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Sulfonate S: A major form of forest soil organic sulfur

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Summary. Several forests of varying elevations, soils and vegetation were studied to evaluate the relative importance of sulfonate S, amino acid S, and ester sulfate as constituents of soil organic S. Suflonate S exceeded 40% of total S in the O1 horizon of all but one site examined, and comprised at least 50% of total S in the O2 horizons of 14 out of 18 study sites examined. Sulfonate pool sizes, on a percentage basis, tended to decrease with increasing sample depth within the mineral horizons, but sulfonate S was still a major form of organic S in the C horizon. Amino-acid S pool sizes were, as a general rule, lower than those for sulfonate in the O1 and O2 horizons, and lower than those for both ester sulfate and sulfonate when mineral soil horizons were considered. In no case did amino-acid S represent >25% of total S. Amino-acid S decreased with increasing depth at all but one site examined. Ester sulfate pool sizes were generally less than those of sulfonate S and greater than those of amino-acid S. This trend was observed with the O1, O2, and A horizons, but it was not apparent with samples from the intermediate and lowest soil horizons, where ester sulfate levels exceeded those for sulfonate S in 4 out of 8 and 5 out of 14 sites, respectively, in these latter horizons. Although there were some exceptions, collectively, the data suggest that sulfonate S is a major form of organic S in forest soils, irrespective of depth.

Key words: Sulfonate – C-bonded sulfur – Ester sulfate – Organic sulfur

The metabolic fate of incoming sulfate from acidic precipitation has been extensively studied (Fitzgerald et al. 1988a). The anion accumulates in forested ecosystems by adsorption (Johnson and Henderson 1979; Johnson et al. 1982) and by incorporation into organic matter (David et al. 1983; Fitzgerald et al. 1988a). Organic S formed by the latter mechanism is present in several forms in forest soils. Ester sulfate consists of S bonded to C through an atom of O. Depending on the chemical nature of the organic moiety, this linkage can be extremely acid-labile (Dodgson and Rose 1970), and this form of organic S is susceptible to reduction by hydriodic acid (Johnson and Nishita 1952). In contrast, C-bonded S consists primarily of amino-acid S (cysteine and methionine) and sulfonate S, and as the nomenclature implies, the C in these compounds is directly bonded to S. The insensitivity of the C-S bond to reduction with hydriodic acid is well established (Johnson and Nishita 1952; Freney et al. 1970), and thus any S not reduced by this acid must be C-bonded S. Amino acid S is subject to reduction by Raney nickel (Freney et al. 1970). Preliminary work demonstrated that a wide range of alkyl sulfonates (Fitzgerald and Franklin 1982) were resistant to reduction by either hydriodic acid or Raney nickel. Thus, any C-bonded S not reduced by the latter catalyst should be sulfonate S.

Organic S is a major form of intrinsic S in litter (O1 and O2) and A horizons (Strickland et al. 1986) as well as in deeper mineral soil horizons (David et al. 1983; Autry et al. 1990). In general, C-bonded S has been the primary form of both organic and total S found at all depths analyzed (Strickland et al. 1986; Bartel-Ortiz and David 1988; Autry et al. 1990). While a good deal is known about the sizes of C-bonded and ester sulfate pools at all depths within a profile, from the uppermost litter horizon (O1) to the lowest mineral soil horizon (B, C), very little is known about the pool sizes of the two constituents comprising C-bonded S at these depths. Most present knowledge about amino-acid and sulfonate S is confined strictly to the O1, O2, and A horizons for forests of the Coweeta basin in North Carolina (Watwood and Fitzgerald 1988, Fitzgerald et al. 1988a). For example, Strickland and coworkers (1986) found that sulfonate S accounted for 24%, 74%, and 79% and that amino-acid S accounted for 49, 6, and 3 of total S in these horizons, respectively. Until the present study, however, there have been no published reports dealing with the fractionation of C-bonded S to amino-acid and sulfonate S in samples collected from the intermediate and lowest mineral soil horizons.

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Owing to the abundance of sulfonate S relative to amino-acid S in the O1, O2, and A horizons examined and since C-bonded S comprises a substantial portion of organic S in all horizons analyzed, further examination of the pool sizes of sulfonate S and amino-acid S in all horizons is warranted to better ascertain which are the primary forms for S retention in forest soils. The main objectives of the present study were, therefore, to characterize the various organic S forms, particularly the C-bonded constituents, at all depths within the soil profile and to correlate these observations with soil physical properties and, concomitantly, with forest productivity and soil fertility.

