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Models of sulfur dynamics in forest and grassland ecosystems with emphasis on soil processes

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Abstract. The major S constituents in terrestrial ecosystems include inorganic SO_4^{2-}, C-bonded S and ester sulfate with the organic fractions constituting the major soil S pools. Conceptual models of S dynamics link inorganic SO_4^{2-} flux to organic sulfur transformations and other elements such as N and C. Mass balance models have been useful in ascertaining whether a system is at steady-state with respect to adsorption processes and/or nutritional demands of vegetation for S. Chemical equilibrium/surface complexation models have been used to evaluate the effects of a complex of factors, including effects of pH on SO_4^{2-} adsorption and precipitation; these models have not generally been integrated into ecosystem models of S dynamics. Models such as ILWAS, Birkenes, Storgama, Trickle-Down and MAGIC were developed to ascertain surface water acidification processes within watersheds; these models incorporated SO_4^{2-} adsorption in some formulation combined with hydrological considerations. None of these models explicitly treat organic S transformations and fluxes. In contrast, grassland ecosystem models detail organic S transformations, but give little attention to adsorption and hydrologic factors. More detailed simulation models of S transformations in forest and grassland soils have recently been developed, but these results have yet to be incorporated into ecosystem and watershed models.

Introduction

Sulfur plays an important role in the functioning of terrestrial ecosystems. It is required by all biotic components as a macronutrient necessary for protein formation (especially the amino acids methionine, cystine and cysteine) as well as other metabolic constituents such as the vitamins biotin and thiamine (Freney 1967; Fitzgerald 1978; Freney & Williams 1983). Deficiencies of this element may limit production as has been documented for agronomic (Tabatabai 1984), grassland (Bettany & Stewart 1983; Millard et al. 1985; Murphy et al. 1983) and forest (Turner & Lambert 1980) systems. Furthermore, oxidized S is a major constituent of acidic deposition and often partially regulates mineral acidity in soil solutions and surface waters. As a result, there has been recent concern over the deleterious impact of

Table 1. Comparison of the treatment of sulfur dynamics in forest and grassland ecosystem models.

Model (Reference)	General model type	Inorganic S dynamics	Organic S dynamics	Hydrology
(McGill & Cole 1981)	Conceptual (General soil)	Two phases (sold and soluble)	Linked to C and N dynamics	Not considered
(Bettany & Stewart 1983; Maynard et al. 1984)	Conceptual (Grasslands)	Adsorbed and occluded sulfate. Precipitated sulfide, elemental S, labile inorganic S	Extension of McGill & Cole (1981) and inclusion of microbial S, labile organic S stable organic S, plant uptake	Not considered
(David et al. 1984)	Conceptual (Forest soil)	Adsorbed sulfate, sulfate in solution	Carbon-bonded S, ester sulfate in solution and solid phases, mineralization, immobilization	Effects of solution transport
(Johnson 1984)	Mass balance (forest ecosystems)	Adsorbed sulfate, soluble sulfate, weathering	Organic constituents combined, plant uptake, decomposition	Leaching effects
MINEQL (Westhall et al. 1985)	Chemical Equilibrium	Complexation and precipitation of some inorganic sulfate constituents	Not considered	Not explicit part of model
ALCHEMI (Driscoll & Schecher 1985)	Chemical Equilibrium	Complexation and precipitation of some inorganic sulfate constituents; pH dependent anion adsorption	Not considered	Not explicit part of model
ILWAS (Chen et al. 1983)	Simulation (forest watershed	Sulfate adsorption fitted to linear isotherm; weathering based on stoichiometric release from minerals	Only mineralization from organic matter and plant uptake based on decomposition rates and plant uptake nutrient needs	Linked to hydrology sub-model
Birkenes (Christophersen & Wright 1981; Wright 1984)	Simulation (forest watershed	Soluble sulfate, combined effect of both organic and inorganic S in solid phase; linear adsorption assumed	See inorganic S	Linked to hydrology sub-model
Storgama Model (Christophersen et al. 1984)	Simulation (forest watershed; Modification of Birkenes	Formulation for removal of water soluble sulfate during snowmelt included which could include both organic and inorganic S transformation	See inorganic S	Linked to hydrology sub-model

Table 1. Contd.

Model (Reference)	General model type	Inorganic S dynamics	Organic S dynamics	Hydrology
Trickle-Down (Schnoor et al. 1984; Schnoor pers. comm.)	Simulation (watershed)	Sulfate adsorption treated as linear isotherm	Not considered	Linked to hydrology sub-model
MAGIC (Cosby et al. 1985)	Simulation (forest watershed	Chemical equilibria reactions used to describe relationships among dissolved and adsorbed ions; some coefficients must be ascertained for each watershed	Not considered	Linked to hydrology sub-model
(Coughenour et al. 1980)	Simulation (grassland)	Sulfate adsorption by Freudlich isotherm	Uptake of sulfate by Michaelis-Menten; elemental ratios in microbes and plants used for determining demand; mineralization function of uptake and microbial S content; ester sulfate formation not integrated directly into model	Linked to soil water sub-model
(Fuller et al. 1986)	Simulation (Spodosols)	Sulfate adsorption by kinetic formulation	Transformation rates of sulfate between ester sulfate and carbn-bonded S fitted to first order reactions	Not considered
(Hunt et al. 1986)	Simulation (grassland soil)	Not considered	Relationships between microbial activity, including esterases, in affecting formation of carbon-bonded S and ester sulfates	Not considered

elevated inputs of this element to various terrestrial systems, especially forests (Drablos & Tollan 1980; Hutchinson & Havas, 1980; Linthurst 1984).

The objectives of this paper are to: a) outline the major S constituents of terrestrial ecosystems; b) present conceptual models of S cycling; c) review some of the major approaches used to incorporate S dynamics in watershed and ecosystem models and assess their limitations; and d) suggest possible areas for advancement.

Sulfur constituents in terrestrial ecosystems

Sulfur is found in terrestrial systems in a wide variety of inorganic and organic forms, each of which may play characteristic biological and chemical roles. The chemical forms of S constituents have been well documented for the biota and include amino acids, sulphonium compounds, ester sulfates, vitamins, antibiotics, inorganic sulfides, and organic sulfides (Freney 1967; Fitzgerald 1978; Dodgson et al. 1982; Rennenberg 1984). In general, most of the organic S found in biotic components occurs as amino acids and their derivatives although ester sulfates may be common in various taxa including soil bacteria and fungi (Fitzgerald 1978; Dodgson et al. 1982). Inorganic sulfate can be a major S constituent of both higher plants and microorganisms, especially if S is in nutritional excess; however, only trace amounts of H_2S have been detected (Cuhel et al. 1981; Rennenberg 1984).

In contrast, individual organic S components in the abiotic portion of terrestrial systems have not been clearly defined. Moreover, these abiotic forms of S compose the major S pools within most terrestrial systems. The contribution of vegetation to the total S content of ecosystems is generally less than 50%, and even less than 10% in systems with elevated S loadings (Meiwes & Khanna 1981; David et al. 1984; Johnson 1984). Similarly, microbial S constitutes less than five % of total soil S, even in microbially active organic horizons (Strick & Nakas, 1984; Nakas 1986).

