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A simulation model of sulfur transformations in forested Spodosols

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Abstract. Transformations of organic and inorganic S in two forested Spodosols from the Hubbard Brook Experimental Forest, New Hampshire and the Huntington Forest in the Adirondack Mts. of New York were investigated using laboratory $^{35}SO_4^{2-}$ incorporation experiments. Sulfur transformations were modeled as a set of three reversible, first-order reactions in which soluble SO_4^{2-} is converted to adsorbed SO_4^{2-}, ester sulfate and carbon-bonded S. Reaction rate contants for $^{35}SO_4^{2-}$ adsorption/desorption and immobilization reactions involving ester sulfate and carbon-bonded S were determined using a fifth order Runge-Kutta-Fehlberg integration routine combined with least squares fitting. Model simulations were able to account for over 93% of the variation in the distribution of ^{35}S in S fractions. A hypothetical application of immobilization rate constants to field situations at the Hubbard Brook Experimental Forest suggests that large quantities of S cycle through organic forms in Northern Hardwood Forest Ecosystems.

Introduction

The cycling of S in terrestrial ecosystems has received increasing attention in recent years due to concern over the effects of atmospheric inputs of sulfuric acid on terrestrial and aquatic ecosystems (Likens et al., 1977; Eaton et al., 1980; Johnson, et al., 1982; David, et al., 1984). Considerable effort has been made to quantify the extent and nature of soil SO_4^{2-} adsorption in forest soils, since transport of SO_4^{2-} in drainage water is accompanied by leaching losses of basic cation nutrients (e.g. Ca^{2+}, K^+) and potentially toxic acidic cations (e.g. H^+, Al^{3+}; Johnson and Cole, 1980; Fuller et al., 1985). However, it has recently been recognized that organic transformations of S may also be important in regulating ecosystem S fluxes (David et al., 1984; Strickland and Fitzgerald, 1984). Processes which buffer SO_4^{2-} concentration or delay SO_4^{2-} efflux from terrestrial ecosystems, such as SO_4^{2-} adsorption and organic sulfur transformations, may allow greater opportunity for neutralization of associated acidity to occur. These processes in turn may be important in explaining why short-term temporal variations in surface water acidity are frequently more highly correlated with changes in nitrate concentrations, even though SO_4^{2-} is the major anion (Johnson et al., 1969; Driscoll and Schafran, 1984).

A number of investigations have attempted to examine rates and pathways of organic S transformations using $^{35}SO_4^{2-}$ as a tracer of soil S movement (Freney et al., 1971; David et al., 1984; Saggar et al., 1981; Maynard et al., 1984; Schindler et al., 1986). While these investigations have provided valuable information on the forms and relative amounts of organic S produced, they have been hampered by an inability to quantify both forward and back (reversible) reactions simultaneously, such as S immobilization and mineralization. Particularly troublesome has been the problem of reimmobilization of previously mineralized isotope. An isotopic tracer may cycle through a pool many times during the course of an experiment. Except for determining *minimum* values (ie. based on initial concentration of soluble sulfate and percent incorporation of ^{35}S; McLaren et al., 1985), it has been very difficult to estimate gross immobilization or mineralization rates.

Sulfur in forest soils

Sulfate generally represents the major pool of inorganic S in most well-drained soils; lesser amounts of S are present in reduced forms (Freney, 1958; David et al., 1982; Maynard et al., 1984). Sulfate is typically present in a water soluble form or absorbed to free Fe and Al in soils (Johnson and Todd, 1983; Fuller et al., 1985). In spodosols, which retain minimal SO_4^{2-} relative to more highly weathered soils (Johnson and Todd, 1983), adsorbed SO_4^{2-} is predominantly located in Bs horizons (Fuller et al., 1985).

The chemical forms of organic S in forest soils are poorly understood, and have been grouped into broadly defined fractions (Maynard et al., 1984). The most important pools of organic S are carbon-bonded S, in which S is directly bonded to a C atom, and organic (HI reducible) sulfates, in which S is bonded to C through an O- or N-linkage of which the ester linkage predominates (Freney, 1970; Landers et al., 1983; Maynard et al., 1984). Carbon-bonded S (subsequently referred to as C-S) typically accounts for the largest concentration of S in forested spodic soils, and is derived largely from plant inputs, although microbial immobilization also contributes (David et al., 1984). Soluble forms of C-S may be mobilized in the forest floor, transported through the soil profile in combination with fulvic or humic acids and illuvially deposited in mineral horizons. This pool contains many metabolites, including the S-containing amino acids (Freney, 1979; Maynard et al., 1984).

Ester sulfates (subsequently referred to as C-O-SO_3) are extremely varied, ranging from simple metabolic storage products to complex structural compounds. The sulfate group is thought to be important in altering the parent molecule due to its acidic character which affects both the conformation of the molecule and counter-ion coordination reactions (Dodgson et al., 1982). Although some plant species contain high concentrations of C-O-SO_3 (Maynard et al., 1984), it is not significant in northern hardwood tree species (David et al., 1984). Therefore, soil C-O-SO_3 is thought to form largely through microbial processes within the soil. Several investigators have hypothesized that ester sulfate is formed as a storage product when concentrations of solution SO_4^{2-} are high, and subsequently serves as a S source when SO_4^{2-} concentrations are low, or when increases in labile C induce greater microbial demand for S (Fitzgerald, 1978; McGill and Cole, 1981; Maynard et al., 1984).

The dynamics of these organic S constituents have different effects on H^+ transport within the terrestrial ecosystem. Immobilization and mineralization of C-S result in the consumption or production of H^+, respectively, whereas formation of ester sulfates can also increase the ability of a soil to retain and exchange cations.

