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Sulfur dynamics in mineral horizons of two northern hardwood soils. A column study with ^{35}S

BHESH R. DHAMALA, MYRON J. MITCHELL & ALAN C. STAM
College of Environmental Science and Forestry, State University of New York, Syracuse, NY 13210, USA

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Abstract. Sulfur dynamics of two Spodosols were ascertained using soil columns constructed from homogenized mineral soil from nothern hardwood ecosystems at the Huntington Forest (HF) in the Adirondack Mountains of New York and Bear Brook Watershed in Maine (BBWM). Columns were leached for 20 weeks with a simulated throughfall solution with $^{35}SO_4^{2-}$. Sulfur constituents were similar to those of other Spodosols, with the organic S fractions (C-bonded S and ester sulfate) constituting over 90% of total S. HF soil columns had higher total S (14.9 μmol S g^{-1}) than that for the BBWM soil columns (7.4 μmol g^{-1}) primarily due to higher C-bonded S in the former.

Initially, adsorbed SO_4^{2-} accounted for 5 and 4% of total S for the BBWM and HF soil columns, respectively. After 20 weeks, adsorbed SO_4^{2-} decreased (81%) in BBWM and increased (33%) in HF soil columns. For both HF and BBWM soil columns, C-bonded S increased and ester sulfate decreased, but only for HF columns was there a net mineralization of organic S (5.6% of total S). The greatest decrease in ester sulfate occurred at the top of the columns.

Leaching of ^{35}S was less than 0.5% of the ^{35}S added due to its retention in various S constituents. There was an exponential decrease in ^{35}S with column depth and most of the radioisotope was found in C-bonded S (70–88 and 70–91% for BBWM and HF, respectively). The rapid turnover of adsorbed SO_4^{2-} was reflected in its high specific activity (834 and 26 kBq μmol^{-1} S for BBWM and HF, respectively). The lower specific activity of adsorbed SO_4^{2-} in HF was attributable to greater isotopic dilution by non-radioactive SO_4^{2-} derived from greater organic S mineralization in the HF versus the BBWM columns.

Both soil columns initially had high levels of NO_3^- which resulted in the generation of H^+ and net retention of SO_4^{2-} in the early phase of the experiment due to pH dependent sulfate adsorption; later NO_3^- decreased and SO_4^{2-} was desorbed. Leaching of NO_3^- and SO_4^{2-} was correlated with losses of Mg^{2+} and Ca^{2+} of which the latter was the dominant cation.

Analyses using both S mass balances and radioisotopes corroborate that for BBWM soil columns, SO_4^{2-} adsorption–desorption dominated the S biogeochemistry while in HF soil columns, organic S mineralization–immobilization processes were more important. It is suggested that similar techniques can be applied to soils in the field to ascertain the relative importances of SO_4^{2-} adsorption processes and organic S dynamics.

Introduction

An understanding of the S cycle in soil is important because SO_4^{2-} is a major anion in acidic deposition, and its mobility in mineral soils is closely associated with leaching of nutrient cations and aluminum (Johnson et al. 1982; Galloway et al. 1983; Krug & Frink 1983; Reuss & Johnson 1986). Transformations and

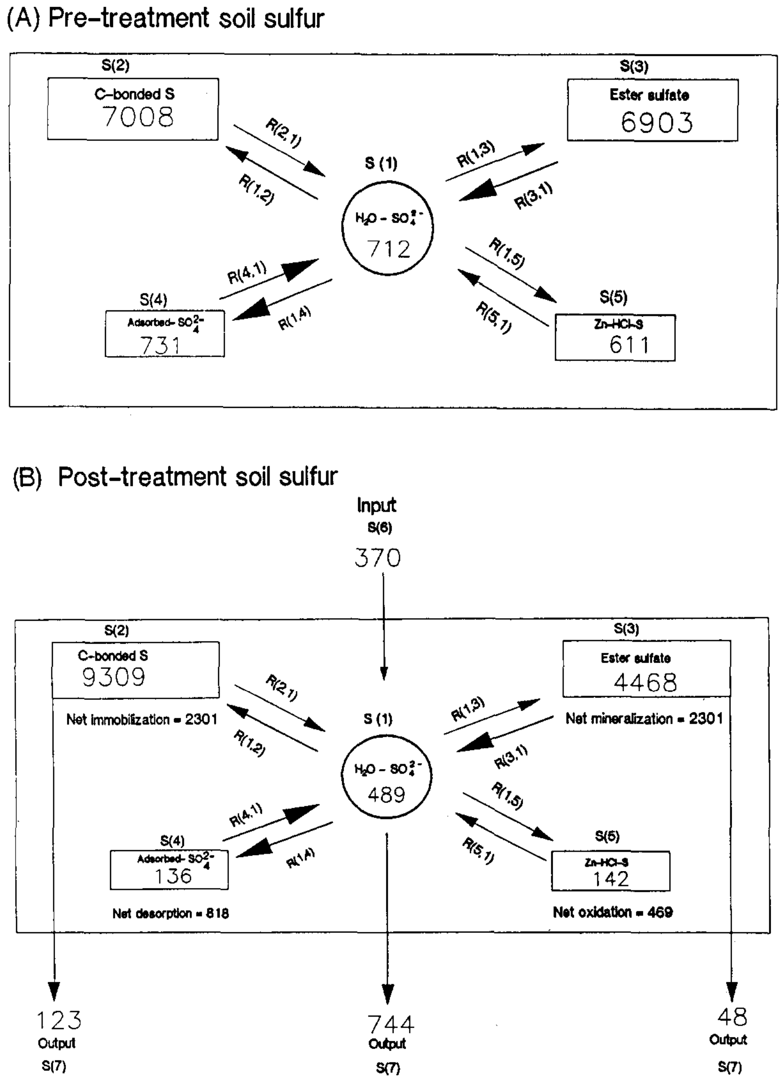
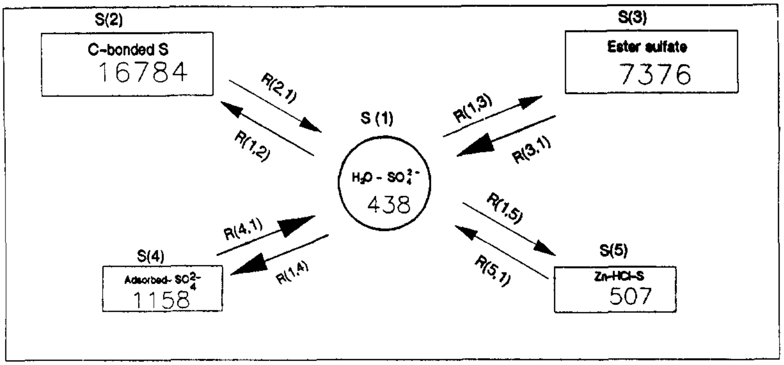