It is generally assumed that SO_4^{2-} is the major inorganic S species in terrestrial systems and there has been considerable effort focused on studying its distribution and dynamics. The retention or release of negatively charged SO_4^{2-} through soils is of special importance due to its interactions with soil particle surfaces and soluble cationic constituents. Although SO_4^{2-} is not chemically bound to most cationic species in soil solutions, anions and cations must move together to maintain charge balance. Thus, if SO_4^{2-} is retained in soils through adsorption to surface sites an equivalent quantity of cations must also be retained. Conversely, if SO_4^{2-} is transferred to surface

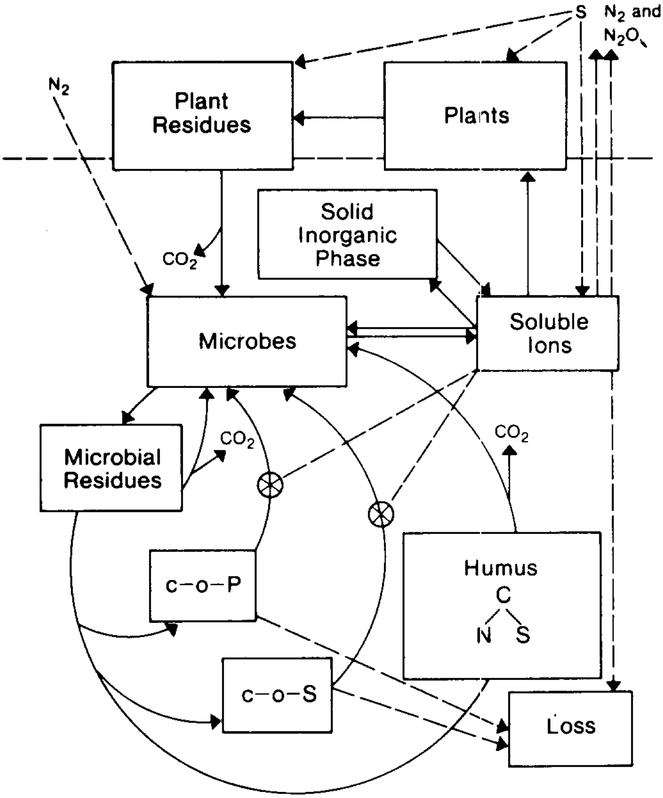


Fig. 1. Schematic illustration of interrelations of C, N, S and P cycling within soil–plant systems (From McGill & Cole 1981).

waters via leaching, basic cation nutrients (e.g. Ca^{2+}, Mg^{2+}) or acidic cations (e.g. H^+, Al^{n+}) must also be transferred (Harward & Reisenauer 1966; Johnson & Cole 1980).

The presence of other inorganic S species has generally not been evaluated except in soils subject to oxygen depletion or soils in xeric environments. Under conditions of oxygen deprivation, such as in submerged rice paddy soils, dissimilatory reduction of SO_4^{2-} to sulfide occurs (Connell & Patrick 1968, 1969). In arid regions, significant quantities of gypsum ($CaSO_4 \cdot H_2O$) and epsomite ($MgSO_4 \cdot 7H_2O$) can occur, in addition to small amounts of sulfide minerals (e.g. sphalerite, ZnS; chalcopyrite, $CuFeS_2$). In sedimentary rocks, such as shales and limestones, pyrites and marcasite (FeS_2) may be found and thus these minerals may be found in soils derived from such parent materials (Freney, 1967). Recent investigations of forest soils (David et al. 1983; Mitchell et al. 1986) and peats (Lowe & Bustin 1985) have shown that other inorganic S constituents (as operationally defined by ZnHCl reduction which recovers various inorganic S species including elemental S and thiosulfate) may occur and these "non-sulfate inorganic S" compounds may constitute a large fraction of the total inorganic S pool.

In almost all terrestrial ecosystems the vast majority of S is contained in organic forms in the soil. In most studies the organic S constituents have been operationally defined into a series of complex analytical fractions. The hydriodic acid (HI) reducible fraction of organic S, as defined by Freney (1958, 1961), is a result of the conversion of ester sulfates (C-O-S linkages) and sulfamates (C-N-S linkages) as well as a few organic sulfites into H_2S (Fitzgerald 1978). It is generally agreed that most of this organic HI-reducible S is in the form of ester sulfates (Freney & Williams 1983; Landers et al. 1983).

There is less agreement on the characterization of the residual organic S fractions which is not reduced by the HI-reduction procedure. Many investigators define this fraction as C-bonded S (Freney et al. 1970; Tabatabai 1982; Landers et al. 1983; Maynard et al. 1984). However, others (Lowe & Delong 1963; Biederbeck 1978) recommend that only the fraction of organic S reducible to H_2S by Raney nickel be considered C-bonded S or amino acid S. This latter method has been criticized because all of the C-bonded S is not reduced by this procedure (Freney et al. 1970; Tabatabai & Bremner 1972) and thus we will use the former definition of C-bonded S (total organic S minus HI reducible S).

Modeling sulfur transformation and transfer

Conceptual models

There have been several attempts to construct descriptive models of terrestrial S dynamics (Table 1). For example, McGill & Cole (1981) developed a conceptual model for linking C, N, P and S transformations in organic matter (Fig. 1). In their model the major organic S constituents, ester sulfates and C-bonded S, are treated separately. It was hypothesized that mineralization of ester sulfates is regulated by the biological requirement for S whereas C-bonded S mineralization is more closely associated with the concomitant mineralization of C and N for energy needs. The model does not encompass adsorption/desorption reactions of inorganic SO_4^{2-}.

In a more comprehensive conceptual model (Fig. 2) of S dynamics, Bettany & Stewart (1983) and Maynard et al. (1984) divided organic S fractions (both C-bonded S and ester sulfates) into labile, clay protected and

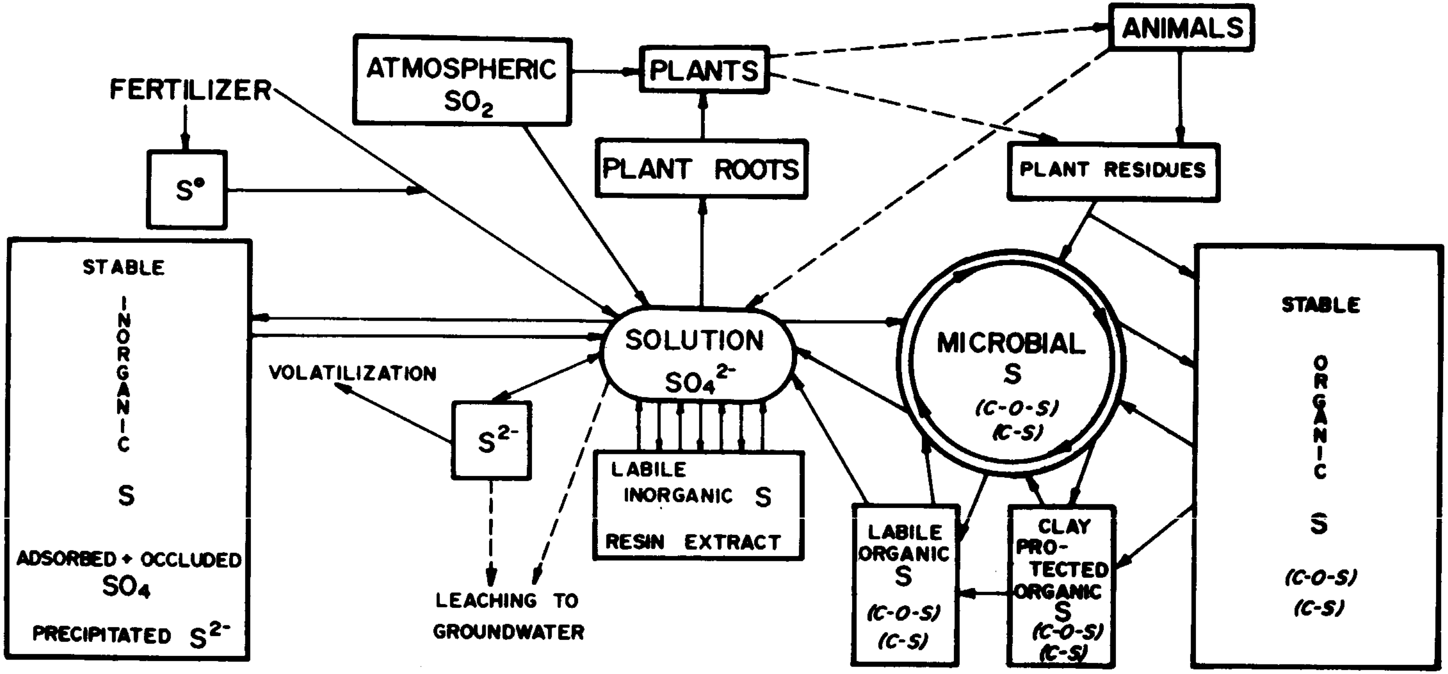


Fig. 2. A conceptual diagram of the main forms and transformations of sulfur in the soil-plant system. (From Maynard et al. 1984.)