Materials and methods

Site description and sampling

A partial description of each of the sites is provided in Table 1. Samples were collected by hand from the O1 and O2 litter layers (where applicable), the uppermost (0–20 cm; primarily A), intermediate (20–40 cm; primarily A/B), and lowest (40+ cm; primarily B, C) mineral soil horizons from excavated pits at each site. The samples were sieved (< 1 cm), and all roots and stones were removed by hand. The samples were maintained, field-moist, in sealed polyethylene bags at 4 °C until analysis.

Characterization of intrinsic organosulfur pool sizes

Intrinsic sulfur fractions were quantified according to the procedures summarized in Fig. 1. Total S was determined by alkaline oxidation

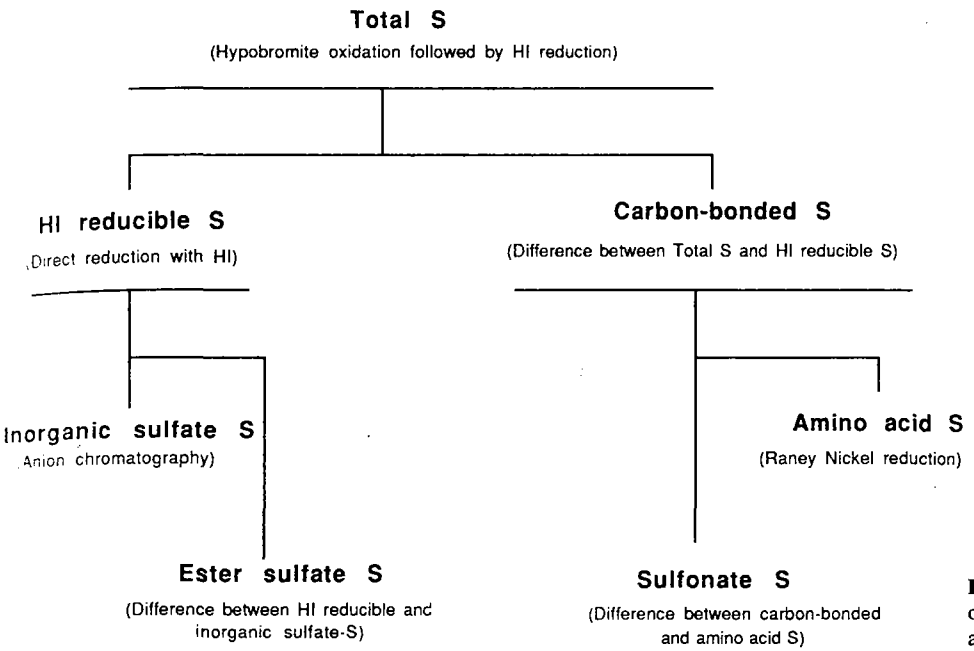

Fig. 1. Procedures for determining organosulfur pool sizes. *HI*, hydriodic acid

Table 1. Forested study sites investigated

Site	Location	Vegetation	Soils	Elevation (m)
Florida	Gainesville, Fla.	Slash Pine	spodosols	0
Douglas Fir	Thompson Forest, Wash.	Douglas fir	Inceptisols	100
Red Alder	Thompson Forest, Wash.	Red alder (mature)	Inceptisols	100
B.F. Grant Forest	Eatonton, Ga.	Loblolly pine	Ultisols	175
Norway Spruce	Nordmonen, Norway	Norway spruce	Entisols	202
Duke Forest	Mebane, N.C.	Loblolly pine	Ultisols	215
Tarklin	Walker Branch, Tenn.	Mixed deciduous	Ultisols	300
Fullerton	Walker Branch, Tenn.	Mixed deciduous	Ultisols	300
Loblolly Pine	Oakridge, Tenn.	Loblolly pine	Ultisols	300
Turkey Lakes	Ontario, Canada	Sugar maple-birch	Spodosols	350
Huntington Forest	Newcomb, N.Y.	Mixed deciduous	Spodosols	530
Camp Branch	Falls Creek, Tenn.	Mixed oak	Ultisols	550
Mixed Deciduous	Coweeta, N.C.	Oak-hickory	Ultisols	700–1000
White Pine	Coweeta, N.C.	White pine	Ultisols	800–1000
Whiteface Mountain	Lace Placid, N.Y.	Spruce-fir	Histosols, Spodosols	1000–1500
Findley Lake	Findley Lake, Wash.	Fir-hemlock	Inceptisols	1800
Becking	Great Smoky Mountains, N.C.	Red spruce, beech	Inceptisols	1800
Indian Gap	Great Smoky Mountains, N.C.	Red spruce, beech	Inceptisols	1800
Nolan Divide	Great Smoky Mountains, N.C.	Red spruce, beech	Inceptisols	1800