Fig. 1. Conceptual model of S fluxes, transformations and budget in soil columns. S(*) and R(*,*) represent pools and transformation/fluxes among pools. Immobilization = R(1, 2) and R(1, 3); Mineralization = R(2, 1) and R(3, 1); Adsorption = R(1, 4). Pre-treatment (*A*) and post-treatment (*B*) S budgets of BBWM soil columns (μmol S).

fluxes of organic and inorganic S in soils are controlled by mineralization–immobilization, adsorption–desorption and oxidation–reduction processes (Neary et al. 1987; Huete & McColl 1984; Rajan 1978) as described in a conceptual model (Figs. 1 and 2). This model is based upon four reversible reactions that represent immobilization–mineralization and adsorption–desorption processes.

(A) Pre-treatment soil sulfur



(B) Post-treatment soil sulfur

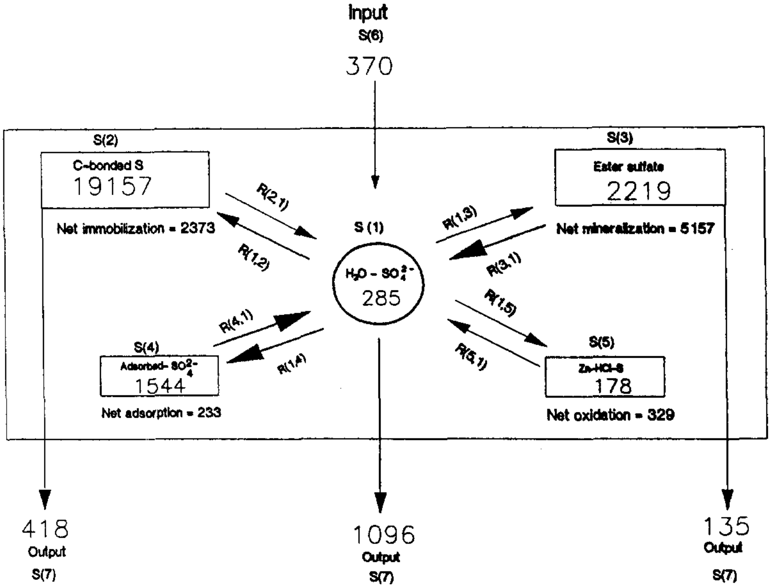


Fig. 2. Pre-treatment (*A*) and Post-treatment (*B*) S budgets of HF soil columns (μmol S).

Soil columns have been used to quantify the effects of different S loading rates on the fluxes of SO_4^{2-} and other ions from soils (Raynal et al. 1980; Bolan et al. 1986; McClenahen 1987). In a few cases, ^{35}S was used as a tracer (Chao et al. 1962; Haque & Walmsley 1974; Freiseleben 1988). None of these studies, however, have considered concomitantly SO_4^{2-} flux, immobilization–mineralization, adsorption–desorption, and the relationships of these processes to the

fluxes of cations and anions. The present study, utilizing soils from two northern hardwood ecosystems, was designed to:
- examine S dynamics in mineral soils using input and output budgets;
- quantify the relationships among cations (H^+, Ca^{2+}, Mg^{2+}, K^+, and NH_4^+) and anions (NO_3^-, and SO_4^{2-}); and
- compare the contributions of S mineralization–immobilization and adsorption–desorption between these soils.

Materials and methods

Soil collection

Soils were collected from northern hardwood forests at Bear Brook Watershed, Maine (BBWM) and Huntington Forest, New York (HF). Soils from these sites were chosen for study because the former site is being used for chemical manipulations as part of the Watershed Manipulation Project (David et al. 1990) and the latter site has had extensive work on biogeochemical cycling (Shepard et al. 1989) with special focus on sulfur dynamics (David et al. 1987).

BBWM is located on the upper southeast-facing slope of Lead Mountain at a maximum elevation of 450 m above sea level. The site is approximately 45 km east of Orono, Maine (44° 51′ N, 68° 6′ W) and about 40 km from the Atlantic Ocean. Soils are derived from glacial till and are well-drained Typic Haplorthods with a fine sandy loam texture and high concentrations of organic matter in the upper mineral horizons. There are five soil series of which the Rawsonville and Mundal series are most common (Erickson 1987). Prominent tree species in the BBWM are American beech (*Fagus grandifolia* Ehrh.), red maple (*Acer rubrum* L.), grey birch (*Betula populifolia* Marsh.), yellow birch (*Betula alleghaniensis* Britton.), red spruce (*Picea rubens* L.), balsam fir (*Abies balsamea* (L.) Mill.), and hemlock (*Tsuga canadensis* L.) (Erickson, 1987). Soil for the present study was collected from a pit at an elevation of about 250 m.