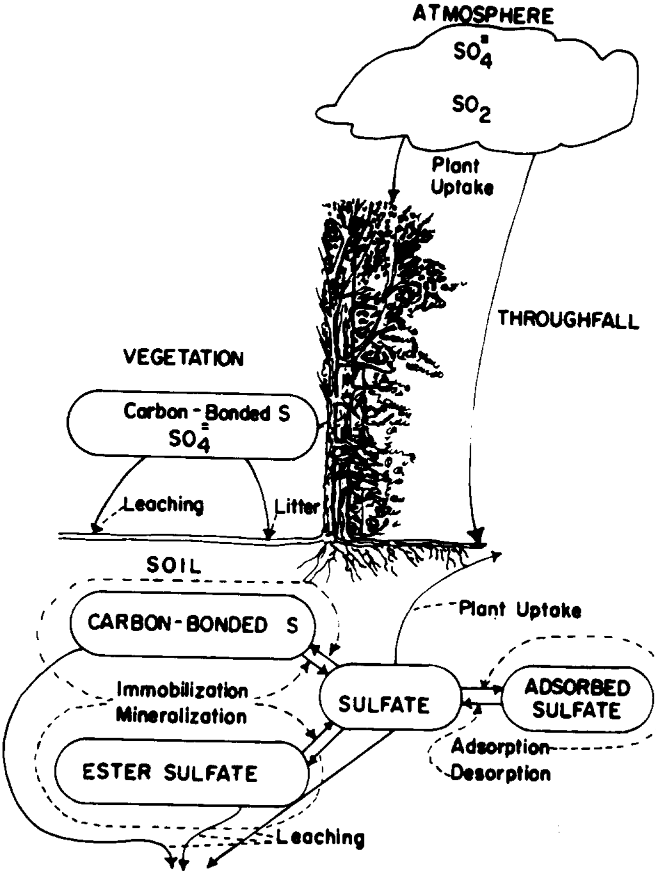


Fig. 3. A conceptual diagram of sulfur cycling in forest ecosystems. (From Nakas 1986.)

stable organic constituents and also included labile inorganic S, solution SO_4^{2-} and stable inorganic S (adsorbed and occluded SO_4^{2-} and precipitated sulfide). Experimental work using radioisotopes has begun to elucidate some of the transformations among these S constituents. For example, Maynard et al. (1984) found in grassland and agronomic systems that under conditions of excess SO_4^{2-} more of the S is incorporated into HI-reducible S (i.e. ester sulfates) versus C-bonded S. Conversely, when S was in short suply the transformation of SO_4^{2-} to C-bonded S was favored. These findings support the hypothesis of McGill & Cole (1981).

Conceptual models have also been employed for examining S interactions in forest ecosystems (Fig. 3). For example, such models have been useful in describing differences in mineralization – immobilization processes in organic versus inorganic soil horizons (David et al. 1983). In the more organic

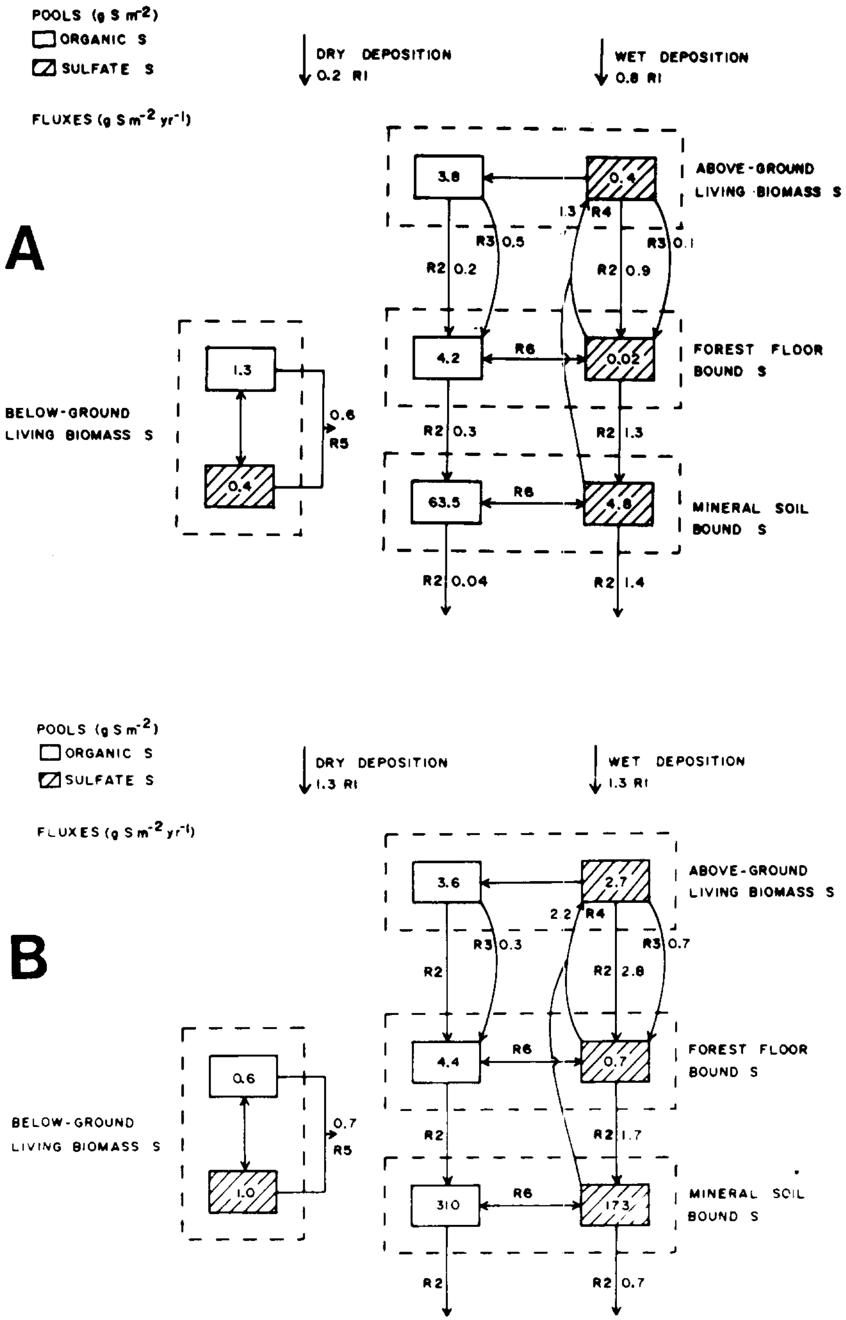


Fig. 4. Mass balance budget for two forest ecosystems (A: Northern Hardwood Forest in Northeast USA; B: Oak-Hickory Forest at Walker Branch Watershed, Tennessee). R1-atmospheric deposition; R2-leaching; R3-litterfall; R4-net plant uptake; R5-root litter and exudates: R6-mineralization-immobilization (from David et al. 1984).

rich Oa and Bh horizons of a hardwood forest soil, C-bonded S mineralization was associated with high mineralization rates of organic C. However, in the Bs1 and Bs2 horizons with low organic matter, SO_4^{2-} desorption and ester sulfate mineralization were of greater importances as sources of SO_4^{2-}. Work with S radioisotopes on the same soil has followed immobilization processes (Schindler et al. 1986) and has shown that ester sulfate turnover is more rapid than C-bonded S.

