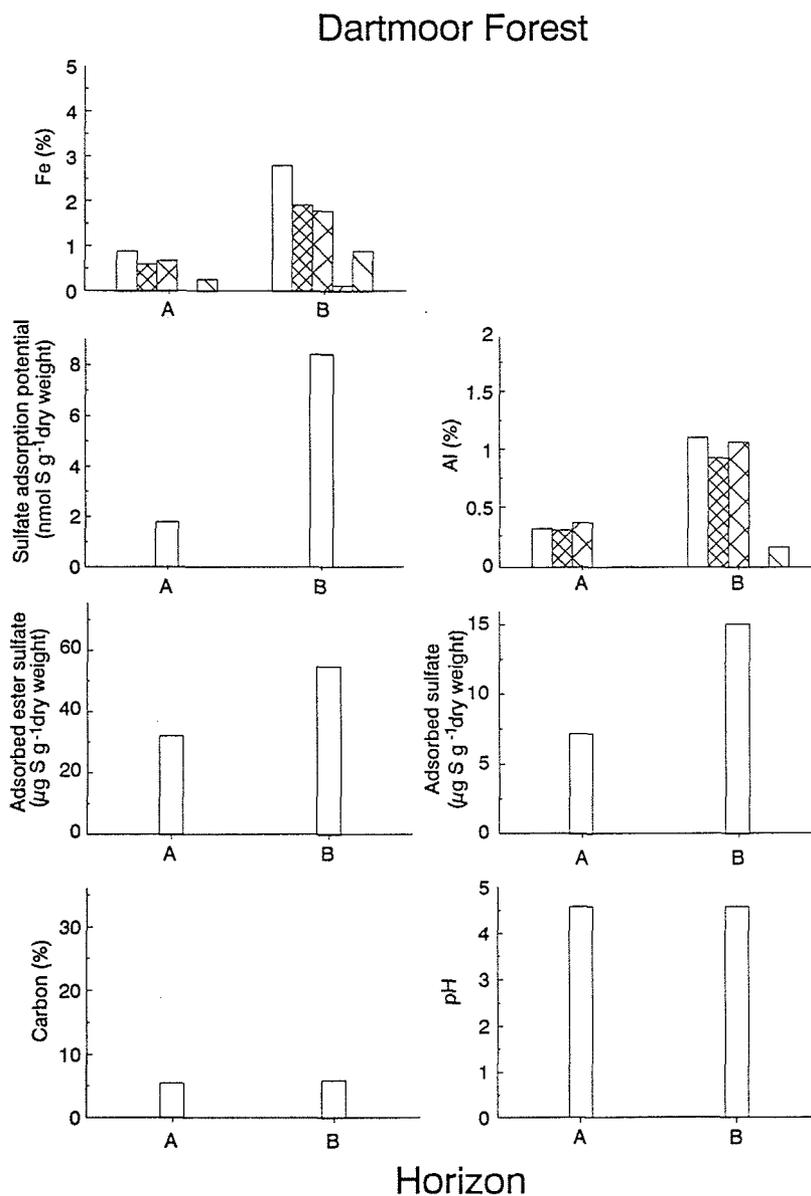
ing mostly of organically bound Fe (Fig. 5). All levels of Al were quite low as was pH, while the C content was high (33.8%). Inorganic amorphous Fe and Al were low in all the sites examined.

Organic S formation potentials were typically greater in the upper soil horizons than in the lower horizons, with the Plynlimon grassland soil exhibiting the greatest rate of formation (Table 1). These upper horizon soils also had higher mobilization capacities. Of the sites examined, the Dartmoor grassland soils had the lowest organic S formation rates $(0.3-0.4 \, \text{nmol S g}^{-1}$ soil dry weight $48 \, \text{h}^{-1}$, respectively), while overall the Plynlimon grassland had the highest formation rates $(1.1-2.1 \, \text{nmol S g}^{-1}$ soil dry weight $48 \, \text{h}^{-1})$. All soils exhibited the potential to accumulate organic S.