The hardwood site at the HF is located at 44° 00′ N, 74° 13′ W at an elevation of 530 m. The dominant soil at this site is a Becket-Mundal coarse-loamy, mixed frigid Typic Haplorthod. The forest is dominated by sugar maple (*Acer saccharum* Marsh.) and American beech. Associated species are yellow birch, red spruce and black cherry (*Prunus serotina* Ehrh.). Further details on this site have been given previously (Raynal et al. 1980; Mollitor & Rynal 1982; David et al. 1982, 1987).

Simulated throughfall solution

A simulated throughfall solution, with a chemical composition similar to throughfall from the hardwood site at HF (Shepard et al. 1989), was formulated using neutral salts and concentrated HNO_3 (Table 1). Carrier-free $^{35}SO_4^{2-}$ (3.7×10^4 MBq mmol^{-1}) was added to the simulated throughfall, and the

Table 1. Chemistry of throughfall solution.

Ion	TF chemistry[a] μeq L^{-1}	Simulated TF chemistry μeq L^{-1}
Cl^-	24.0	24.0
NO_3^-	44.0	44.0
SO_4^{2-}	80.0	80.0
H^+	24.0	17.0
NH_4^+	19.0	13.5
Na^+	42.0	29.7
K^+	48.0	34.0
Ca^{2+}	52.0	36.9
Mg^{2+}	24.0	17.0

[a] Shepard et al. 1989

resultant solution's radioactivity was 7.90 MBq L^{-1}. The ^{35}S–SO_4^{2-} constituted 0.004% of the total SO_4^{2-}.

Sampling and experimental design of soil columns

At both BBWM and HF field sites, mineral soil (E to Bs3 horizons, depth of 70 cm) was collected from 3 × 3 m plots representing soils from Tunbridge (David et al. 1990) and Becket-Mundal series, respectively. Both soils were typic Haplorthods (Spodosol) but were not necessarily representative of all soils found at each of these sites. Each soil was homogenized and sieved through a 6-mm screen, brought to the laboratory and stored at 4 °C until it was used for soil column construction. Soil samples were collected in June 1987 and the laboratory experiment was initiated in March 1988.

For each soil, three plexiglass columns (20 cm height × 15.2 cm diameter) were packed with mineral soil at a bulk density of 0.86 Mg m^{-3} which approximated field conditions. A Nalgene bottle was attached to the base of each column and maintained at − 10 kPa for collecting leachates. Simulated throughfall with ^{35}S–SO_4^{2-} was applied at a rate of 2.54 cm $week^{-1}$ (463 ml) which is similar to the precipitation input at HF (2.04 cm $week^{-1}$; Shepard et al. 1989). Columns were maintained at 1 °C for 20 weeks and leachates were collected weekly. This low temperature was used to decrease microbial activity.

Statistical analyses were performed using Student's *t*-test and Analysis of Variance (ANOVA) with the Statistical Analysis System at 0.05 level of significance (SAS, 1985). Comparisons among means were performed using Duncan's multiple-range test (Sokal & Rohlf 1981).

Chemical analyses

Total sulfur in solution, hydriodic acid-reducible sulfur (HI–S) and zinc-hydrochloric acid-reducible sulfur (ZnHCl–S) were determined using the modified version of digestion–distillation apparatus of Johnson & Nishita (1952) that was used by Landers et al. (1983). Total S in soil was analyzed using a LECO-135 S analyzer (David et al. 1989). Extractable S fractions (PO_4-SO_4^{2-} and H_2O-SO_4^{2-}) were obtained by shaking the soil samples for 1 h in a solution to soil ratio of 20:1 and 10:1, respectively, with either 15 mmol l^{-1} NaH_2PO_4 or deionized distilled water, respectively. Sulfate was determined using a Dionex ion chromatograph.

Soil analyses for total S and different S fractions were performed prior to constructing the soil columns and at the end of the leaching experiment. Analyses were performed on freeze-dried samples to minimize changes in sulfur fractions associated with sample handling (David et al. 1989). Soil moisture was determined by weighing the soil before and after freeze-drying, and converting the value to percent water on a dry mass basis. Sulfur fractions were calculated as follows:

C-bonded S = (Total S) − (HI-S)

Ester sulfate = (HI-S) − (PO_4 − SO_4^{2-})

Total inorganic SO_4^{2-} = (PO_4-SO_4^{2-})

Inorganic S = (PO_4-SO_4^{2-}) + (ZnHCl-S)

Adsorbed SO_4^{2-} = (PO_4-SO_4^{2-}) − (H_2O-SO_4^{2-})

It is possible that some of the ester sulfate calculated by this procedure may be occluded sulfate, and thus the ester sulfate pool may be overestimated (Williams 1975). All soil leachates were stored at 1 °C upon sampling. A glass electrode was used to determine pH (Corning Digital pH meter, Model 130); NO_3^- was determined by ion chromatography (Dionex); and Ca^{2+}, Mg^{2+}, and K^+ were quantified by atomic absorption spectrometry (Perkin-Elmer, Model 703). Ammonium was analyzed by a Wescan ammonia analyzer (Scott et al. 1989).

Determination of ^{35}S

The total activity of ^{35}S in the soil was determined by digesting the soils in sodium hypobromite solution (Landers et al. 1983). The digestion flask was heated to dryness in a sand bath (250 °C). The residue was dissolved in distilled deionized water and neutralized with formic acid. The solution was centrifuged, and the activity of ^{35}S in the supernatant was determined using liquid scintillation.

For the determination of ^{35}S activity in HI-S and ZnHCl-S fractions in soil and leachates, subsamples were taken after Johnson-Nishita digestion and activity determined. For ^{35}S activity in PO_4-SO_4^{2-} and H_2O-SO_4^{2-}, subsamples were taken and counted after respective extraction procedures. The specific

Table 2. Mean concentrations of soil sulfur fractions (μmol S g^{-1}) in pre-treatment soil (difference between soils by Student's *t*-test).