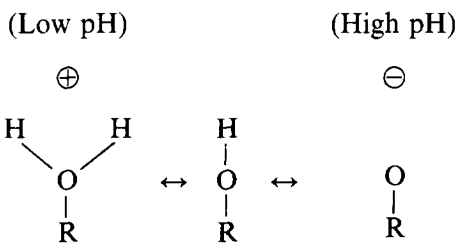
Mass balance models

Mass balance models (Fig. 4) have been useful in ascertaining whether a system is at steady state with respect to nutritional demands for S and SO_4^{2-} adsorption (Likens et al. 1977; Johnson et al. 1982a, b; Haines 1983; Johnson 1984). In glaciated Spodosols of the Northeastern U.S., S may act conservatively if there is no net biochemical retention of S and SO_4^{2-} is in "steady state" with respect to a weak adsorption complex (Johnson & Todd 1983; Fuller et al. 1985), such that S inputs to an ecosystem are matched by S outputs. In contrast, non-glaciated Ultisols of the Southeastern U.S. have high SO_4^{2-} adsorption capacities and exhibit net retention of atmospheric S inputs (Johnson 1984; Richter et al. 1983; Rochelle et al. 1987). However, it has recently been recognized that there is also significant cycling of S through various organic constituents within forest systems which may result in short–term retention or release of S (Swank et al. 1984; Schindler et al. 1986; David & Mitchell 1987). It is difficult to utilize annual mass balance information to ascertain how biotic S retention affects seasonal variations in S cycling or to predict long term changes in S dynamics in forest systems where biochemical S transformations dominate, especially if there are changes in S inputs.

Chemical equilibrium surface complexation models

One shortcoming evident in many models of ecosystem S transformations is their failure to account for pH-dependent SO_4^{2-} adsorption. Nodvin et al. (1986), for instance, found that Spodosol B horizons adsorbed substantially more SO_4^{2-} when acidified with HNO_3 and desorbed SO_4^{2-} when solution pH was raised. This factor may account for the observed negative correlations between $[H^+]$ and $[SO_4^{2-}]$ in streams draining the Hubbard Brook Experimental Forest in New Hampshire (Fuller et al. 1987). Hydrologic residence time, basic cation release, soil pCO_2 and N transformations appeared to exert more influence on soil solution pH than short-term variability in SO_4^{2-} flux, and thus ultimately affect seasonal variability in SO_4^{2-} concentrations through pH-dependent adsorption processes. Forest clearcutting, which results in stream acidification by stimulating nitrification and decreasing vegetation uptake of NO_3^-, may thus result in SO_4^{2-} retention (Fuller et al. 1987).

Sulfate is thought to adsorb largely to free (non-silicate bound) Al and Fe in mineral soil horizons (Johnson & Todd 1983; Fuller et al. 1985; Reuss & Johnson 1986). These constituents behave much like a weak acid/base system, in that they can consume or donate protons in response to changes in soil solution pH:



(1)

where ROH represents a hydroxyl group on a free Al or Fe surface (R). Protonation of surface sites at the oxide/water interface can be modeled using equilibrium constants, as can retention of adsorbing anions (Davis et al. 1978) on the positively charged surface:

$$ROH + H^+ + SO_4^{2-} \leftrightarrow ROH_2^+ - SO_4^{2-} \qquad (2)$$

$$ROH + 2H^+ + SO_4^{2-} \leftrightarrow ROH_2^+ - HSO_4^- \qquad (3)$$

Chemical equilibrium models, such as MINEQL (Westall et al. 1985) and ALCHEMI (Driscoll & Schecher 1985; Schecher & Driscoll 1987), have been used to evaluate complexation of constituents in solution (e.g. $AlSO_4^+$), precipitation of hydroxide, hydroxysilicate and hydroxysulfate mineral phases, and adsorption of anions such as SO_4^{2-}. These models typically use numerical methods such as a Newton-Raphson technique to solve the system of equilibrium equations while maintaining electroneutrality, mass balance and accounting for the effects of temperature and ionic strength on ion activity. Utilizing batch titration experiments, pH-dependent SO_4^{2-} adsorption was evaluated in a Bs2 horizon from a forested Spodosol in New Hampshire. This experiment was used to calibrate surface complexion constants in ALCHEMI (Driscoll & Schecher 1985; Schecher & Driscoll 1987) which was able to accurately assess SO_4^{2-} adsorption across a range of soil solution pH values.

Precipitation of aluminum hydroxy sulfate minerals such as jurbanite have also been hypothesized to control solution SO_4^{2-} and Al concentrations (Prenzel 1983). Analysis of lysimeter solutions from the Hubbard Brook Experimental Forest both prior to and following clearcutting have shown that soil solutions were undersaturated with respect to jurbanite, even though SO_4^{2-} was being retained through adsorption reactions (Fuller et al. 1987). However, in areas of Europe with high SO_4^{2-} deposition, lower solution pH, and higher Al concentrations in soil solution, precipitation of aluminum hydroxy sulfate minerals has been shown to control SO_4^{2-} concentrations (Prenzel 1983).

Simulation models

Forest ecosystems. There has been increasing interest in the use of S models as tools for interpreting the effects of acidic deposition. A major focus has been on linking S inputs to SO_4^{2-} concentrations in limnetic waters and the release of basic cations via weathering and exchange reactions, because it has been shown that there are correlations among these factors and lake acidification (Almer et al. 1978; Church & Turner 1986). Acidification models of watersheds have not generally detailed processes regulating S dynamics (Table 1), but rather model SO_4^{2-} flux based on measurements of wet deposition, estimated dry deposition, assumed mineralization rates, and approximated SO_4^{2-} adsorption-desorption relationships (Christopherson & Wright 1981; Christopherson et al. 1982). It has been proposed that these models may be useful in assessing how changes in atmospheric inputs of anthropogenic S will affect watershed responses to acidification processes (Church & Turner 1986; Reuss & Johnson 1986) and thus model predictions may ultimately affect regulatory decisions on the control of air pollutants.

ILWAS model. The ILWAS (Integrated Lake-Watershed Acidification Study) model (Fig. 5) was developed to simulate biogeochemical processes within a watershed to ascertain the role of acidic deposition on surface water chemistry (Chen et al. 1983; Gherini et al. 1985). The model divides the ecosystem into a series of connected homogeneous compartments including distinct soil layers. Litter decay and thus S mineralization was assumed to follow first order kinetics dependent on substrate mass with stoichiometric conversions to account for transformations from one stage to another. Litter decay followed four stages:

1. litter → fine litter
2. fine litter → humus + cations
3. humus → fulvic (organic) acid + NH_4^+ + SO_4^{2-} + H^+ + CO_2
4. fulvic (organic) acid → CO_2 + NH_4^+ + SO_4^{2-} + H^-