(Tabatabai and Bremner 1970) followed by hydriodic acid reduction. Hydriodic acid-reducible S, consisting of both ester-linked and inorganic sulfate, was measured by direct hydriodic acid reduction (Freney 1961). Inorganic sulfate was extracted with 0.02 $M Na_2HPO_4$ and measured by anion chromatography (Dick and Tabatabai 1979). Total ester sulfate was calculated as the difference between hydriodic acid-reducible S and inorganic sulfate S.

C-bonded S was calculated as the difference between total S and hydriodic acid-reducible S. Amino-acid S was quantified by Raney nickel reduction (Freney et al. 1970). Sulfonate S was calculated as the difference between C-bonded S and amino-acid S.

Soil pH was determined on a 1:5 soil:water solution. Total C was determined using a Leco Total Carbon Analyzer. All direct analyses were performed in triplicate and in no case did the standard error exceed 15%.

Results

In general, the sulfonate linkage was the primary constituent of organic S, accounting for a larger percentage of the organic S than did either ester sulfate or amino-acid S. In the O1 horizon, sulfonate S accounted for more organic S than did ester sulfate or amino acid S in 15 out of 17 sites examined (Table 2), the only exceptions being the Coweeta White Pine and the Findley Lake sites, where the ester sulfate levels exceeded those of both sulfonate S and amino-acid S. Sulfonate S was also the dominant form of organic S in the O2 horizon for 16 out of 18 sites examined (Table 3). The only exceptions in this case were the Coweeta Mixed Deciduous and the Whiteface sites, where the ester sulfate levels exceeded those of both sulfonate S and amino-acid S. In the uppermost mineral soil horizon, sulfonate S was the dominant form of organic S in 10 out of 17 horizons examined (Table 4), although a greater percentage of sites (41%) had larger ester sulfate pools than those of both sulfonate and amino-acid S in this horizon compared with the O1 or O2 horizons. For example, in the A horizon of the Turkey Lakes site sulfonate S represented 74% of total S, while ester sulfate and amino-acid S represented only 16 and 7% of total S, respectively. In contrast, in the uppermost soil horizon at the Duke, Nolan Divide, Coweeta White Pine, B.F. Grant Forest, and Indian Gap sites, ester sulfate exceeded 50% of total S, while sulfonate S accounted for <37%. In the intermediate (20–40 cm; primarily A/B) soil horizons, the dominance of the sulfonate linkage as the primary form of S was not apparent, and only 4 out of 9 horizons showed higher levels of sulfonate S than ester sulfate S (Table 5). Similar findings were made for the lowest mineral soil horizon, where sulfonate S pool sizes exceeded those ester sulfate S in only 8 out of 14 horizons examined (Table 6).

Amino-acid S pools were generally smaller than both ester sulfate and sulfonate pools in all horizons examined. In the O1 layer, amino-acid S comprised between 7% and 25% of total S in 13 out of 17 horizons examined (Table 2). For example, at the Douglas Fir site amino-acid S represented 21% of total S. The exceptions to this trend included the Coweeta Mixed Deciduous, Huntington Forest, Findley Lake and Turkey Lakes sites, all of which showed amino-acid pools representing <6% of total S. In the O2 horizon, the amino-acid S levels ranged from 1% to 24% of total S (Table 3), although at most of the sites (14 out of 18) the amino-acid S pools represented ≤15% of total S. The exceptions to this trend were the Duke Forest, Camp Branch, Nolan Divide, and Whiteface sites, in which the amino-acid S levels constituted 17, 20, 23, and 24, respectively, of total S. In the uppermost mineral horizons, similar findings were made, with amino-acid S comprising ≤15% of total S in 13 out of 17 horizons examined (Table 4). For exmaple, at the Norway Spruce and Findley Lake sites, the intrinsic amino-acid S pool sizes comprised 0.5% and 3%, respectively, of total S. In the intermediate soil horizons, amino-acid S represented ≤12% of total S in all horizons exam-