Soil sulfur transformations

Recently a number of watershed models have been developed to simulate the concentration and transport of acidic components in forested ecosystems (Christopherson and Wright, 1981; Chen et al., 1984; Schnoor et al., 1984; Cosby et al., 1985). None of these models, however, have included a comprehensive depiction of S transfer due to a lack of reliable information on relevant pools and rate data. The objective of this study was to evaluate a technique for quantifying kinetic expressions of soil S transformations which could eventually be incorporated into simulation models describing transformations of acidity in forested ecosystems. Our approach to this problem was to use $^{35}SO_4^{2-}$ incubation experiments to trace the movement of S into solid phase S constituents.

Investigations of S cycling in a variety of soils have shown a rapid conversion of added $^{35}SO_4^{2-}$ to organic ^{35}S, followed by an asymptotic approach to an apparent steady state (Freney et al., 1971; Fitzgerald et al., 1983; McLaren et al., 1985). Conversely, the specific activity of the $^{35}SO_4^{2-}$ has been shown to decline initially, followed by a gradual approach to a steady state (Maynard et al., 1983). We concur with the interpretation of McLaren et al. (1985), that these patterns suggest that S mineralized during the steady state period originated largely from a pool of recently immobilized organic S with the same specific activity as the SO_4^{2-} pool (Maynard et al., 1983). Moreover, apparently only a small fraction (3–6%; McLaren et al., 1985) of the organic S pool participates in concurrent immobilization and mineralization reactions. This fraction may include only microbial S or perhaps a small pool of labile extracellular S, while the bulk of the organic S pool is recalcitrant.

A simplified conceptual flow diagram (Figure 1) of S transformations occurring in a soil horizon was used for modeling purposes, based on the concepts of Maynard et al. (1984) and Bettany and Stewart (1983). Several important mechanisms of sulfur transfer (Maynard et al., 1984; David et al., 1984) including plant uptake, solution transport into and out of a horizon, and inorganic non-sulfate S reactions were not considered in this conceptual model. However, since laboratory incubation experiments in the well-aerated forest soils used in the present study should not be greatly affected by these

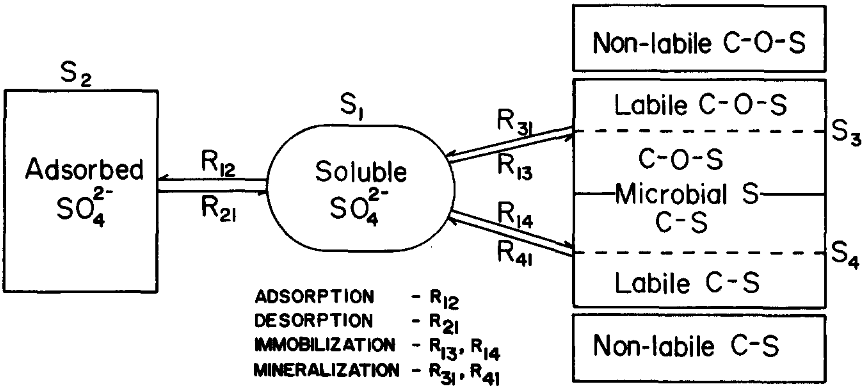

Figure 1. A conceptual model of S transformations occurring in a forest soil horizon. S_{1-4} refer to S pools used in modeling of S transformations. R_{ij}'s refer to reaction rate constants. S transfer to and from the horizon. (e.g. plant uptake, leaching) is not considered in this model.

processes, this model was considered adequate for describing the observed S transformations. The model is characterized by three sets of reversible reactions involving SO_4^{2-}, including adsorption/desorption, immobilization/mineralization of C-O-SO_3, and immobilization/mineralization of C-S. All forward reactions were assumed to proceed from soluble SO_4^{2-} as a reactant, therefore the direct interconversion of solid phase organic constituents was not considered.

While immobilization and mineralization proceed largely to and from microbial and labile forms of organic S (McLaren et al., 1985), analytical determinations of C-S and C-O-SO_3 are capable of distinguishing only total pools (Figure 1). Moreover, although microbial S can be estimated (Saggar et al., 1981), even a portion of the microbial biomass may be inactive. Only analyses of ^{35}S activity within the total organic fraction gives an accurate index of the rapidly cycling labile plus microbial pool. The size of these labile organic S pools have been estimated as the ^{35}S content of the organic S pool of interest divided by the specific activity of the $^{35}SO_4^{2-}$ pool at steady state (McLaren et al., 1985).

Materials and methods

Study sites

Data from a previously described $^{35}SO_4^{2-}$ incubation experiment (Schindler et al., 1986) were used to develop kinetic rate constants for S transformations. In this study, soil samples were collected from two sites: the Hubbard Brook Experimental Forest (watershed five) in the White Mts. of New Hampshire (HB), and the Huntington Forest in the Adirondack Mts. of

New York (HF). Both sites are characterized by Northern Hardwood vegetation, in which American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*) and yellow birch (*Betula alleghaniensis*) are the dominant species. Soils of both areas are classified as Typic Haplorthods or Fragiorthods (Fuller et al., 1985). Following excavation of soil pits, samples were sieved (2 mm) and stored at 3°C in a field-moist condition until the initiation of laboratory incubation experiments within one to three months (the latter period corresponded to soil samples collected in November and represented an artificial overwintering).

Experimental methods

Soil S transformations were evaluated in three horizons from each site (Oa, Bh, Bsl) using laboratory incubation experiments at 20°C for 56 days. In these experiments, carrier-free sodium ^{35}S-SO_4^{2-} (3.7×10^4 MBq per mmol., Amersham, Inc.) was added while mixing to field moist soil (200–500 g.) These samples were incubated in a sealed container with an elevated water vapor pressure to maintain their moisture status. Details of the experimental design and results are available from the original study (Schindler, 1984; Schindler et al., 1986).