Forms of sulfur	Soil	
	BBWM	HF
Total S[a]	7.42 (0.23)**	14.88 (1.14)
HI-S[a]	4.17 (0.07)**	5.37 (0.05)
ZnHCl S[a]	0.28 (0.00)	0.29 (0.00)
PO_4-SO_4^{2-} S[b]	0.67 (0.00)	0.90 (0.22)
H_2O-SO_4^{2-} S[b]	0.33 (0.01)*	0.25 (0.01)
C-bonded S	3.26 (1.31)**	9.51 (1.45)
Ester sulfate	3.21 (0.56)*	4.18 (0.80)

[a] $n = 3$
[b] $n = 2$
() = Standard deviation
** = $p \leqslant 0.01$
* = $p \leqslant 0.05$

activity of ^{35}S in each S fraction was calculated as disintegrations of ^{35}S (Bq) divided by the S concentration (μmol S) of each respective fraction.

All determinations of ^{35}S activity used 10 ml of Fisher Scinti-Verse Universal LSC cocktail and a spectrum window from 0–0.156 MeV in a Beckman liquid scintillation counter. Counts were corrected for radioactive decay, internal standards used to determine counting efficiency and results expressed as disintegrations (Bq).

Results and discussion

Initial soil characteristics

Soils taken from BBWM and HF differed ($p \leqslant 0.05$) in concentrations of total S, C-bonded S, ester sulfate, and H_2O-SO_4^{2-} (Table 2). Total S, C-bonded S and ester sulfate concentrations of the BBWM soil were substantially less than that of the HF soil. Carbon bonded S (44 and 64% of total S for BBWM and HF, respectively) and ester sulfate (43 and 28% of total S for BBWM and HF, respectively) were the dominant S constituents in both soils, with inorganic S fractions constituting less than 10% of the S pools.

For the same soil from BBWM, David et al. (1990) reported a concentration of 8.7, 3.4 (39% of total S) and 1.4 (16% of total S) μmol S g^{-1} soil for total sulfur, C-bonded S and ester sulfate, respectively. Similar concentrations for total S and C-bonded S were found in the present study but the concentration of ester sulfate was higher. David et al. (1983) reported that the Bh and Bs1 horizons of soil from the HF had total S concentrations of 16 and 23 μmol S g^{-1} soils and C-bonded S concentrations of 83% and 70% of total S, respectively. In general, the S concentrations and relative proportion of S constituents in the two soils used in the present study were similar to those found by other studies at these sites and are typical of other Spodosols (David et al. 1982; Schindler et al. 1986; Johnson et al. 1986, van Loon et al. 1987).

Adsorbed SO_4^{2-} accounted for 5% of total soil S in the BBWM soil and 4% of total S in the HF soil. These SO_4^{2-} concentrations were higher than previously reported from these soils (David et al. 1982, 1990), probably due to the accumulation of mineralized SO_4^{2-} during storage. Inorganic non-sulfate S (ZnHCl–S) was the smallest S pool ($<4\%$ of the total S).

Sulfur budgets of soil columns

After leaching, ZnHCl–S decreased by 21% and 35%, in the BBWM and the HF soil columns, respectively. These decreases may be attributed to the oxidation of partially reduced inorganic S species that constitute much of this fraction (Aspiras et al. 1972). In the BBWM soil columns, adsorbed SO_4^{2-} decreased by 81%, while in the HF soil columns it increased by 33%. The large decrease in the BBWM soil was likely due to desorption of SO_4^{2-} during the 20-week incubation. Changes in the inorganic S constituents constituted about 8 and 0.4% of the initial S pools in the BBWM and HF soils, respectively.

Carbon-bonded S increased (33 and 14% for BBWM and HF soil columns, respectively) and ester sulfate decreased (45 and 70% for the BBWM and HF soil columns, respectively) afer leaching (Figs. 1, 2). Thus, there was a net immobilization of C-bonded S and net mineralization of ester sulfate. For BBWM soil columns, there was no net change in the total organic S pool, while for HF there was 12% net mineralization.

The greater lability of ester sulfate was expected, because it is more easily mineralized than C-bonded S which is associated with a relatively strong aromatic ring structure of humic acid (Bettany et al. 1980; Biederbeck 1978). McLaren and Swift (1977) have also suggested that the HI-reducible form of soil organic S, which is predominantly ester sulfate, has a more rapid turnover rate than C-bonded S. Freney et al. (1975) and Schindler et al. (1986) also reported that ester sulfate is more labile than C-bonded S in soil.

Net mineralization–desorption and oxidation–reduction rates (based on the total amount of SO_4^{2-} collected in the leachates) for the BBWM soil and the HF soil were 3.9% and 5.6% of total S, respectively, for the 20 weeks of incubation. Schindler and Mitchell (1987) reported a similar net mineralization rate of 2.5% of S for 20 weeks of leaching of a Bs1 horizon soil from HF using smaller amounts of soil (15 g) in laboratory incubations.

Depth distribution of S constituents after incubation

Total S and C-bonded S did not show any change (ANOVA, $p \geqslant 0.05$) with depth in either the BBWM or HF soil columns at the end of the experiment. Ester sulfate concentrations differed ($p \leqslant 0.05$) with soil depth and generally were lowest at the top of the columns (Table 3). These results suggest that either net mineralization rates of ester sulfate were greater near the top of the columns

Table 3. Duncan's grouping of mean ester sulfate and Zn-HCl S (μmol S g^{-1}) within the BBWM and the HF soil columns.