Table 2. Organosulfur status of O_1 litter layers of various forested sites[a]

Site	S content (μg g^{-1} dry weight)[b]				
	Total	Total organic	Amino acid	Sulfonate	Ester sulfate
Douglas Fir	1446	1439	302 (21)	1078 (75)	59 (4)
Red Alder	1543	1491	391 (25)	953 (62)	147 (10)
B.F. Grant Forest	712	662	149 (21)	450 (63)	63 (9)
Norway	670	618	50 (8)	288 (43)	280 (42)
Duke Forest	478	395	60 (13)	324 (68)	11 (2)
Tarklin	1600	1557	235 (15)	948 (59)	374 (23)
Fullerton	2213	2179	158 (7)	1635 (74)	386 (17)
Loblolly	1083	1083	141 (13)	785 (73)	157 (15)
Turkey Lakes	2662	2605	139 (5)	1943 (73)	523 (20)
Huntington Forest	20537	20529	242 (1)	19249 (94)	1038 (5)
Camp Branch	832	804	163 (20)	375 (45)	266 (32)
Coweeta Mixed Deciduous	481	477	7 (1)	356 (74)	114 (24)
Coweeta White Pine	263	252	24 (9)	111 (42)	117 (45)
Whiteface	2279	2166	433 (19)	1263 (55)	470 (21)
Findley Lake	6505	6450	173 (3)	2334 (36)	3943 (61)
Becking	2130	1986	227 (11)	1302 (61)	457 (22)
Nolan Divide	1678	1542	344 (21)	757 (45)	441 (26)

[a] Samples collected in 1985 for all sites except Norway, which was sampled in 1987

[b] Results expressed as means with $n = 3$, and standard error < 15% in all cases; parentheses show percentage of total S

ined (Table 5). In the lowest soil horizon, similar trends were observed, and the amino-acid S levels comprised < 10% of total S in all 14 horizons examined (Table 6). For example, the Duke Forest and Camp Branch sites had no detectable amino-acid S. Although there was some variability among horizons, the amino-acid S pools were generally the smallest of the organic S pools, in most cases smaller than those of sulfonate S and ester sulfate S.

The ester sulfate levels were generally lower than the sulfonate S levels, but higher than those of amino-acid S. In the O1 horizon, this trend was observed in 11 out of 17 horizons examined (Table 2), with ester sulfate S comprising < 40% of total S in 14 out of the 17 horizons examined (Table 2). The main exceptions to this observation included the Coweeta White Pine, Findley Lake, and Norway Spruce sites, where total ester sulfate constituted 45%, 61%, and 42%, respectively, of total S. In samples collected from the O2 horizon, this trend was again observed; at 15 out of the 18 sites examined the ester sulfate S levels were < 40% of total S (Table 3). The exceptions to this trend were the Coweeta Mixed Deciduous, Findley Lake, and Whiteface sites. The ester sulfate levels were lower than those of sulfonate S but higher than those of amino-acid S in 13 out of the 18 sites examined (Table 3). Exceptions to this trend included the Douglas Fir, Red

Table 3. Organosulfur status of O_2 litter layers of various forest study sites[a]

Site	S content ($\mu g\ g^{-1}$ dry weight)[b]				
	Total	Total organic	Amino acid	Sulfonate	Ester sulfate
Florida	627	596	44 (7)	389 (62)	163 (26)
Douglas Fir	1121	1092	169 (15)	884 (79)	39 (4)
Red Alder	2594	2564	309 (12)	2148 (83)	107 (4)
B F Grant Forest	721	575	63 (9)	459 (64)	53 (7)
Norway	845	821	56 (7)	473 (56)	292 (35)
Duke Forest	585	561	97 (17)	319 (54)	145 (25)
Tarklin	1394	1366	209 (15)	825 (59)	332 (24)
Fullerton	1481	1444	146 (10)	1015 (69)	283 (19)
Loblolly	1561	1543	127 (8)	1124 (72)	292 (19)
Turkey Lakes	2315	2265	153 (7)	1435 (62)	677 (29)
Huntington Forest	33190	33081	382 (1)	30932 (93)	1767 (5)
Camp Branch	953	916	199 (20)	412 (43)	305 (32)
Coweeta Mixed Deciduous	284	272	39 (14)	39 (14)	194 (68)
Coweeta White Pine	485	460	11 (2)	264 (55)	185 (38)
Whiteface	1467	1452	352 (24)	479 (33)	621 (43)
Findley Lake	5245	5240	365 (7)	2742 (52)	2133 (41)
Becking	1438	1341	209 (15)	794 (55)	338 (24)
Nolan Divide	1361	1289	311 (23)	527 (39)	451 (33)