After periods of 1 hour, and 1, 7, 14, 28 and 56 days, subsamples were analyzed for S concentration and ^{35}S activity in soluble SO_4^{2-}, adsorbed SO_4^{2-}, C-O-SO_3 and C-S fractions. The ^{35}S activity was measured in a 500 μl subsample of the S trapping or extracting solution with a Packard 3375 TriCarb liquid scintillation spectrometer. Details of the S extraction procedures (Landers et al., 1983) and the recovery and counting of ^{35}S (Schindler et al., 1986) are given elsewhere.

Model derivation and assumptions

Organic S transformations are controlled by a number of enzyme systems, which together contribute to the formation of the operationally defined fractions of C-S and C-O-SO_3. Our initial premise was that for each transformation, all of the contributing enzyme systems could be lumped into a single rate limiting step, which could be modeled in terms of Michaelis-Menten kinetics. For the mineralization of C-^{32}S, for instance, the velocity of the reaction (ν) is represented as:

$$\nu = \frac{V_{\mathrm{max}}}{K_{\mathrm{m}} + [^{32}\mathrm{S}]} [^{32}\mathrm{S}] \qquad (1)$$

where: V_{max} is the maximum velocity of the reaction at high substrate concentrations, K_{m} is the Michaelis-Menten rate constant, and [^{32}S] indicates substrate concentration. This reaction is first-order at low substrate concentrations, and becomes zeroth-order at high concentrations. The same reaction involving an isotopic tracer (ν'), however, shows the following form, when it is assumed that the enzyme (E) tracer complex is negligible relative to the enzyme substrate complex ($E^{35}S << E^{32}S$):

$$v' = \frac{V_{\max}}{K_m + [^{32}S]} \ [^{35}S] \tag{2}$$

Most soil systems are characterized by reversible reactions (e.g. adsorption/desorption, immobilization/mineralization) which tend to approach steady-state over time and help buffer changes in the absolute size of ^{32}S pools. If we assume that the size of the carbon-bonded ^{32}S pool for the above reaction was approximately constant over the course of an experiment, then equation (2) reduces to the following:

$$v' = R\,[^{35}S] \tag{3}$$

where: R is a lumped constant equal to $V_{\max}/(K_m + [^{32}S])$. Thus, even if the overall ^{32}S reaction is at $V_{\max}$ (zeroth order), the tracer will follow first-order kinetics if the ^{32}S pool remains constant. In addition, the lumped constant (R) is applicable to ^{32}S transformation rates, but only for the specific ^{32}S pool sizes under which it was derived.

A Michaelis-Menten approach would be attractive for modeling organic S transformations but for two constraints: (1) The functional pool size (that fraction of the organic ^{32}S involved in rapid turnover) cannot be measured. (2) Fitting two rate constants ($V_{\max}$ and K_m) for each reaction is extremely difficult, yielding an overall model with ten constants. However, by assuming that all ^{32}S pool sizes remained constant throughout incubation experiments (ie. ^{32}S pools were at steady state), only consideration of the organic ^{35}S concentrations, which are realistic estimates of the rapidly cycling organic S pools, is necessary, and an overall model with six rate constants can be utilized. This assumption was somewhat tenuous for several horizons (Schindler et al., 1986), particularly the Oa horizons, in which net mineralization appeared to occur in one horizon (HF-Oa) and net immobilization in another (HB-Oa).

Model structure

Transformations of ^{35}S were evaluated using a first-order kinetic model (Figure 1), consisting of four S pools and 3 reversible reactions. Changes in S pools (S_1–S_4) with time were represented by the following set of differential equations,

$$\frac{dS_1}{dt} = R_{21}\,S_2 + R_{31}\,S_3 + R_{41}\,S_4 - S_1(R_{12} + R_{13} + R_{14}) \tag{4}$$

$$\frac{dS_2}{dt} = R_{12}\,S_1 - R_{21}\,S_2 \tag{5}$$

$$\frac{dS_3}{dt} = R_{13}\,S_1 - R_{31}\,S_3 \qquad (6)$$

$$\frac{dS_4}{dt} = R_{14}\,S_1 - R_{41}\,S_4 \qquad (7)$$

where R_{ij} refers to the rate constant for the reaction of component i to component j. Note that this model is for both ^{32}S and ^{35}S reactions, but that ^{32}S reactions are assumed to be at steady state (e.g. $d^{32}S/dt = 0$). Also note that ^{35}S concentrations are very small relative to ^{32}S concentrations and thus should not affect total S transformations.

This set of equations was integrated numerically to solve for ^{35}S distribution at any time for a given set of rate constants. Optimum fits for the rate constants were determined using an iterative procedure to minimize residual sums of the squared deviations from predicted values. This technique has been used in pharmacokinetic studies of drug uptake in humans (e.g. Kaplan et al., 1972) and a convenient set of computer software is available in the PAR procedure of the BMDP statistical software (Dixon, 1981). PAR is a derivative free, nonlinear least squares fitting routine, in which the fitted function can be replaced by a fifth-order Runge-Kutta-Fehlberg numerical integration program (Shampine et al., 1976) available in the BMDP statistical library (Ralston et al., 1979). Rate constants were constrained to a minimum value of zero and a maximum value of 20. The latter constraint was necessary for successful integration, and was only applicable to SO_4^{2-} adsorption/desorption reactions. During the iterative routine, the ratio of the rate constants for adsorption/desorption (R_{12}/R_{21}) approached a constant value, while the magnitude of the two constants varied due to inadequate data in the early phases of the experiment. This variation had little effect on the determination of organic S transformation rate constants.

To illustrate this technique, a hypothetical two compartment model with a single reversible reaction is used (e.g. SO_4^{2-} and C-O-SO_3 linked by immobilization and mineralization; Figure 2), with a tracer added at time zero to compartment one (SO_4^{2-}). At equilibrium, the ratio of tracer in compartments one and two (C_1/C_2; Figure 2) will equal the ratio of the rate constants for mineralization and immobilization (R_{21}/R_{12}) reactions. The rate at which equilibrium is reached, however, is a function of the absolute magnitude of the rate constants. Thus, with adequate data in the accruing phase of compartment two, gross mineralization and immobilization rates can be predicted from the rate constants, although neither can be measured independently.