Depth (cm)	BBWM Mean[1]	HF Mean
	Ester sulfate	
1	1.22 c	1.20 a b
3	1.91 b	0.63 b
8	1.77 b c	0.85 b
10	2.40 a b	0.97 b
14	2.70 a	2.29 a
16	2.12 a b	1.81 a b
	Zn–HCl sulfur	
1	0.03 d	0.07 c
3	0.06 c	0.09 b c
8	0.06 b c	0.10 b
10	0.09 a	0.11 a b
14	0.08 a b	0.11 a b
16	0.04 d	0.13 a

[1] Means within a column with the same letter are not significantly different at $p \leqslant 0.05$.

and/or ester sulfate was being leached down the columns. In Spodosols, the relative importance of ester sulfate as a fraction of total S increases with horizon depth (David et al. 1982), and the leaching of organic S constituents may play an important role in sulfur accumulation (Mitchell et al. 1989).

Total inorganic SO_4^{2-} and H_2O–SO_4^{2-} concentrations did not differ significantly with depth ($p \geqslant 0.05$). The concentration of ZnHCl-S was generally lower at the top of the columns ($p \leqslant 0.05$) (Table 3) which may be a reflection of greater exposure to ambient air and hence oxidation of chemically reduced S.

Fluxes and transformations of ^{35}S

Total recovery of ^{35}S averaged 95%. Total activity of ^{35}S in the soil columns was estimated by counting soil samples digested in sodium hypobromite solution and extrapolating for those depths for which samples were not taken with an exponential function (Fig. 3). From 92–108% of the ^{35}S added to the six columns could be accounted for in the soil columns. The output of ^{35}S in the leachate was less than 0.5% of the amount added in the simulated throughfall solution.

The fate of the ^{35}S can be ascertained by examining its distribution with column depth in various sulfur fractions (Table 4a). Highest ^{35}S activity (> 90% of total ^{35}S added) was recorded from 0 to 3 cm depth for both soils, and activity declined exponentially with column depth. This pattern of ^{35}S activity was similar for all S fractions (total S, C-bonded S, ester sulfate, total inorganic SO_4^{2-} and adsorbed SO_4^{2-}) except ZnHCl-S for which no activity was detected. Organic S accounted for most of the ^{35}S activity in the soil, and it ranged from 70–88% and 70–91% of the total activity in the BBWM and HF soil, respective-

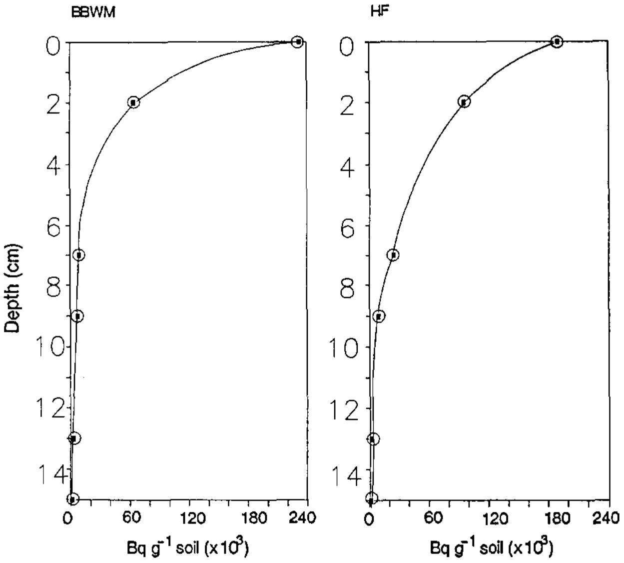


Fig. 3. Mean activity of ^{35}S in BBWM and HF soil columns after 20 weeks of leaching.

ly. Previous studies using ^{35}S have also demonstrated that SO_4^{2-} may be rapidly immobilized into organic S fractions (Schindler et al. 1986; Fitzgerald et al. 1982). Generally, C-bonded S accounted for about 80% of the total ^{35}S activity. Ester sulfate had a higher specific activity in HF than BBWM soil columns (Table 4b) which suggests a higher turnover rate of ester sulfate in the former columns.

Among the ^{35}S fractions, inorganic SO_4^{2-} (adsorbed SO_4^{2-} and total inorganic

Table 4a. Mean ^{35}S activity (kBq g^{-1} soil) of soil columns at different depths after decay correction (n = 3).

Site	Depth (cm)	Total S	C-bonded S	Ester sulfate	Total SO_4^{2-}	Adsorbed SO_4^{2-}
BBWM	1	232.5 (76.3)	199.6 (72.6)	5.2 (4.2)	27.7 (1.9)	20.9 (3.3)
	3	63.8 (25.4)	44.7 (28.3)	8.7 (2.6)	10.4 (2.9)	7.9 (4.0)
	8	9.1 (3.7)	3.9 (2.6)	2.5 (0.9)	2.7 (0.6)	2.1 (0.5)
	10	7.2 (4.2)	5.4 (4.6)	0.6 (0.6)	1.2 (0.2)	0.2 (0.2)
	14	2.6 (2.2)	1.6 (2.4)	0.6 (0.4)	0.4 (0.2)	0.3 (0.1)
	16	1.3 (1.2)	0.7 (1.2)	0.4 (0.2)	0.2 (0.1)	0.1 (0.1)
HF	1	189.7 (57.0)	141.3 (52.6)	16.1 (9.1)	32.2 (1.6)	19.3 (3.0)
	3	95.1 (3.1)	62.3 (2.6)	4.4 (1.8)	28.4 (1.9)	16.1 (4.8)
	8	24.1 (17.6)	14.1 (13.1)	4.3 (2.0)	5.6 (3.8)	3.5 (2.5)
	10	8.3 (4.3)	6.7 (4.1)	0.6 (0.1)	1.1 (0.7)	0.6 (0.5)
	14	1.3 (0.9)	0.5 (0.7)	0.7 (0.3)	0.1 (0)	0.1 (0)
	16	0.5 (0.2)	0.2 (0.2)	0.3 (0.0)	0 (0)	0 (0)

Table 4b. Average specific activity (kBq μmol^{-1} S) of ^{35}S in soil columns at different depths ($n = 3$).