[a] Samples collected in 1985 for all sites except Norway (1987) and Florida (1988)
[b] See footnote to Table 2

Table 4. Organosulfur status of uppermost mineral horizons of various forest study sites

Site and horizon	Date sampled	S content ($\mu g\ g^{-1}$ dry weight)[b]							
		Total	Total organic	Amino acid	Sulfonate	Ester sulfate	pH	C ($mg\ g^{-1}$ dry weight)	C:S ratio
Douglas Fir A	1985	355	340	72 (20)	211 (59)	57 (16)	5.1	30.5	86:1
Red Alder A	1985	987	979	113 (11)	633 (64)	233 (24)	4.5	48.7	49:1
B F. Grant Forest A	1988	108	85	11 (10)	2 (2)	72 (67)	4.2	8.7	81:1
Norway Spruce E	1987	216	194	1 (0.5)	158 (73)	35 (16)	3.9	36.5	169:1
Duke Forest A	1985	67	59	8 (12)	17 (26)	34 (51)	3.8	8.5	127:1
Tarklin A1	1986	247	217	43 (18)	69 (28)	105 (43)	4.0	18.3	74:1
Fullerton Ap	1986	480	449	10 (2)	371 (77)	68 (14)	4.9	13.5	28:1
Loblolly A	1986	178	167	16 (9)	90 (51)	61 (34)	5.1	11.6	65:1
Turkey Lakes A	1985	1260	1228	94 (8)	931 (74)	203 (16)	4.7	16.7	13:1
Camp Branch A	1985	171	152	47 (27)	53 (31)	52 (30)	4.7	31.5	184:1
Coweeta Mixed Deciduous A	1985	226	210	56 (25)	89 (39)	65 (29)	4.8	28.3	125:1
Coweeta White Pine A	1985	150	138	20 (13)	29 (19)	89 (59)	4.7	28.1	187:1
Whiteface A	1987	603	557	37 (6)	327 (54)	193 (32)	4.0	112.5	187:1
Findley Lake A2	1985	1725	1715	40 (2)	1148 (67)	527 (31)	4.0	26.4	15:1
Becking A	1986	607	577	67 (11)	241 (40)	269 (44)	3.6	40.8	67:1
Indian Gap A	1986	529	505	62 (12)	59 (11)	384 (73)	4.0	57.8	109:1
Nolan Divide A	1986	485	474	58 (12)	45 (9)	371 (77)	3.8	60.6	125:1

[b] See footnote to Table 2

Alder, B. F. Grant Forest, Coweeta Mixed Deciduous, and Whiteface sites. In the uppermost mineral soil horizon, this trend was not apparent, with only 9 out of 17 sites exhibiting ester sulfate levels that were lower than those of sulfonate S and higher than the amino acid S levels, while 7 out of the 17 sites had larger ester sulfate pools than sulfonate S and amino-acid S pools (Table 4). For example, at the Red Alder site, the ester sulfate levels lay between those of sulfonate and amino-acid S, but at the Nolan Divide, Coweeta White Pine, and Tarklin sites, the ester sulfate levels consistently exceeded those of both amino-acid and sulfonate S. Nevertheless, ester sulfate still represented ≤40% of total S in 10 out of the 17 uppermost horizons examined (Table 4). In the intermediate (A/B) and lowermost (B, C) horizons, neither trend was readily apparent. For example, in only 4 out of 9 intermediate and only 8 out of 14 lowermost horizons examined were the ester sulfate pools smaller than those of sulfonate S and larger than those of amino-acid S. Further, in only 5 out of 9 intermediate and 8 out of 14 lowermost horizons, were the ester sulfate levels ≤40% of total S (Tables 5 and 6).