At least 96% of the total S was in the form of organic S at all sites for all horizons (Table 2). Total S was the highest in the A horizon of both Plynlimon soils.

Sulfonate S was not always dominant (Table 2); insoluble ester S was sometimes higher. Soluble ester sulfate was not detected in many of the horizons.

Discussion

The effect of Fe and Al on sulfate adsorption was greatest in the B horizons in the soils examined. A similar relationship between Fe and Al and sulfate adsorption has also been observed in several other soils (Johnson and Todd 1983; Singh 1984; Harrison et al. 1989). The organic fraction of Fe was positively related to sulfate adsorption potentials in all soil horizons $(r = 0.74, \; P \le 0.02)$. Crystalline Fe and Al also positively influenced sulfate adsorption potentials $(r = 0.73, \; P \le 0.04; \; r = 0.85, \; P \le 0.007$, respectively). Johnson and Todd (1983) observed a correlation between crystalline Fe and adsorbed

Fig. 4 Fe and Al fractions, sulfate adsorption potentials, adsorbed sulfate, adsorbed ester sulfate, C, and pH of Plynlimon grassland soils. Dithionite–citrate–bicarbonate extractable Fe and Al were not determined for the A horizon. Adsorbed ester sulfate was not detected in the C horizon. For descriptions of Fe and Al fractions, see Fig. 2
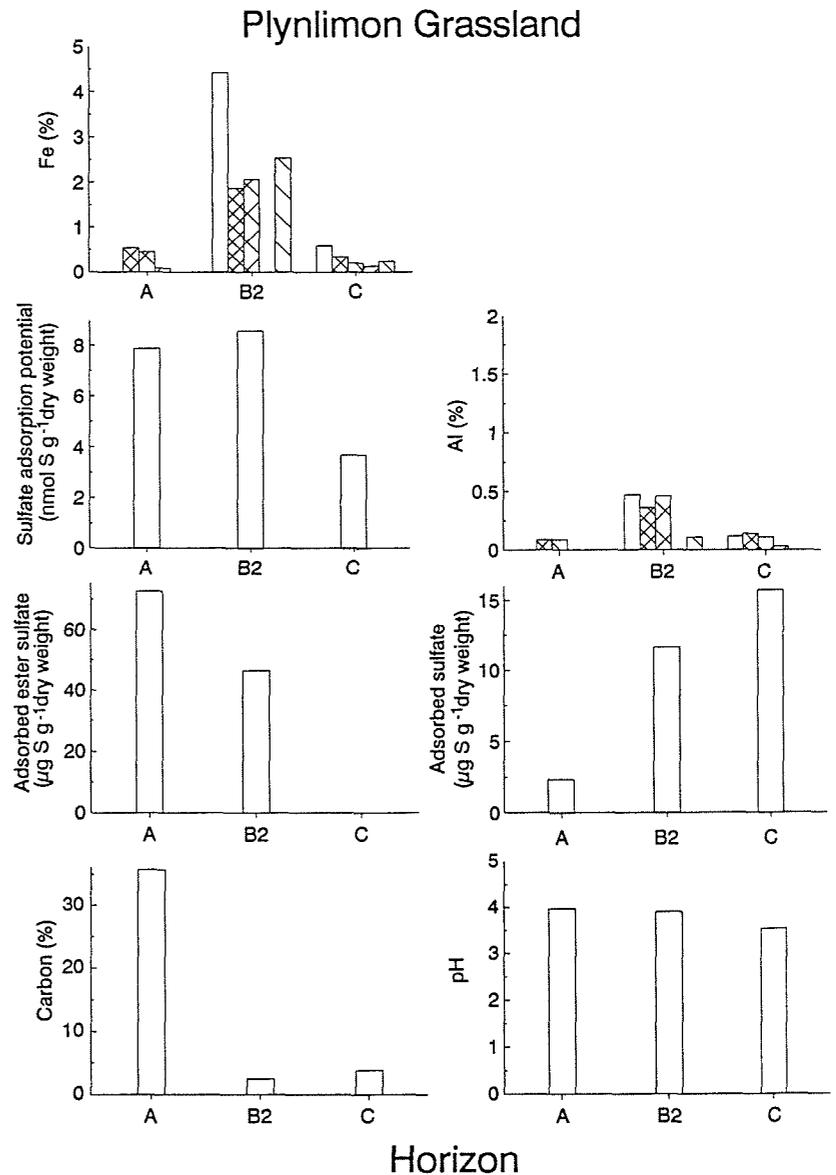
Fig. 5 Fe and Al fractions,
sulfate adsorption potentials,
adsorbed sulfate, adsorbed
ester sulfate, C, and pH of
Plynlimon forest soils.
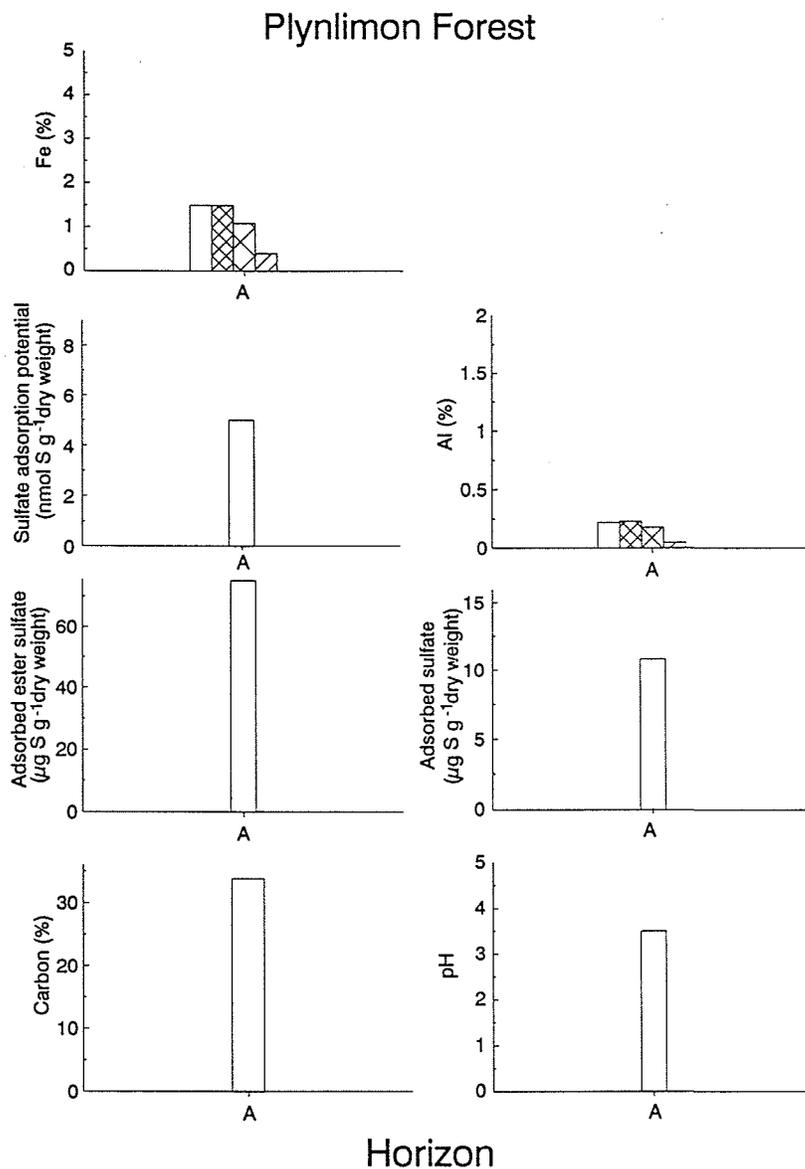For descriptions of Fe and Al
fractions, see Fig. 2