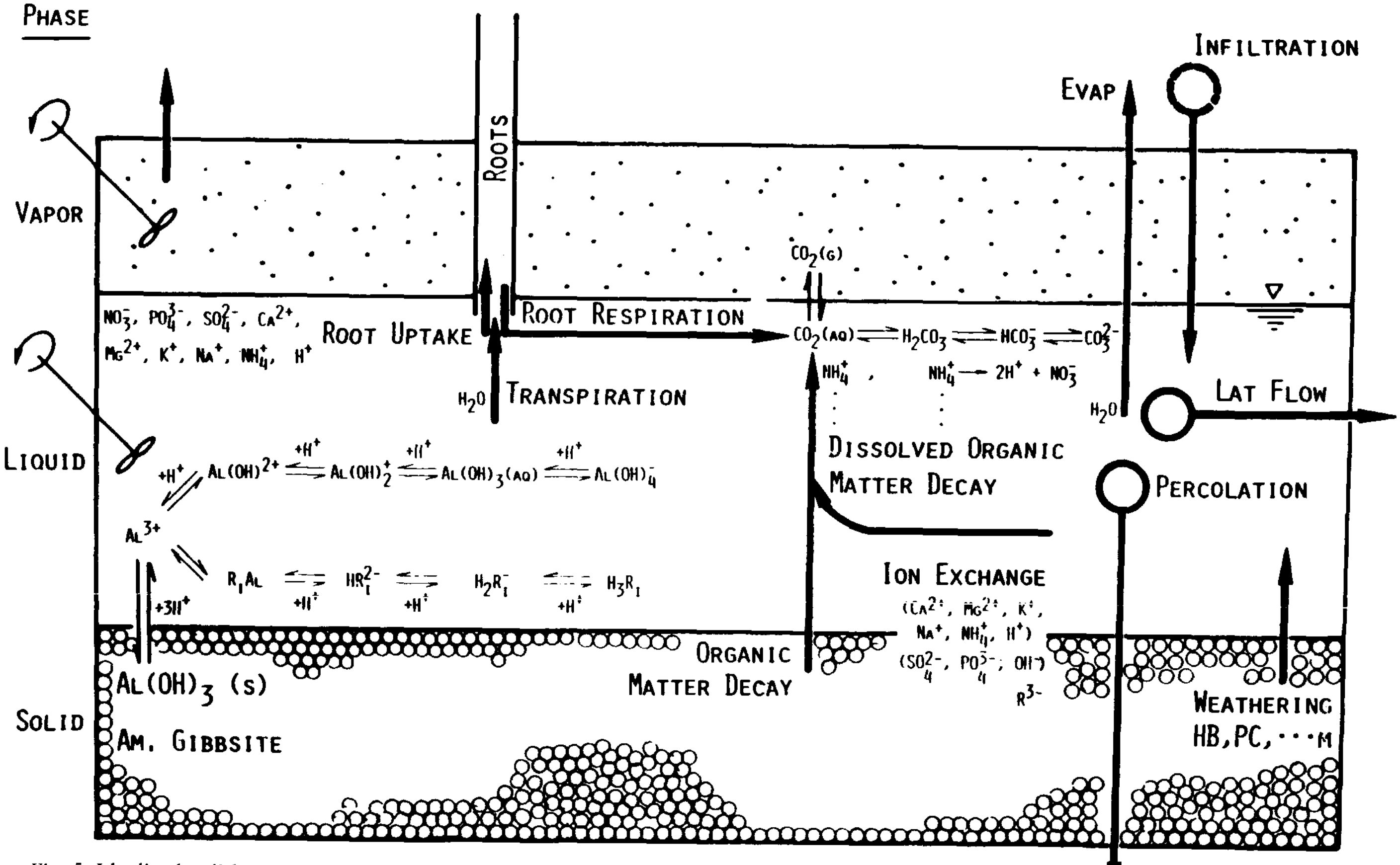


Fig. 5. Idealized soil layer showing major processes considered in ILWAS (from Gherini et al. 1985).

	Upper Reservoir	Lower Reservoir
H_2O	Precipitation, evapotranspiration, infiltration to lower reservoir, discharge to stream	Infiltration, evapotranspiration, discharge to stream
SO_4	Wet and dry deposition, adsorption/desorption, mineralization	Adsorption/desorption
Ca + Mg	Ion exchange	Release by weathering and adsorption/desorption
H^+	Ion exchange and equilibrium with gibbsite	Consumption by weathering, adsorption/desorption, equilibrium with gibbsite
Al^{3+}	Equilibrium with gibbsite	Equilibrium with gibbsite, adsorption/desorption

Fig. 6. Summary of Processes included in Birkenes model (from Wright 1984).

The effect of temperature on decomposition rate was modeled using an exponential relationship. Demand for any nutrient, including S, was a function of annual productivity indexed to a monthly nutrient demand. It was assumed that nutrient demand by higher plants is a function of the chemical composition of the bole and leaves. If the availability of any nutrient is below that needed, the uptake of nutrients is proportionally reduced. There is no mechanism for excess S uptake and speciation of S into organic and inorganic fractions in the plant. The relative importance of these internal plant processes depends on S availability and nutritional demands (Rennenberg 1984) and their contributions will affect the biogeochemical cycling of S (David et al. 1984). It was assumed in the ILWAS model that SO_4^{2-} adsorption fits a linear isotherm:

$$C = K \cdot C_s \tag{4}$$

where C = aqueous concentration of the anion; C_s = concentration of the anion on the solid; and K = an adsorption coefficient. Alterations of SO_4^{2-} adsorption associated with changes in pH, organic matter interference, or saturation of adsorption sites are not considered. Weathering was modeled using coefficients applied to the masses of individual mineral components and was assumed to occur stoichiometrically by chemical species. Element flux was linked to a hydrologic sub-model.

Birkenes model. Another model (Birkenes) developed for examining the effects of acidic deposition was used in Norway (Christophersen & Wright 1981; Wright 1984). Because of their importance in acidification chemistry and the need for simplicity, only the cations H^+, Mg^{++}, and Al^{+n} and the anion SO_4^{2-} were included in this model (Fig. 6). The Birkenes model is divided into two layers or reservoirs (Fig. 7). In the upper reservoir, wet and dry deposition, adsorption/desorption and mineralization of S were considered, while within the lower reservoir only SO_4^{2-} adsorption/desorption was included. It was assumed that:

— all S entering the catchment as wet deposition is SO_4^{2-};
— dry deposition includes SO_2 gas and SO_4^{2-} aerosols;
— S exits only as dissolved SO_4^{2-} in stream water.

Dry deposition was estimated using mean concentrations in the air multiplied by deposition velocity. It was stated by Christophersen & Wright (1981) that:

processes such as biological activity and mineralization of sulfur compounds thus cannot be considered quantitatively but are included indirectly in the model.

Their model assumes that SO_4^{2-} of atmospheric origin accumulating in the upper zone remains potentially water soluble. The aqueous concentration of SO_4^{2-} is only a function of the total amount of SO_4^{2-} in the solid phase as indicated by the following relationship, which may implicitly include organic S transformations as well as adsorption-desorption reactions:

$$C_a = K_a \cdot F_a \tag{5}$$

where K_a is a linear, equilibrium SO_4^{2-} adsorption-immobilization term in $m^2 \cdot l^{-1}$; C_a ($mg \cdot l^{-1}$) is solution SO_4^{2-} concentration; and F_a is the solid phase SO_4^{2-} concentration ($mg \cdot m^{-2}$). This formulation is the same as that used in the ILWAS model described previously. For the lower reservoir, it was assumed that SO_4^{2-} concentration follows an exponential path to a fixed equilibrium value (non-equilibrium adsorption) when inputs are absent.

Storgama model. The Birkenes model has been modified in subsequent formulations such as that applied to the Storgama watershed (Fig. 8; Christophersen et al. 1984). This model includes the removal of water soluble SO_4^{2-} during snowmelt which Christophersen et al. (1984) stated was "sulfate reduction/adsorption" but is probably better described as immobilization/adsorption because SO_4^{2-} can be incorporated into ester forms without being chemically reduced. A temperature parameter, which is only operative when drainage occurs (Fig. 9), controls the rate of reduction

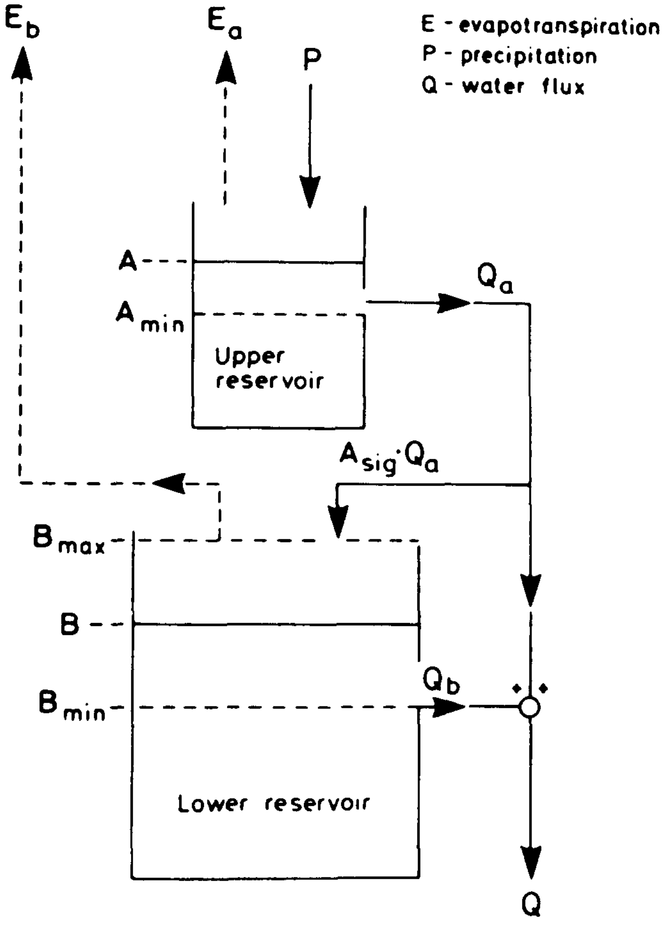


Fig. 7. Birkenes hydrologic submodel. Q^a and Q_b are drainage from upper (upper soil horizons) and lower (lower soil layers) reservoirs, respectively; E_a and E_b are evapotranspiration; P is precipitation; A_{sig} is a routing parameter (from Wright 1984).

which increases F_a (Eq. 5). It is assumed that reduction is dissimilatory and is associated with wet conditions. However, there was no evidence presented that this process occurred or that the soils have depressed redox conditions. It is more likely that decreases in soluble SO_4^{2-} can be accounted for by S immobilization which includes assimilatory as well as some dissimilatory processes. This model has been recently employed in examining elemental fluxes in a stream in Canada (Seip et al. 1985). Although the Storgama model may adequately simulate SO_4^{2-} flux in streams in specific watersheds during certain seasons, the model formulations for soil S dynamics are probably not accurate process level representations of the major S transformations and thus may not be broadly applicable.