Soil pH appeared to follow a relatively narrow range within horizons. For example, in the uppermost soil horizons, pH values ranged from 3.6 for the Becking A horizon to 5.1 for the Douglas Fir and Loblolly A horizons (Table 4). Similar ranges of 3.9–5.0 and 3.8–5.5 were observed in the intermediate (Table 5) and lowest (Table 6) soil horizons, respectively. Collectively, the data suggest that increasing depth exerts no effect on soil pH. Soil C contents, in contrast, tended to decline with increasing depth. In the uppermost soil horizons, 12% of the horizons examined had <10 mg total C g^{-1} dry weight. This proportion increased to 78% for the intermediate (Table 5) and 64% for the lowest (Table 6) soil horizons. C:S ratios also decreased with increasing depth. For example, 24% of the uppermost soil horizons examined had C:S ratios of $<50:1$ (Table 4), while 67% and 93% of the intermediate and lowest soil horizons, respectively, had C:S ratios of $<50:1$ (Tables 5 and 6, respectively).

Table 5. Organosulfur status of intermediate soil horizons of various forest study sites

Site and horizon	Date sampled	S content (μg g^{-1} dry weight)[b]					pH	C (mg g^{-1} dry weight)	C:S ratio
		Total	Total organic	Amino acid	Sulfonate	Ester sulfate			
B.F. Grant Forest A/B	1988	213	97	4 (2)	92 (43)	1 (1)	4.1	4.8	23:1
Norway Spruce Bs	1987	143	83	8 (6)	66 (46)	9 (6)	4.2	10.5	73:1
Norway Spruce BC	1987	112	95	3 (3)	60 (53)	32 (29)	4.7	7.4	66:1
Tarklin A/B	1986	239	193	28 (12)	10 (4)	155 (65)	5.0	5.4	23:1
Fullerton A/B	1986	257	229	5 (2)	97 (38)	127 (49)	4.7	6.4	25:1
Coweeta Mixed Deciduous B	1985	184	153	ND[a]	ND[a]	40 (22)	5.0	11.5	63:1
Becking A/B	1986	827	782	43 (5)	482 (58)	257 (31)	4.1	8.5	10:1
Indian Gap A/B	1986	718	672	17 (2)	204 (28)	451 (63)	4.6	2.6	4:1
Nolan Divide A/B	1986	385	367	44 (11)	151 (39)	172 (45)	3.9	3.1	8:1

[a] ND, not determined; carbon-bonded S not fractionated for this horizon
[b] See footnote to Table 2

Table 6. Organosulfur status of lowest soil horizons of various forest study sites

Site and horizon	Date sampled	S content (μg g^{-1} dry weight)[b]					pH	C (mg g^{-1} dry weight)	C:S ratio
		Total	Total organic	Amino acid	Sulfonate	Ester sulfate			
Florida C	1988	433	396	7 (2)	331 (77)	58 (13)	4.7	5.4	12:1
Red Alder B3	1987	267	241	22 (8)	112 (42)	107 (40)	5.5	28.9	108:1
B.F. Grant Forest Bt	1988	179	38	NT[c]	6 (3)	32 (18)	4.9	6.2	35:1
Norway C	1987	91	74	6 (7)	45 (49)	23 (25)	4.6	2.7	30:1
Duke Forest B2	1987	1300	889	NT[c]	540 (42)	349 (27)	4.6	2.7	2:1
Tarklin B	1986	240	209	9 (4)	92 (38)	108 (45)	5.0	2.4	10:1
Fullerton B	1986	360	324	3 (1)	311 (86)	10 (3)	4.8	4.5	13:1
Loblolly B	1986	130	114	8 (6)	27 (21)	79 (61)	5.2	4.0	31:1
Camp Branch C	1987	340	307	NT[c]	194 (57)	113 (33)	4.8	1.3	4:1
Coweeta Mixed Deciduous C	1985	268	216	ND[a]	ND[a]	171 (64)	5.0	2.0	7:1
Whiteface Bs	1987	1140	1094	7 (1)	871 (76)	216 (19)	3.8	51.1	45:1
Becking B	1986	495	389	16 (3)	162 (33)	211 (43)	4.1	20.0	40:1
Indian Gap B	1986	661	435	12 (2)	133 (20)	290 (44)	4.8	15.7	24:1
Nolan Divide B	1986	572	315	14 (3)	237 (41)	64 (11)	4.7	20.9	37:1