Site	Depth (cm)	Total S	C-bonded S	Ester sulfate	Total SO_4^{2-}	Adsorbed SO_4^{2-}
BBWM	1	31.6 (10.1)	34.1 (12.7)	3.6 (3.1)	146.3 (30.5)	834.2 (35.9)
	3	9.5 (4.8)	10.2 (7.6)	4.3 (0.9)	34.8 (13.0)	68.9 (140.8)
	8	1.3 (0.6)	0.9 (0.7)	1.3 (0.3)	9.4 (2.6)	21.5 (3.9)
	10	1.3 (0.9)	2.0 (1.8)	0.2 (0.2)	4.8 (1.4)	26.5 (1.5)
	14	0.4 (0.3)	0.3 (0.5)	0.2 (0.2)	1.6 (0.1)	4.7 (4.3)
	16	0.2 (0.2)	0.1 (0.4)	0.2 (0.1)	0.6 (0.1)	1.2 (1.1)
HF	1	14.0 (3.3)	12.3 (3.7)	12.7 (6.1)	40.1 (11.4)	25.9 (8.5)
	3	8.3 (1.2)	6.6 (0.9)	7.3 (2.9)	26.3 (7.6)	15.4 (6.6)
	8	1.9 (1.6)	1.4 (1.4)	5.8 (4.2)	4.1 (3.4)	2.5 (9.5)
	10	0.6 (0.3)	0.5 (0.3)	0.7 (0.4)	3.2 (4.0)	0.9 (0.8)
	14	0.1 (0.1)	0.1 (0.1)	0.3 (0.1)	0.3 (0.2)	0.1 (0)
	16	0 (0)	0 (0)	0.2 (0.1)	0.1 (0.1)	0.1 (0.1)

( ) Standard deviation

SO_4^{2-}) showed the highest specific activity in both soils (Table 4b). The high specific activity of ^{35}S in the inorganic SO_4^{2-} pool of both soils indicates that this S pool has the most rapid incorporation and turnover of $^{35}S\text{-}SO_4^{2-}$. This adsorption process is abiotic, and the transfer of SO_4^{2-} from the soil water to the adsorption phase approaches equilibrium almost instantaneously (Fuller et al. 1987). The lower specific activity of $PO_4\text{-}SO_4^{2-}$ in the HF soil columns could be due to greater isotopic dilution of this constituent due to higher net mineralization rates of ester sulfate in the HF versus the BBWM soil columns (Figs. 1, 2). The specific activity for the C-bonded S is substantially lower than that of inorganic SO_4^{2-} probably due to its large endogenous pool size and slower turnover rate. Higher specific activity of C-bonded S compared with ester sulfate in BBWM soil is a reflection of the net immobilization of S in C-bonded S versus the net mineralization of ester sulfate. Decreasing specific activity with column depth can be attributed to SO_4^{2-} desorption and S mineralization both of which would contribute to SO_4^{2-} in solution and thus result in isotopic dilution of $^{35}SO_4^{2-}$. Similar results have also been found in field application of $^{35}SO_4^{2-}$ where activity also declined with soil depth (David & Mitchell 1987).

It has been established in other studies using ^{35}S labeled soil constituents that recently formed insoluble organic S constituents may be depolymerized and released into soluble forms (Strickland et al. 1984). For leachates in the present study, ester sulfate had higher ^{35}S specific activity, 40.7 and 9.77 Bq g^{-1}/μmol-S for the BBWM and the HF soil columns, respectively, than C-bonded S indicating that newly formed ester sulfates are more easily leached from the soil than C-bonded S. This confirms the observations of the non-radioactive S mass balances and depth distribution of ester sulfate.

Leachate chemistry

In the early phase of the experiment (weeks 1 through 4) concentrations of total S and SO_4^{2-} in solution were low. This was followed by peak concentrations in weeks 5 through 11 and relatively uniform concentrations in subsequent weeks. Carbon-bonded S and ester sulfate concentrations in solution did not vary ($p > 0.05$) through the experimental period. Mean values of C-bonded and ester sulfate for BBWM and HF leachates were 11.1, 5.3 and 49.4, 17.4 μmol S L^{-1}, respectively. Such results are similar to those of previous laboratory (Schindler and Mitchell, 1987) and field studies (David et al. 1987; Mitchell et al. 1986, 1989) that also showed that organic S constituents contribute to the total S of solutes from forest ecosystems.

The BBWM and HF soil columns initially had high leaching rates of NH_4^+ and NO_3^- derived from ammonification and nitrification. Some of this inorganic N may have accumulated during soil preparation and prior to experimentation. During the first week, NO_3^- was five times greater than the concentration of other anions for both BBWM and HF leachates (Fig. 4). Previous stuides with soil columns also found that nitrification was stimulated by soil disturbance during column construction and continued up to nine months (Freiesleben 1988). Absence of a vegetation sink for N uptake (Vitousek et al. 1979) also may have contributed to the NO_3 leaching in the present study. Nitrification produces H^+ (a depression of soil pH), thereby enhancing SO_4^{2-} adsorption (Chao et al. 1964). Sulfate was retained in the early phase of this experiment during column acidification (Fig. 5). The subsequent increase in SO_4^{2-} concentration coincided with a decrease in H^+ production for both BBWM and HF soil columns. The importance of pH-dependent SO_4^{2-} adsorption has been shown for Spodosols from northern hardwoods in both laboratory (Mitchell et al. 1989) and field studies (Nodvin et al. 1988; Mitchell et al. 1989). In the latter phase of the study when NO_3^- concentration decreased, this adsorbed SO_4^{2-}, including a portion that was derived from S mineralization, was released, and resulted in a net loss of S from the soil columns (Fig. 5).