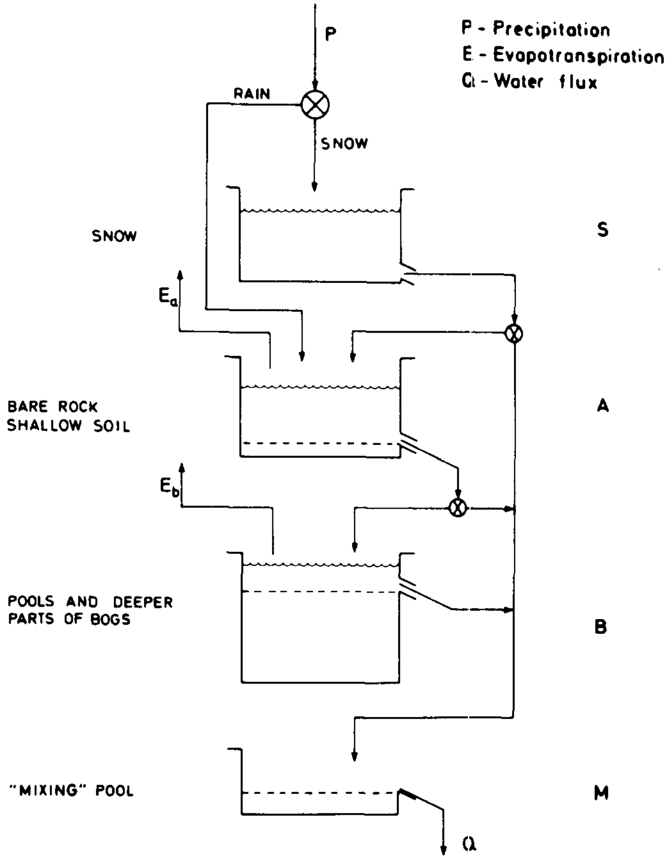


Fig. 8. Storgama hydrologic reservoir model; (from Christophersen et al. 1984).

Trickle-Down. The Trickle-Down model is based on the continuity of mass within a compartmentalized volume and was originally formulated to examine the effects of acidic deposition on seepage lakes in the upper Midwest US (Schnoor et al. 1984). Denitrification, sulfate reduction, SO_4^{2-} adsorption, NO_3^- uptake and chemical weathering reactions, all of which increase the acid neutralizing capacity, were combined within a single kinetic formulation for each compartment (snow, soil unsaturated zone, surface waters, groundwater aquifer and bedrock aquifer). Similarly, a general kinetic formulation for acidifying processes combining nitrification, sulfide oxidation, base cation uptake and soil exchange was also utilized. Alkalinity, acid generation and base generation were linked to a hydrologic sub-model. Thus, the original formulation did not include explicit considerations of organic S transformations or SO_4^{2-} adsorption (Schnoor et al. 1984). In its most recent form, however, (Schnoor, pers. comm.) SO_4^{2-} adsorption has

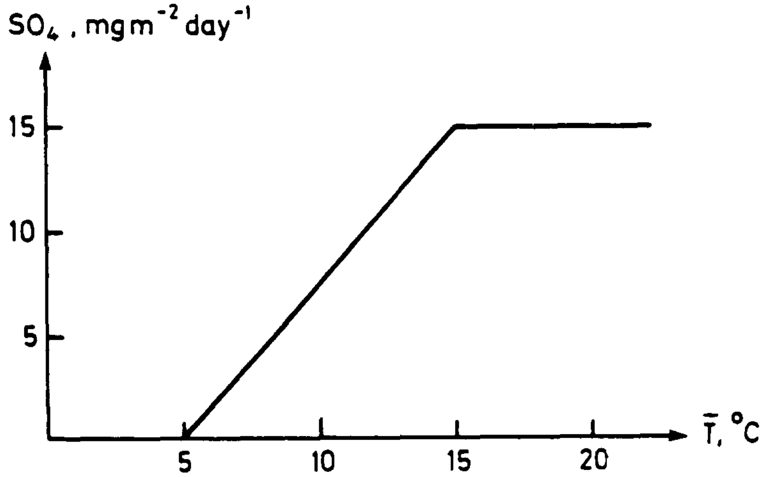


Fig. 9. Assumed relationship between mean daily temperature and daily amount of water-soluble sulphate reduced/adsorbed in the A-reservoir of the Storgama model. Reduction/adsorption only takes place when drainage occurs from reservoir. (From Christophersen et al. 1984.)

been incorporated as a simple linear function of solution SO_4^{2-} concentration.

MAGIC model. MAGIC (Model of Acidification of Groundwater in Catchments) uses a series of chemical equilibria reactions similar to those used by Reuss & Johnson (1985), describing relationships among dissolved and adsorbed ions in the soil-water system focusing on pH, alkalinity, base cations and Al relationships (Cosby et al. 1985a, b, c). A major objective of the model is to utilize a lumped approach for predicting surface water acidification which incorporates as little detail as necessary in both the inclusion of biogeochemical reactions (i.e. no biological transformations are included) as well as the spatial and temporal scales (i.e. soil chemical processes are uniform with depth) within a watershed. MAGIC uses 21 parameters of which 16 are thermodynamic constants derived from literature values. There are also cation selectivity coefficients and a solubility constant for the solid Al phase which must be estimated for each catchment being studied and the results linked to a hydrologic sub-model. It is assumed that SO_4^{2-} adsorption follows a Langmuir isotherm:

$$E_s = E_{mx} \cdot 2 \cdot [SO_4^{2-}]/(C + 2 \cdot [SO_4^{2-}]) \qquad (6)$$

where E_s = adsorbed SO_4^{2-} concentration, E_{mx} is the maximum adsorption capacity of the soil; $[SO_4^{2-}]$ = solution SO_4^{2-} concentration; and C = half-saturation constant for the adsorption process.

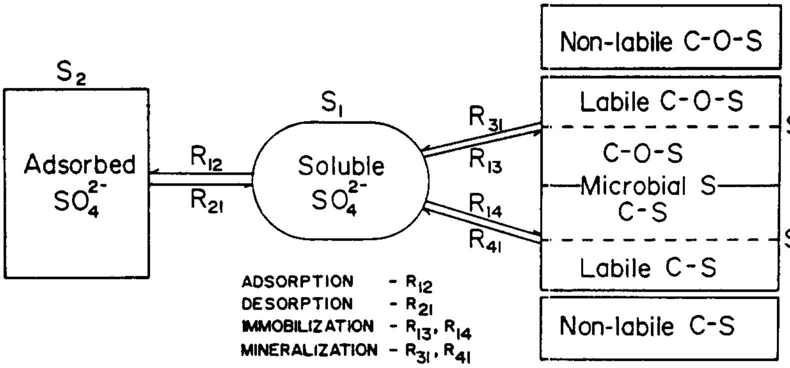


Fig. 10. A conceptual model of S transformations occurring in a forest soil horizon. $S_{1\text{-}4}$ refer to S pools used in modeling S transformations. R_{ij}'s refer to reaction rate constants. (From Fuller et al. 1986.)