Results and discussion

First-order rate constants for the six reactions (Figure 1) are presented in Table 1 for the ^{35}S-SO_4^{2-} incorporation experiment. Model simulations

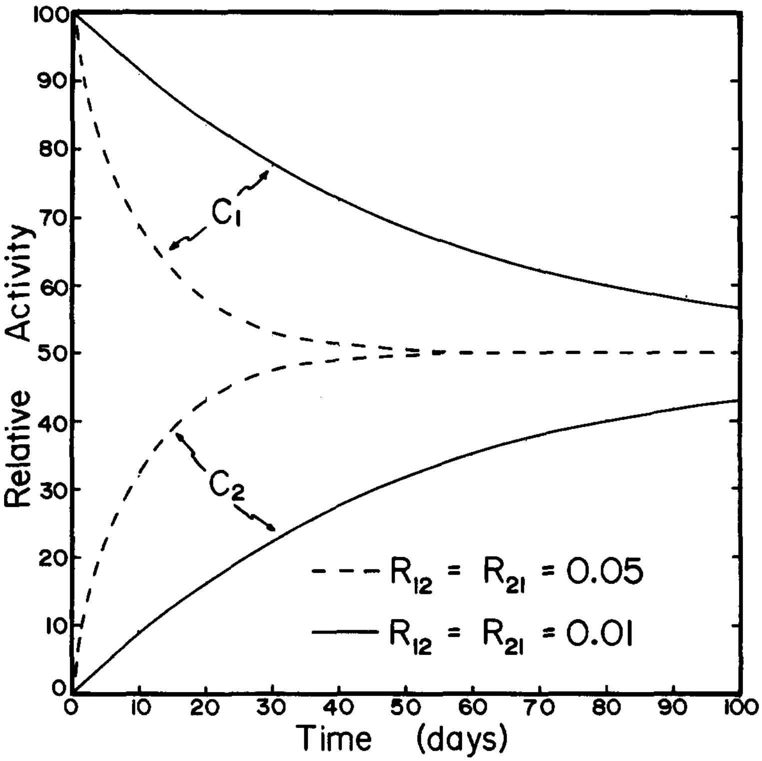

Figure 2. Changes in the relative distribution of an isotope added to compartment one (C_1; e.g. soluble $^{35}SO_4^{2-}$) at time zero for a hypothetical two compartment model linked by a reversible reaction (e.g. mineralization and immobilization of C-O-SO_3; C_2). When the absolute value of the rate constants (R_{12} and R_{21}) are larger (dashed lines), the system approaches equilibrium more rapidly.

were generally in close agreement with experimental data (Figures 3 and 4). Deviations from predicted values were probably due to a combination of sources, which include error in the fractionation and analysis of both S and ^{35}S and imprecise model formulation. However, for all horizons, the model was able to account for over 93% of the variation in ^{35}S distribution among the four S fractions (Table 1). Since adsorbed $^{35}SO_4^{2-}$ was the largest fraction in several horizons, we were concerned that this constituent may have unrealistically inflated the observed correlation coefficients. However, when the adsorbed SO_4^{2-} fraction was removed from correlation analyses, the model still accounted for over 81% of the variation in ^{35}S in soluble SO_4^{2-}, C-O-SO_3 and C-S (Table 1).

As expected, $^{35}SO_4^{2-}$ rapidly equilibrated with the adsorbed SO_4^{2-} pool (Singh, 1984). Subsequently, both of these fractions declined as slower organic transformations depleted soluble $^{35}SO_4^{2-}$ (Figure 4). Adsorption rate constants (R_{12}) and the ratio of adsorption/desorption rate constants

Table 1. First order rate constants for the reactions depicted in Figure 1 for Hubbard Brook (HB) and Huntington Forest (HF) soil horizons. Standard error estimates are given in parentheses below each rate constant. The first correlation coefficient is for predicted vs. measured ^{35}S distribution for all four S pools, whereas the second omits adsorbed sulfate.

		Rate constant (days^{-1})							
Site	Horizon	R_{12}	R_{21}	R_{13}	R_{31}	R_{14}	R_{41}	r^2	r^2
HB[a]	Oa	0.48	5.94	0.016	0.021	0.019	0.016	0.97	0.96
		(22.5)	(279.7)	(0.005)	(0.015)	(0.004)	(0.009)		
HF	Oa	0.44	1.06	0.025	0.020	0.037	0.000	0.93	0.95
		(0.21)	(0.60)	(0.008)	(0.016)	(0.004)	(b)		
HB	Bh	1.99	1.41	0.033	0.089	0.0035	0.000	0.97	0.94
		(1.26)	(0.95)	(0.023)	(0.081)	(0.0019)	(b)		
HF	Bh	0.87	0.94	0.025	0.035	[c]	[c]	0.96	0.97
		(0.25)	(0.31)	(0.010)	(0.024)				
HB	Bsl	20	4.08	0.091	0.060	0.013	0.000	0.99	0.86
		(b)	(0.44)	(0.032)	(0.027)	(0.004)	(b)		
HF	Bsl	5.84	0.89	0.110	0.190	0.050	0.002	0.99	0.81
		(14.3)	(2.20)	(0.170)	(0.330)	(0.019)	(0.010)		

[a] Failed to converge, parameters are best estimates only
[b] Rate constants limited to less than 20 and greater than 0, therefore no S.E.
[c] Not determined due to inadequate data; set to 0 for modeling other constants

(R_{12}/R_{21}) increased with soil depth, corresponding to higher SO_4^{2-} adsorption capacities with soil depth observed in Spodic soils (Fuller et al., 1985). The ratio R_{12}/R_{21} ranged from 0.08 to 0.41 for Oa horizons, 0.92 to 1.41 for Bh horizons, and 4.9 to 6.6 for Bsl horizons. Note that for rapid reactions, like adsorption/desorption, equilibrium may be established very rapidly, and rate constants for adsorption had to be constrained to less than twenty to allow for numerical integration. Nevertheless, this approach allowed for adequate prediction of soluble $^{35}SO_4^{2-}$; which at equilibrium is proportional to the R_{21}/R_{12} ratio, analogous to a distribution coefficient (Rhodes, 1957).