Calcium was the dominant basic cation in both BBWM and HF leachates followed by Mg^{2+} and K^+. In the BBWM soil leachate, the concentrations of Ca^{2+}, Mg^{2+} and K^+ were as high as 658, 358 and 224 μeq L^{-1}, respectively, during the early weeks of experiment. The HF soil leachate also had a similar pattern, but lower concentrations of the respective cations. The concentrations of these cations declined with time and their flux from the columns was directly related to the total flux of the mobile anions, NO_3^- and SO_4^{2-}. In BBWM and HF soil leachates, the total of NO_3^- plus SO_4^{2-} concentrations were positively related to Ca^{2+} (BBWM: $r^2 = 0.38$, $n = 20$, slope = 0.33, $p \leqslant 0.05$; HF: $r^2 = 0.41$, $n = 20$, slope = 0.31, $p \leqslant 0.05$) as well as Mg^{2+} (BBWM: $r^2 = 0.66$, $n = 20$, slope = 0.18, $p \leqslant 0.05$; HF: $r^2 = 0.66$, $n = 20$, slope = 0.13, $p \leqslant 0.05$) but not significant for K^+ ($p > 0.05$). The HF soil had a higher loss rate of SO_4^{2-} than the BBWM columns causing greater loss rates of basic cations. For both BBWM and HF soil columns, the concentrations of Ca^{2+}, Mg^{2+}, and K^+ declined with time, as the fluxes of NO_3^- and SO_4^{2-} decreased.

For the HF site, Mollitor and Raynal (1982) and Shepard et al. (1989) also reported that SO_4^{2-} and Ca^{2+} were the dominant anion and cation in soil

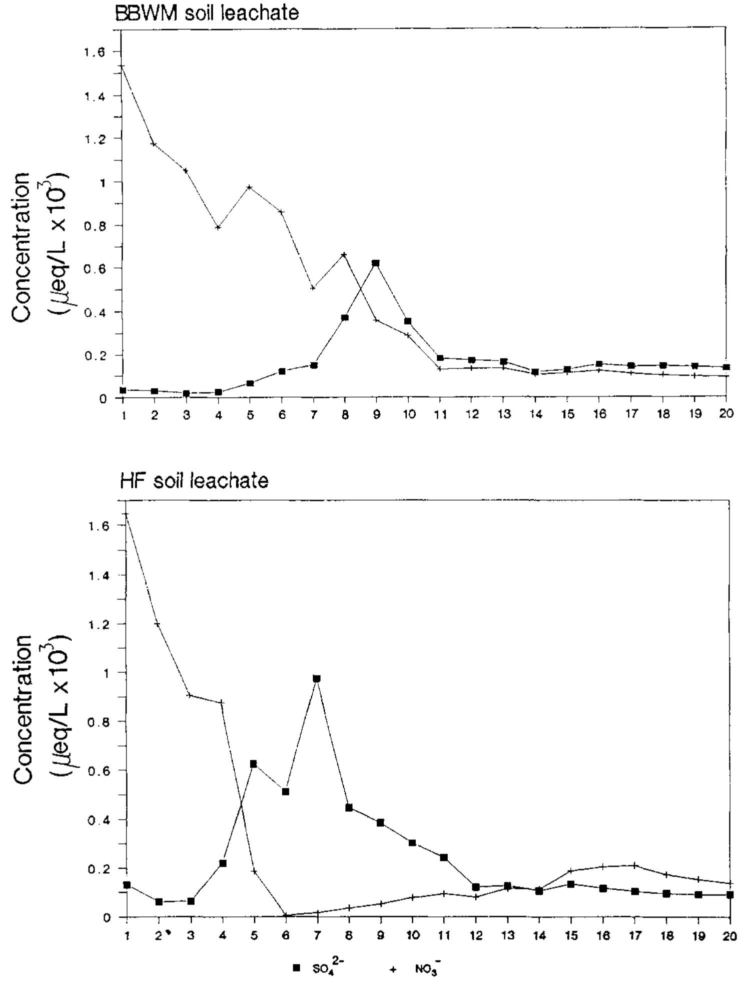


Fig. 4. Leachate concentrations of SO_4^{2-} and NO_3^- from BBWM and HF soil columns.

solutions, respectively. At the end of the present study, leachate concentrations from the BBWM and HF soils columns were similar to concentrations found in the field for most ions except NO_3^-, K and NH_4^+ which were substantially higher in column leachates (Fig. 6).

Sulfur dynamics of soils from BBWM and HF

The results of the study show that adsorption–desorption, mineralization–immobilization and oxidation–reduction of organic S differed between the HF and BBWM soil columns. In BBWM soil columns, although there were net