The relationship between adsorbed and dissolved sulfate has been utilized in formulating a model which is a subset of the larger, more comprehensive MAGIC model. This simplified model has been used for predicating changes in acidic deposition inputs and surface water sulfate concentration (Cosby et al. 1986; Hornberger et al. 1986). It is recognized that neither the MAGIC model nor its simplified version explicitly consider transformation of organic S, pH-dependent SO_4^{2-} adsorption or organic matter blockage of adsorption sites and thus these models serve as a "baseline" case which can be compared with more complex formulations (Cosby et al. 1986). In addition, biologically mediated processes such as microbial immobilization and plant uptake of sulfate may be included implicitly as part of the non–linear asymptotic storage represented by the adsorption isotherm.

Fuller et al. (1986) model. For quantitatively assessing transformation rates of S constituents in forested Spodosols, Fuller et al. (1986) developed a simulation model utilizing a set of three reversible, first-order reactions formulated as differential equations which incorporated transfers among soluble SO_4^{2-}, adsorbed SO_4^{2-}, ester sulfate and C-bonded S (Fig. 10). Model calibration was performed using a numerical integration routine for the system of differential equations, combined with least squares fitting of kinetic rate constants for individual soil horizons (Oa, Bh and Bs1) using $^{35}SO_4^{2-}$ incubation experiments from Schindler et al. (1986). The model was able to account for most of the temporal variation in the interconversions among the four ^{35}S pools (Fig. 11). The results of the model simulation concur with previous studies which have ascertained that only a small portion of the organic S pool is rapidly cycled through labile forms

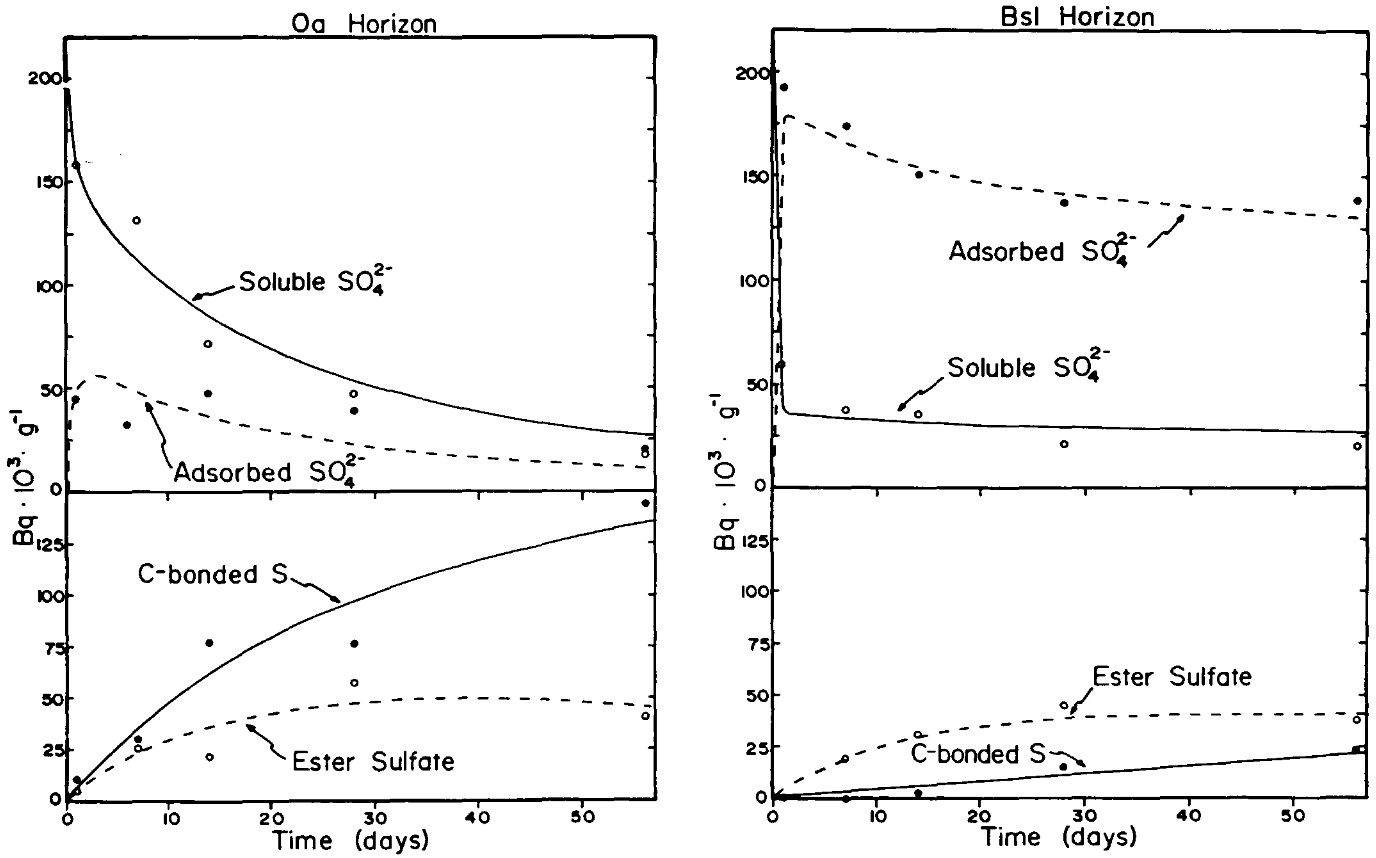


Fig. 11. Model simulation of ^{35}S reaction kinetics in a Huntington Forest Oa horizon (above) and Hubbard Brook Bs1 horizon (below). Solid lines refer to model simulations. (From Fuller et al. 1986.)

(McLaren et al. 1985). The results also indicate that analytical constraints in distinguishing labile and recalcitrant organic S fractions within the ester sulfate and C-bonded S pools limit our ability to quantify organic S dynamics.

The importance of these labile pools in affecting S transformation rates was demonstrated by Schindler (1984) who included leaching as a factor in examining the transfer of $^{35}S\text{-}SO_4^{2-}$ in various horizons of the same soil used by Fuller et al. (1986a) and Schindler et al. (1986). In laboratory experiments in which the soils from different horizons were subjected to leaching of a simulated soil solution, all of the C-bonded S formed from SO_4^{2-} immobilization was leached from the soil as organic S (Fig. 12, Schindler 1984). Under field conditions it can be hypothesized that this soluble organic S would be deposited in illuvial B horizons. Confirmation of this hypothesis has been obtained from soil solutions sampled by lysimeters at the Huntington Forest (New York) in which transfer of organic S from O horizons with subsequent deposition and/or mineralization in the mineral B horizons was observed (David et al. 1984). Significant (12–19% of total S) transport of organic S within streams of the Adirondacks of New York (David & Mitchell 1985) and in an alpine watershed in Alberta, Canada (Mitchell et al. 1986) has also been shown.

Grassland models. Various simulation models of grassland ecosystems have been generated to predict primary production and its linkage to soil processes (Innis 1978; McGill et al. 1981; Van Veen & Paul 1981; Hunt & Parton 1986). In general these models have concentrated on predicting changes in C and N constituents since these elements have a major role in regulating nutrient dynamics and productivity in grassland ecosystems. However, S can also be a limiting nutrient to grassland ecosystems in various locations throughout the world (Murphy et al. 1983; Tabatabai 1984; Maynard et al. 1984) and thus the inclusion S dynamics in models of these ecosystems may be essential. Such models can serve to assess the needs for S fertilization and to determine the influence of S from atmospheric deposition on ecosystem processes.