Plynlimon Forest

Horizon

Table 1 Sulfur processing potential of Dartmoor and Plynlimon soils. All values given as means (SEM), $n = 3$

Site	Horizon	Organic S formation (nmol S g^{-1} dry weight 48 h^{-1})	Organic S mobilized (% 24 h^{-1})	Organic S accumulated (nmol S g^{-1} 24 h^{-1})
Dartmoor grassland	A1	0.3 (0.08)	52.7 (3.6)	0.2 (0.05)
	A2	0.4 (0.01)	39.0 (1.0)	0.3 (0.09)
	Bs	0.3 (0.01)	48.9 (3.1)	0.2 (0.02)
Dartmoor forest	A	1.0 (0.5)	55.7 (2.1)	0.4 (0.2)
	B	0.7 (0.1)	53.3 (3.4)	0.3 (0.08)
Plynlimon grassland	A	2.1 (0.2)	64.3 (3.9)	0.8 (0.1)
	B2	1.1 (0.2)	55.8 (3.0)	0.5 (0.05)
	C	1.4 (0.3)	56.5 (1.7)	0.6 (0.1)
Plynlimon forest	A	1.7 (0.2)	66.3 (5.4)	0.6 (0.1)

Table 2 Sulfur constituents and pool sizes of Dartmoor and Plynlimon soils. Values given as means (SEM), $n = 3$ (ND, not detected)

Site	Horizon	S content ($\mu g\,S\,g^{-1}$ dry weight)							
		Total		Organic	Amino acid	Sulfonate	Soluble ester	Soluble sulfate	Insoluble ester
Dartmoor grassland	A1	280.9	·(7.8)	250.2	15.0 (2.7)	87.1	2.4	8.2 (0.1)	138.0
	A2	1086.4	(106.9)	1067.4	44.9 (6.0)	811.7	3.2	10.6 (0.3)	161.6
	Bs	139.2	(27.8)	128.1	9.8 (1.6)	40.1	ND	3.6 (0.1)	74.9
Dartmoor forest	A	540.0	(32.7)	522.4	27.4 (2.5)	230.0	ND	11.1 (0.1)	232.7
	B	2257.5	(818.5)	2233.0	22.4 (0.9)	2085.7	ND	10.4 (0.4)	70.1
Plynlimon grassland	A	13921.3	(3696.0)	13883.2	450.3 (47.7)	10432.3	3.0	35.8 (0.6)	2924.6
	B2	460.9	(67.9)	441.8	9.72 (0.5)	174.3	ND	9.3 (0.1)	211.3
	C	427.6	(40.3)	413.6	43.8 (1.5)	155.6	ND	5.4 (0.2)	214.1
Plynlimon forest	A	2703.0	(178.5)	2677.7	180.4 (3.3)	1481.4	ND	20.5 (0.6)	940.1

sulfate content, while in other studies (Parfitt and Smart 1978; Rajan 1979; Singh 1984) sulfate adsorption was more closely related to inorganic amorphous Fe than crystalline. In the present study, only minor amounts of amorphous Fe were detected. The Al content in all soils was lower than the Fe content, suggesting that Al is not as important as Fe in sulfate adsorption. A similar trend was noted by Singh (1984), but it was suggested that the extraction procedure for Fe also released Al, so that levels of Fe might be overestimated. This situation might also be true for the Fe and Al content in the soils in the current study.

In most cases in the present study, sulfate adsorption potentials were reflected in naturally occurring levels of adsorbed sulfate and adsorbed ester sulfate. For example, samples from the B horizon of the Dartmoor forest soil had high adsorption potentials and high amounts of adsorbed sulfate and ester sulfate. The capacity for a soil to adsorb sulfate is dependent on the amount of sulfate already adsorbed (Johnson et al. 1980). Therefore, a soil might have a low adsorption potential, yet have substantial amounts of adsorbed sulfate, indicating that maximum sulfate adsorption of the soil has been reached, as in the C horizon in the Plynlimon grassland soil where adsorbed sulfate was already important. Because the potential of soils in the present study reflected naturally occurring levels of sulfate and ester sulfate, it is likely that these soils have the capacity to adsorb more sulfate and ester sulfate.