[a] See footnote to Table 5
[b] See footnote to Table 2
[c] NT, no trace detected

Discussion

In summary, although there were some exceptions, the sulfonate linkage was the major constituent of organic S at all depths examined. This is in agreement with results of studies on other forested ecosystems (Strickland et al. 1986; Watwood et al. 1986; Watwood and Fitzgerald 1988) in which sulfonate S was a major S pool. This is somewhat surprising, because although the chemical stability of the linkage is well established (Busby 1966), this form of organic S is very biologically labile. Arylsulfonates, including *p*-toluene sulfonate and benzene sulfonate, are subject to rapid and complete degradation by bacteria in pure cultures (Benarde et al. 1965; Focht and Williams 1970). Moreover, Martelli (1967) demonstrated that endogenous populations of aquatic bacteria near the Amazon Basin were capable of oxidizing a wide variety of arylsulfonates. Further, Strickland and Fitzgerald (1983) found that 6-sulfoquinovose, the S-containing moiety of the plant sulfolipid (a natural sulfonate) was subject to rapid mineralization when incubated with forest soil and litter. They also found that sulfonate levels generally tended to decrease on an absolute basis with increasing depth, possibly because many naturally occurring sulfonates are constituents of the plant sulfolipid (Harwood and Nicholls 1979; Harwood 1980), and this material concentrates in the O1, O2, and A horizons. The decrease in sulfonate pool sizes may have been due to a decrease in total S levels with declining depth. This notion is supported by the relatively constant proportion of sulfonate to total S observed in the present study at all depths within the mineral soil profile.

In general, amino-acid S was a minor constituent of organic S at all depths analyzed. This correlates well with results of previous studies, which showed that amino-acid S was only a small component of total S in the O1, O2, and A horizons (Strickland et al. 1986; Watwood et al. 1986; Watwood and Fitzgerald 1988). These results may reflect the fact that both methionine and cysteine are mineralized at all dephts within the soil profile (Fitzgerald and Andrew 1984; Fitzgerald and Watwood 1988; Fitzgerald et al. 1988b). A rapidly mineralizable substrate is generally associated with small intrinsic pool sizes if immobilization rates are consistently low. Amino-acid S levels decreased with increasing depth, except for soil samples taken from the Norway Spruce site where slight increases in the amino-acid S pool sized occurred. This was probably due to the localization of amino acids in leaf protein, which, like the sulfolipid, is concentrated in the upper horizons. In some instances, ester sulfate was a major form of organosulfur. However, this observation was not consistent among sites or with increasing depth.

The acidic pH of all mineral soil horizons examined suggests that although some ester sulfate hydrolysis may occur chemically in the soil, the sulfonate pool, by virtue of its insensitivity to a low pH (Busby 1966), is not likely to be abiotically degraded in these systems. Soil pH was not significantly correlated with sulfonate S levels in the uppermost ($r = 0.04$; $P < 0.87$) or intermediate ($r = -0.45$; $P < 0.26$) soil horizons. A slightly inverse relationship between these parameters was observed in the lowest soil horizons ($r = 0.67$; $P < 0.01$), which is consistent with the chemical reactivity of this form of sulfur (Busby 1966). Over the mineral soil profile as a whole, however, there was no significant correlation between soil pH and sulfonate S pool sizes ($r = -0.19$; $P < 0.25$), probably due to the narrow range of soil pH found in the soils studied. The large pools of sulfonate S observed at all depths within the soil profile further support the theory that any sulfate liberated from sulfonate is due to biological mineralization and not chemical catalysis. Further, the rapid biological mineralization rates observed for 6-sulfoquinovose, an environmentally relevant sulfonate (Strickland and Fitzgerald 1983), suggest that this pool is dynamic rather than static in nature, and that in situ immobilization/deposition rates exceed the in situ mineralization rates thus maintaining a large sulfonate S pool. The C:S ratio, which indicates potential mineralization of S, tended to decline with increasing depth, indicating that biological S mineralization may occur at a higher rate in deeper horizons; this may also account for the decrease in sulfonate pool sizes with increasing depth. Sulfonate S, therefore, simultaneously enriches soil fertility and enhances forest productivity in that it is a major, chemically stable source of soil S, and is able to undergo biological mineralization to sulfate, a biologically available form of S, which can then be used to satisfy tree S requirements.

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