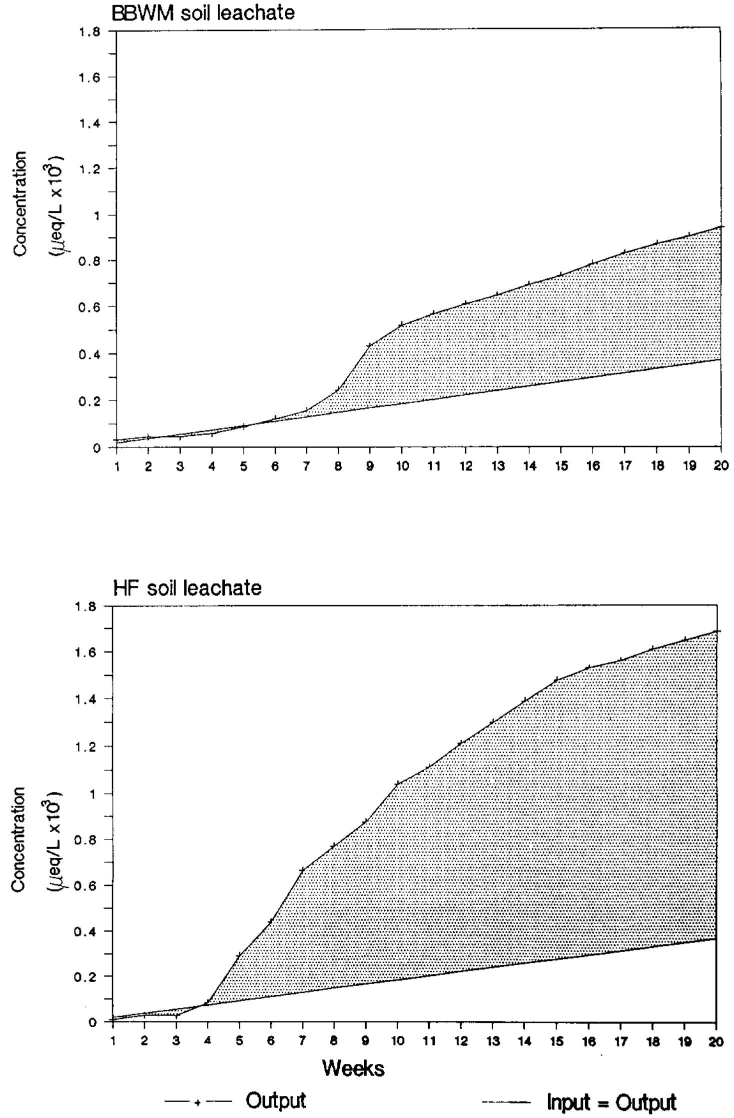


Fig. 5. Cumulative input versus output of sulfate in BBWM and HF soil columns.

changes in the relative sizes of the ester sulfate and C-bonded S pools, the adsorption–desorption of SO_4^{2-} was the major factor regulating the net leaching of SO_4^{2-} (Fig. 1). In contrast, SO_4^{2-} leaching from the HF soil columns is attributed to the mineralization of ester sulfate (Fig. 2).

In both BBWM and HF soil columns, SO_4^{2-} was probably retained due to pH-dependent SO_4^{2-} adsorption. These results indicate that SO_4^{2-} may be retained at both BBWM and HF if there is a decrease in soil pH. Therefore, for

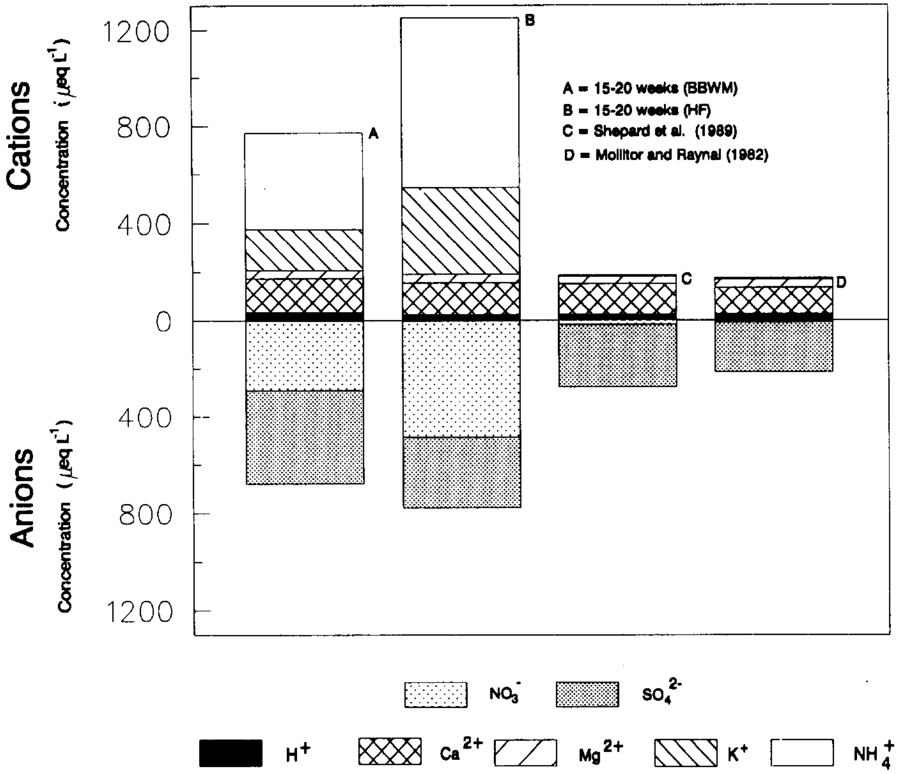


Fig. 6. Leachate chemistry of soil columns (weeks 15–20) compared with soil solution collected by lysimeters in the field.

predicting the effect of changes in SO_4^{2-} input to these ecosystems it is critical that pH-dependent SO_4^{2-} adsorption be included in models that predict S flux (Mitchell et al. 1989).

These results suggest that organic S pools may play an important role in regulating the S dynamics of these sites, especially at HF where organic S serves as both as a source and sink for S. Such results are similar to those of previous studies at HF that have indicated that SO_4^{2-} fluxes from soils are not in equilibrium with atmospheric inputs due to changes in organic S pools (David et al. 1987; Shepard et al. 1989). The mass balance analyses and dynamics of ^{35}S show that there was a net formation of C-bonded S that may serve as a long term storage pool for S in Spodosols as has been suggested by Schindler et al. (1986) and Mitchell et al. (1989). Conversely, the ester sulfate pool is more labile and may contribute substantially to SO_4^{2-} flux. The fate of the organic S pools has to be ascertained because these are the major storage forms of S in these soils. If these pools are not in steady state, they may markedly affect SO_4^{2-} flux and alter the movement of other ions including basic cations in the ecosystem.

Although the processes that regulate S dynamics in laboratory columns also occur in the field, the actual rates need to be interpreted and used with caution because they may not reflect actual field conditions. Field studies of S dynamics are thus required to confirm these conclusions. These studies need to be linked to other processes, such as cation leaching, which are important in affecting soil solution and surface water chemistry in northern hardwood forest ecosystems.

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