Rate constants for mineralization of C-O-SO_3 were generally greater than or nearly equal to those for immobilization, suggesting that large pools of this constituent should not accumulate in the soil, and that steady-state conditions should be attained relatively quickly. Rate constants for mineralization of C-S were generally much lower than those for immobilization, suggesting that significant quantities of this constituent may have accumulated through microbial immobilization during soil development. It is now likely, however, that mineralization and immobilization of C-S occur at more nearly equal rates since the C-S pool is much larger than the soluble SO_4^{2-} pool (Schindler et al., 1986). It should also be noted that much of the C-S in soil is derived largely from plant turnover, rather than microbial immobilization. Mineralization reactions probably proceed from a larger pool of both labile and non-labile forms of C-S, whereas immobilization reactions probably interact with a relatively small labile pool of C-S (Figure 1; Schindler, 1984).

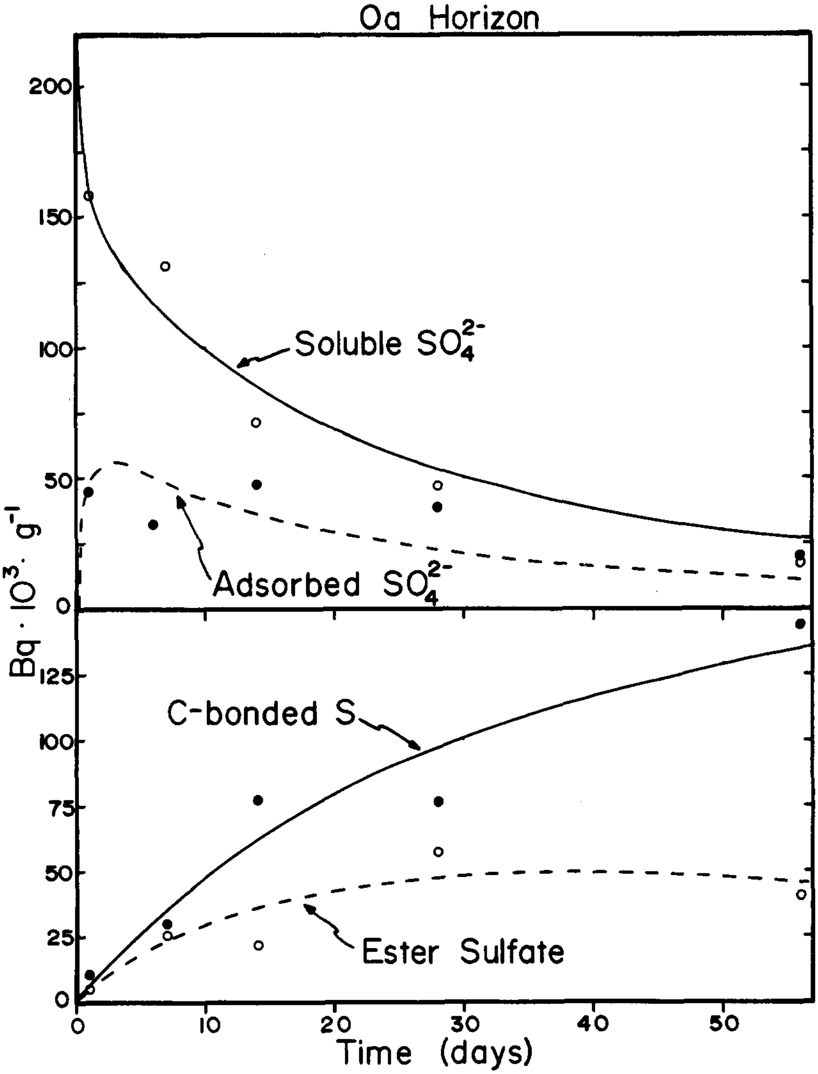

Figure 3. Model simulations of ^{35}S reaction kinetics in the Huntington Forest Oa horizon. Solid and dashed lines refer to model simulations of ^{35}S distribution, whereas data points depict measured ^{35}S distribution in laboratory incubation experiments (from Schindler et al., 1986).

Rate constants for immobilization and mineralization of $C\text{-}O\text{-}SO_3$ both increased whith soil depth (Table 1), suggesting more rapid cycling of this component in the mineral soil. Note that larger net quantities of ^{35}S $C\text{-}O\text{-}SO_3$ formed in the Oa horizon than in the B horizons (Figure 3; Schindler et al., 1986). The large immobilization rate constants estimated for Bsl horizons resulted from moderate quantities of ^{35}S $C\text{-}O\text{-}SO_3$ being formed