Another soil variable that influences sulfate adsorption is organic matter. It was proposed that organic matter can block adsorption sites (Johnson and Todd 1983) and that Spodosols adsorb sulfate poorly due to the abundance of organic matter associated with these soils (Johnson et al. 1980; Johnson and Todd 1983). Other research has suggested that organic matter may have a positive effect on sulfate adsorption (Haque and Walmsley 1974; Patil et al. 1989). Organic matter, measured as total C in the present study, had an overall positive effect on adsorption potentials. The A horizon soils from the Plynlimon grassland and forest had substantial amounts of C and large absorption potentials. However, most of

the Fe and Al in the soils investigated was organically bound, and in soils that had high adsorption potentials ($r = 0.74$, $P \leq 0.02$), adsorbed ester sulfate was also quite large. These observations further indicate that organic matter had a positive affect on sulfate adsorption. It has been suggested that due to the amphoteric nature of organic matter, positive charges can develop, causing sulfate to adsorb (Singh 1984). This explanation might account for the influence of organic matter on sulfate adsorption in Spodosols in the current study.

The C content and organic S formation rates of the A horizon soil from the Plynlimon grassland and forest were considerably higher than in other soils. The positive relationship between soil C, used as an indicator of energy, and organic S formation has been established by previous research (Strickland and Fitzgerald 1984; Stanko and Fitzgerald 1990), and is further substantiated by the data in the present study ($r = 0.95$, $P \leq 0.0001$).

As mentioned previously, organic S mobilization is mediated by preformed enzymes (sulfatases and depolymerases) and it has been suggested that higher in situ levels of sulfate might repress the synthesis of these enzymes, thus decreasing mobilization (Fitzgerald and Strickland 1987). Stanko and Fitzgerald (1990) observed that low mobilization rates were associated with high amounts of sulfate, which tends to support this idea. However, the opposite relationship between mobilization and sulfate has been observed in other soils (Stanko-Golden and Fitzgerald 1991). In most cases, the data in the present study supports the latter relationship ($r = 0.62$, $P \leq 0.07$). These higher soluble sulfate levels in the current study may be reflect mobilization, and hence, the mineralization of organic S.

The organic S pool was the dominant pool in soils from all horizons, which appears to be common in many other soils (David et al. 1982; Mitchell et al. 1986). The fact that sulfonate S was the most abundant form of organic S has also been established in other soils (Watwood et al. 1988; Autry and Fitzgerald 1990). The sulfonate S linkage is found in the plant sulfolipid, primarily in photosynthetic tissues, and to a smaller extent in other tissues (Harwood 1980; Stuiver et al. 1978), which explains why

sulfonate levels were highest in the surface horizons, with the exception of the Dartmoor forest soils, than in the deeper horizons. This relationship was more apparent in the grassland soils. Grassland vegetation typically has shallower root systems than forest vegetation (Pritchett and Fisher 1987), which tends to concentrate plant material above ground rather than below ground. This might explain the greater amounts of sulfonate S in the grassland soils in the present study compared to the forest soils. Sulfonate S appears to be the pool responsible for the high S content in the Dartmoor forest B horizon soil. A high rate of root turnover might explain this seemingly high sulfonate content.

In conclusion, all soils exhibited the ability to immobilize sulfate by both sulfate adsorption and organic S formation. Sulfate adsorption was primarily responsible for sulfate retention in subsurface soils (B horizon), but was also important in the A horizons. Organic S formation was more influential in the surface horizons, but was also important as a sulfate retention mechanism in the subsurface horizons.

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