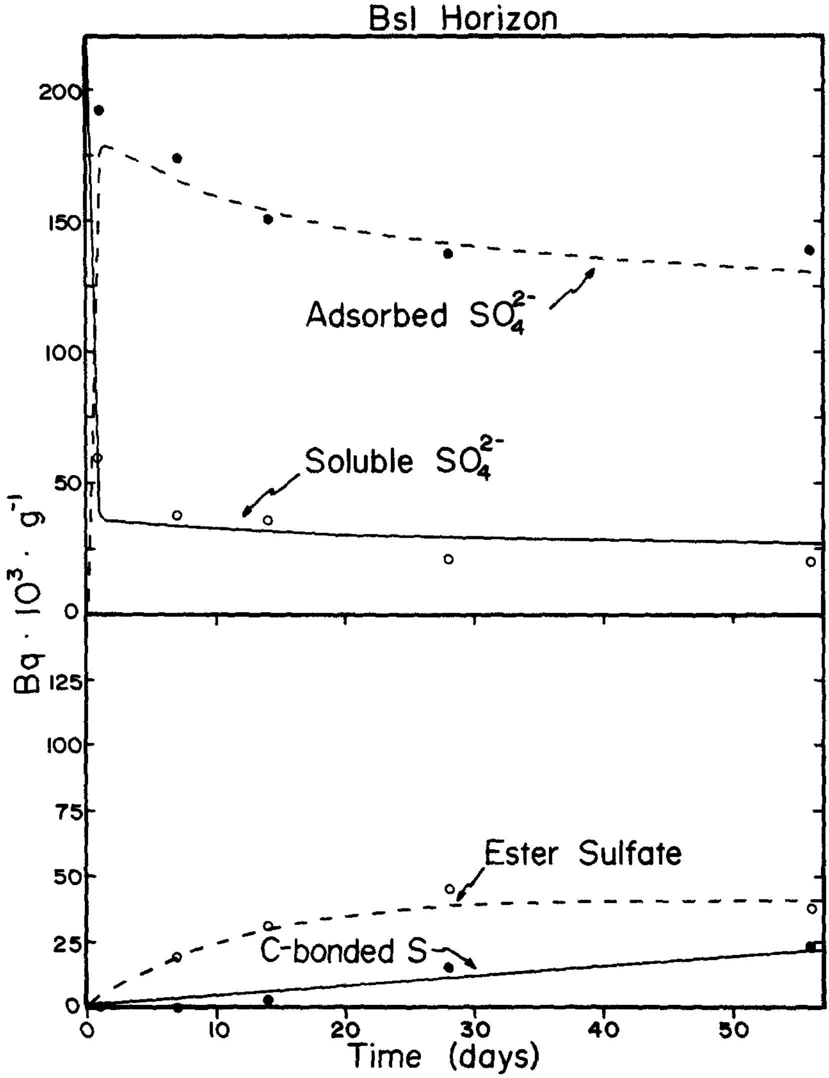

Figure 4. Model simulations of ^{35}S reaction kinetics in the Hubbard Brook Bsl horizon. Solid and dashed lines refer to model simulations of ^{35}S distribution, whereas data points depict measured ^{35}S distribution in laboratory incubation experiments (from Schindler et al., 1986).

from a relatively small soluble $^{35}SO_4^{2-}$ pool, which in turn was due to greater adsorption of $^{35}SO_4^{2-}$ in mineral horizons (Figure 4). Although it seems odd that organic S transformation rate constants should increase in the mineral soil, several lines of evidence suggest that these apparent trends are reasonable. David et al. (1982) found that sulfohydrolase activity was greater in the Bh horizon of a northern hardwood forest soil than in the Oa but much less than in the Oie. This pattern should be anticipated since the Oa horizon consists largely of residual, recalcitrant C. Moreover, in field $^{35}SO_4^{2-}$ amendment experiments, David and Mitchell (1985) found that 75% of the added ^{35}S which was converted to organic S, was found in mineral soil horizons.

Model application

Experimentally derived rate constants are applicable only to the limited set of experimental conditions under which they were derived. In order to apply them accurately to the ^{32}S cycle under field conditions, a detailed understanding of the effects of temporally and spatially variable parameters is necessary. Among these are the effects of temperature (Fitzgerald et al., 1983), moisture content, microbial activity, availability of other potentially limiting nutrients, and suitable substrate.

McGill and Cole (1981) advanced the hypothesis that C-S is mineralized largely as a by-product of C utilization as an energy source, whereas C-O-SO$_3$ is mineralized in response to metabolic demand for S and is retarded by end-product (SO_4^{2-}) inhibition. These concepts can be directly incorporated into a kinetic approach:

$$\frac{d[\text{C-O-SO}_3]}{dt} = R_{12}\,[\text{SO}_4^{2-}] - \frac{R_{21}\,[\text{C-O-SO}_3]}{K_{mi} + [\text{SO}_4^{2-}]} \tag{8}$$

$$\frac{d[\text{C-S}]}{dt} = R_{13}\,[\text{SO}_4^{2-}] - R_{31}\,[\text{C}]\,[\text{C-S}] \tag{9}$$

where: $[SO_4^{2-}]$, [C-O-SO$_3$], and [C-S] refer to labile S concentrations, K_{mi} is a half-saturation constant for the end-product inhibitor (SO_4^{2-}) and [C] refers to a labile organic carbon pool. However, note that when soluble SO_4^{2-} concentrations and labile carbon concentrations remain constant, these equations reduce to a first-order model.

Lacking quantitative information on the effects of these factors on S transformations, laboratory derived rate constants should be applied to field ^{32}S transformations only with great care. Mineralization of C-O-SO$_3$ and C-S, for instance, both occur from solid-phase constituents which are not uniformly mixed with freshly immobilized ^{35}S. McLaren et al. (1985) determined that only 5.9 to 11.8% of the ester sulfate fraction, 0.5 to 4.5% of the C-S fraction, and 2.8 to 6.3% of the total organic S fractions were involved in the short-term cycling of S, utilizing steady state values for $^{35}SO_4^{2-}$ incorporation. They noted that their values for the relative amounts of rapidly cycling S in unamended soils were comparable to estimates by Saggar et al. (1981) for biomass-S in unamended soils. Similar estimates can be made using the rate constants derived in this study by determining predicted equilibrium ^{35}S distribution based on mineralization to immobilization rate constant ratios (see Figure 2). Using this method, the fraction of the C-O-SO_3 pool involved in short-term cycling ranged from 2.1% for an Oa horizon to 8.5% for a Bsl horizon. The latter figure is very close to that calculated by McLaren et al. (1985) for their unamended mineral soil (8.4%). Estimates of a rapidly cycling pool of C-S were not attempted since few of these horizons approached equilibrium (ie. $R_{14} >> R_{41}$). Without independent estimates of the fraction of each organic ^{32}S pool involved in short-term cycling, it is incorrect to extend mineralization rate constants to the ^{32}S cycle.

For immobilization reactions, it is reasonable to assume that experimental rate constants derived for ^{32}S transformations are applicable to the ^{32}S cycle, since the isotope is completely mixed with the reactant, soluble SO_4^{2-}. A *hypothetical* calculation of the *daily gross* immobilization of S at the Hubbard Brook Experimental Forest is presented in Table 2. These projections suggest that as much as 0.38 kg S ha^{-1} day^{-1} may be immobilized into organic forms, predominantly C-O-SO_3, in surface organic and mineral horizons. Immobilization rates for the Bs2 horizon, which includes the bulk of the mineral soil, are unknown, but are probably very low (David and Mitchell, 1985). These projections for gross immobilization are much greater than average daily inputs of S in bulk deposition at HBEF (0.034 kg S ha^{-1} yr^{-1}; calculated from Likens et al., 1977). However, note that rates of immobilization are probably matched by mineralization rates, so that little net accumulation of organic S would necessarily occur. These laboratory incubation experiments are performed under nearly optimal conditions of temperature and moisture. As a result, these should be considered estimates of maximal daily gross S immobilization, which will decline with lower temperatures in winter, and soil drying in summer. Nevertheless, it can be concluded that during periods of optimal microbial activity, substantial quantities of S are cycled through organic forms.

These projections assume, of course, that reaction rates observed in laboratory incubation experiments were not grossly exaggerated by the effects of sample treatment. David and Mitchell (1985), in six week field incubation experiments, observed 41% of the added $^{35}SO_4^{2-}$ incorporated into organic S fractions, suggesting that organic S transformations can indeed cycle large quantities of soil S.

Conclusions

These experiments suggest that ^{35}S transformations can be modeled using reversible expressions that are depicted as first-order reactions. These rate expressions can potentially be applied to field conditions if adequate information on the effects of abiotic and biotic factors on S transfer rates is included with further quantification of reaction kinetics and advances in our

Table 2. Approximation of maximal daily rates of gross S immobilization at the HBEF for horizons in which immobilization rate constants have been derived. Inclusion volumes were calculated from a 21.7 m trench for stone volume (data courtesy of T. Siccama) and root volume (Wood, 1980). Soluble sulfate concentrations were taken from Schindler et al. (1986).

Horizon	Depth (cm)	Horizon weight (T ha^{-1})	Soluble sulfate (μg g^{-1})	R_{13} (day^{-1})	Ester sulfate immobilization (kg ha^{-1})	R_{14} (day^{-1})	Carbon-bonded S immobilization (kg ha^{-1})
Forest floor	-	60	16.9	0.016	0.016	.019	0.019
E	3.4	325	–	??	??	??	??
Bh	3.9	264	6.6	0.033	0.058	.004	0.007
Bsl	5.5	320	8.5	0.091	0.248	.013	0.035
Bs2	40.0	3,029	–	??	??	??	??
Total					0.322		0.061

ability to analytically determine labile organic S pools. Once available, this information will allow for the incorporation of organic S transformations into integrated models of ecosystem acidity transformations.

A hypothetical extension of these rate constants to field conditions suggested that large quantities of S cycle through organic fractions during the growing season when temperature and moisture conditions are conducive to rapid biological turnover. These transformations may buffer concentrations of SO_4^{2-}, thus delaying the transfer of associated acidity to surface waters and allowing neutralization to occur through basic cation release. This process may be an important factor in explaining why short-term temporal variations in surface water acidity are frequently more highly correlated with changes in NO_3^- even though SO_4^{2-} is the major anion (Johnson, et al., 1969; Driscoll and Schafran, 1984).

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References

Bettany, JR and JWB Stewart. 1983. Dynamics of organic sulphur in semi-arid agroecosystems. In: More, A.I. (ed), Sulphur-82: Proceedings of the International Conference, Vol. II, pp. 767–785. British Sulphur Corporation, London.

Chen CW, SA Gherini, JD Dean, RJM Hudson and RA Goldstein. 1984. Development and calibration of the integrated lake-watershed acidification study model, pp. 155–173 *In:* JL Schnoor (ed.) Modeling of Total Acid Precipitation Impacts, Acid Precipitation Series, V.9, Butterworth, Boston.

Christopherson N and RF Wright. 1981. Sulphate budget and a model for sulphate concentrations in stream water at Birkenes, a small forested catchment in southernmost Norway. Water Resources Research, 17(2):377–389.

David MB and Myron J Mitchell. 1985. Transformations of organic and inorganic sulfur: importance to sulfate flux in an Adirondack forest soil. Paper 85-3.5 In: Proceedings of the Air Pollution Control Association. 78th Annual Meeting, Detroit, Michigan. June 16–21, 1985.

David MB, MJ Mitchell and JP Nakas. 1982. Organic and inorganic sulfur constituents of a forest soil and their relationship to microbial activity. Soil Science Society of America Journal 46:847–852.

David MB, MJ Mitchell and SC Schindler. 1984. Dynamics of organic and inorganic sulfur constituents in hardwood forest soils. pp. 221–246 *In* EL Stone (ed.) Forest Soils and Treatment Impacts, Sixth North American Forest Soils Conference, Knoxville, TN, 1983.

Davis JA and JO Leckie. 1980. Surface ionization and complexation at the oxide/water interface. 3. Adsorption of anions. J. Colloid. Int. Sci. 74:32–43.

Dixon WJ 1981. BMDP Statistical Software. University of California Press, Berkeley. 726 p.

Dodgson KS, GF White and JW Fitzgerald. 1982. Sulfatases of Microbial Origin. Volume I. CRC Press Incorp., Boca Raton, Florida.

Driscoll CT and GC Schafran. 1984. Short-term changes in the base neutralizing capacity of an acidic Adirondack, New York lake. Nature 310:308–310.

Eaton JS, GE Likens and FH Bormann. 1980. Wet and dry deposition of sulfur at Hubbard Brook. pp. 69–75. *In:* TC Hutchinson and M Havas (eds.). Effect of Acid Precipitation on Terrestrial Ecosystems. NATO Conf. Series 1: Ecology 4. Plenum Publishing Corp.

Fitzgerald JW 1978. Naturally occurring organo sulfur compounds in soils. In: Nriagu JO (ed.), Sulfur in the Environment, Part II., Ecological Impacts, pp. 391–443. John Wiley and Sons, New York.

Fitzgerald JW, JT Ash, TC Strickland and WT Swank. 1983. Formation of organic sulfur in forest soils: a biologically mediated process. Canadian Journal of Forest Research 13:1077–1082.

Freney JR 1958. Determinations of water soluble sulfate in soils. Soil Science 86: 241–244.

Freney JR 1979. Sulfur transformations. pp. 536–544 *In* Fairbridge RW and Finkl CW (eds.) The Encyclopedia of Soil Science, Part 1: Physics, Chemistry, Biology, Fertility and Technology. Dowden, Hutchinson and Ross, Inc., Stroudsberg, PA.

Freney JR, GE Melville and CH Williams. 1971. Organic sulphur fractions labelled by addition of ^{35}S-sulphate to soil. Soil Biology and Biochemistry 3:133–141.

Fuller RD, MB David and CT Driscoll. 1985. Sulfate adsorption relationships in forested Spodosols of the northeastern U.S.A. Soil Science Society of America Journal 49:1034–1040.

Galloway JN and EB Cowling. 1978. The effects of precipitation on aquatic and terrestrial ecosystems: A proposed precipitation chemistry network. Journal of the Air Pollution Control Association 28:229–235.

Johnson DW and DW Cole. 1980. Anion mobility in soils: relevance to nutrient transport from forest ecosystems. Environment International 3:79–90.

Johnson DW, GS Henderson, DD Huff, SE Lindberg, DD Richter, DS Shriner, DE Todd and J Turner. 1982. Cycling of organic and inorganic S in a chestnut oak forest. Oecologia, 54:141–148.

Johnson DW and DE Todd. 1983. Relationships among iron, aluminium, carbon, and sulfate in a variety of forest soils. Soil Science Society of America Journal 47: 792–800.

Johnson KJ 1980. Numerical Methods in Chemistry. Marcel Dekker, Inc., New York. 503 pp.

Johnson NM, GE Likens, FH Bormann, DW Fisher and RS Pierce. 1969. A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. Water Resources Research 5:1353–1363.

Johnson NM, CT Driscoll, JS Eaton, GE Likens and WH McDowell. 1981. Acid rain, dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire. Geochimica et Cosmochimica Acta 45:1421–1437.

Kaplan SA, RE Weinfeld, CW Abruzzo and M Lewis. 1972. Pharmacokinetic profile of sulfoxazole following intravenous, intramuscular, and oral administration to man. Journal of Pharmacological Science 61:773–778.

Landers DH, MB David and MJ Mitchell. 1983. Analysis of organic and inorganic sulfur constituents in sediments, soils and water. International Journal of Environmental and Analytical Chemistry 14:245–256.

Likens GE, FH Bormann, RS Pierce, JS Eaton and NM Johnson. 1977. Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York.

Maynard DG, JWB Stewart and JR Bettany. 1983. Sulfur and nitrogen mineralization in soils compared using two incubation techniques. Soil Biology and Biochemistry 15: 251–256.

Maynard DG, JWB Stewart and JR Bettany. 1984. Sulfur cycling in grassland and parkland soils. Biogeochemistry 1:97–111.

McGill WG and CV Cole. 1981. Comparative aspects of cycling of organic C, N, S and P through soil organic matter. Geoderma 26:267–286.

McLaren RG, JI Keer and RS Swift. 1985. Sulphur transformations in soils using sulphur labelling. Soil Biology and Biochemistry 17:73–79.

Ralston ML, RI Jennrich, PF Sampson and FK Uno. 1979. Fitting pharmacokinetic models with BMDPAR. Technical Report No. 58. BMDP Statistical Software, Dept. of Biomathematics, Univ. of California, Los Angeles.

Rhodes DW 1957. The effect of pH on the uptake of radioactive isotopes from solution by a soil. Soil Science Society of America Proceedings 21:389–392.

Saggar S, JR Bettany and JWB Stewart. 1981a. Measurement of microbial sulfur in soil. Soil Biology and Biochemistry 13:493–498.

Saggar S, JR Bettany and JWB Stewart. 1981b. Sulfur transformations in relation to carbon and nitrogen in incubated soils. Soil Biology and Biochemistry 13:499–511.

Schindler SC 1984. Sulfur transformations and movement in an Adirondack forest soil. M.S. Thesis, SUNY Coll. of Environ. Sci. and Forestry, Syracuse, New York. 172 pp.

Schindler SC, MJ Mitchell, TJ Scott, RD Fuller and CT Driscoll. 1986. Incorporation of ^{35}S-sulfate into inorganic and organic sulfur constituents of two forest soils. Soil Science Society of America Journal 50:457–462.

Schnoor JL (ed.) 1984. Modeling of Total Acid Precipitation Impacts. Butterworth Publishers, Boston, Mass. 222 pp.

Shampine LF, HA Watts and SM Davenport. 1976. Solving nonstiff ordinary differential equations – the state of the art. SIAM Review 18:376–441.

Singh BR 1984. Sulphate sorption by acid forest soils: 3. Desorption of sulfate from adsorbed surfaces as a function of time, desorbing ion, pH, and amount of adsorption. Soil Science 138:346–353.

Strickland TC and JW Fitzgerald. 1984. Formation and mineralization of organic sulfur in forest soils. Biogeochemistry 1:63–78.