Sulfur model for mixed prairie. Coughenour et al. (1980) developed a simulation model of some of the major factors affecting S fluxes in a grassland ecosystem in a mixed prairie (Fig. 13). Sulfate is removed from solution by the biota following Michaelis-Menten kinetics. Rate of SO_4^{2-} uptake, f_3, is influenced by the effects of soil water and temperature on microbial metabolism and on the microbial demand for S as determined by the C/S ratio such that:

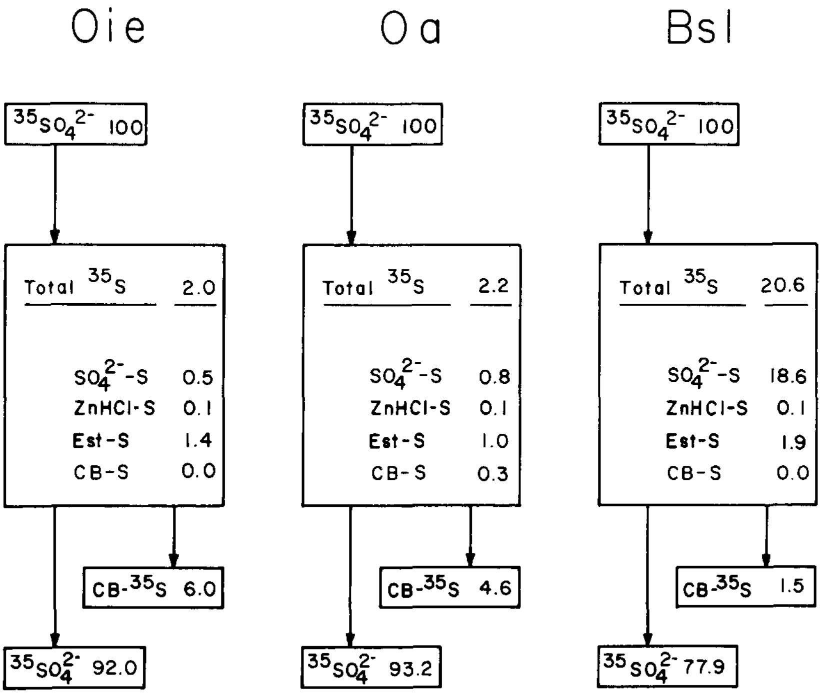


Fig. 12. Percentage of ^{35}S-activity in simulated soils solution and sulfur constituents after 20 week mineralization experiment for three soil horizons; upper compartments = ^{35}S added; middle compartments = ^{35}S in soil; lower compartments = ^{35}S leached. [SO_4-S = sulfate; ZnHCl-S = Zn HCl reducible S; Est-SO_4 = ester sulfate; CBS = carbon bonded S](from Schindler 1984).

$$a_3 = E_m(T) \cdot E_m(W) \cdot E_u(CS_m) \quad \text{and} \tag{7}$$

$$f_3 = a_3 \cdot C_m \cdot V_{max} \cdot [SO_4]/(K_m + [SO_4]) \tag{8}$$

where a_3 = effect of temperature (T); water (W) and C/S ratio (CS_m); V_{max} = maximum uptake rate; $[SO_4]$ = concentration of SO_4^{2-} in soil solution; C_m = microbial biomass; K_m = half-saturation constant.

Excessively high microbial S pools and model instability resulted from the use of published values of V_{max} and K_m and possibly from the relatively large simulation interval of one day. This interval is greatly in excess of the fast turnover rates of microbial S (Fitzgerald et al. 1982; Strickland et al. 1984). Consequently, model constants were tuned to produce more reasonable C/S ratios.

Net mineralization of S was modeled as a function of microbial death formulated in a "decomposer submodel" and the release of S is dependent

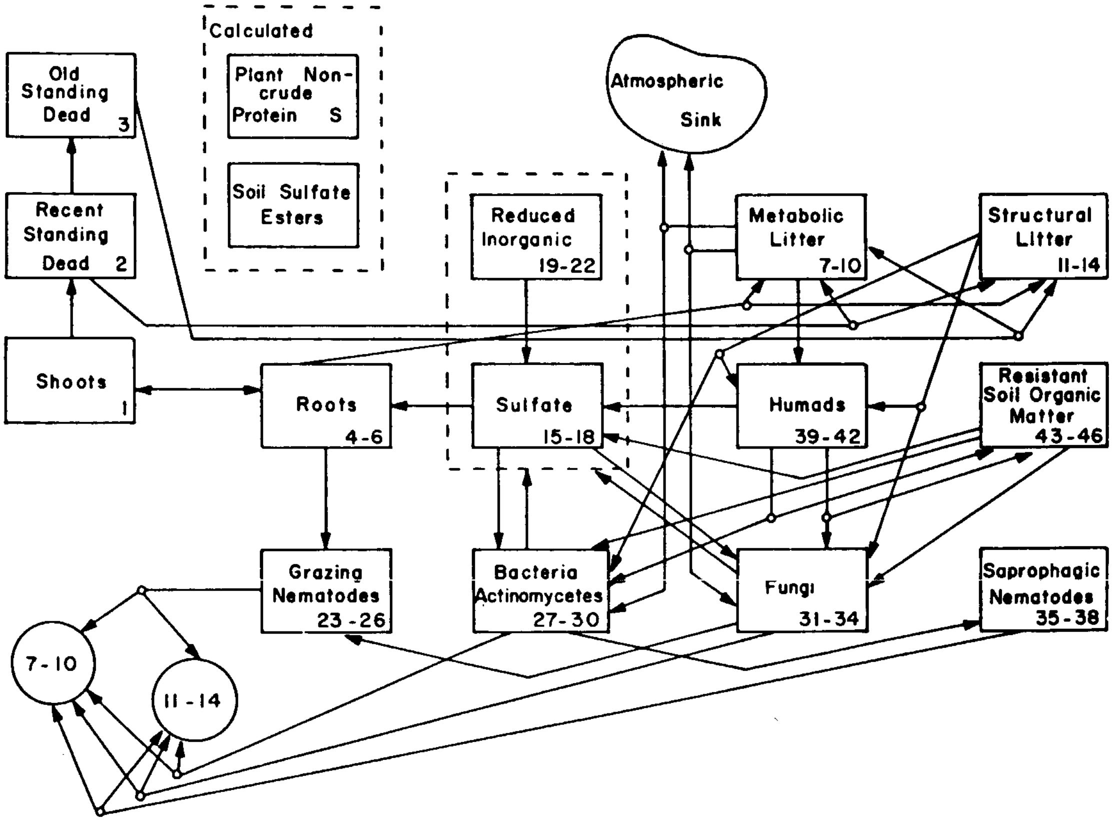


Fig. 13. Flow diagram showing structure of grassland sulfur cycle model of Coughenour (1981).

on a fixed C/S ratio. In the model construction it was recognized that it is difficult to predict mineralization processes unless the biochemical structure of a substrate is known. Nevertheless, mineralization was modeled as being affected by the similar factors which affect uptake (Eq. 7). The net mineralization rate, f_4, was a function of the maximum uptake rate (V_{max}) and the microbial S content (S_m) such that net mineralization was the amount of S in excess of biotic demand. It was assumed that the product of mineralization was either SO_4^{2-} or sulfide depending on degree of aeration and the oxidation of sulfide to SO_4^{2-} was controlled by soil aeration and bacterial metabolism. Volatilization of S during decomposition was formulation as a fraction of litter decomposition with a small decrease with declining aeration. The dynamics of ester sulfates were not integrated into the model; instead the amount of ester sulfate present was a function of total S and total C using a regression approach.

The model includes SO_4^{2-} adsorption-desorption as formulated by the Freudlich isotherm:

$$S = b[SO_4^{2-}]^{1/n} \tag{9}$$

where S is the amount of SO_4^{2-} adsorbed; and b and n are empirical constants. The Freudlich isotherm was preferred to a Langmuir isotherm because no adsorption maximum was found and increasing concentrations of SO_4^{2-} in solution seemed to activate additional adsorption sites. Since adsorption constants were determined empirically, it is possible that the results were confounded by biological immobilization process.

Similar formulations of this model have been used for examining the effects of SO_2 emissions on grassland systems (Coughenour 1981; Heasley et al. 1984). In the soil process sub-model, the major assumption is that most C, N and S reactions occur in parallel. Soil organic matter was divided into slowly decomposing, low-N-content substrates and high-N-content substrates. Utilization of these substrates was dependent on the physiological states of the microbiota as a function of their C:N, C:S, N:S ratios, and on soil temperature and moisture (McGill et al. 1981). Uptake of S and N by plants was assumed to be a function of soil solution concentrations of SO_4^{2-}, NH_4^+, or NO_3^- and followed Michaelis-Menten kinetics modified by soil temperature, soil moisture and root content of labile S and N. S content of tissues in plants was based on fixed C:S ratios and varied with age. There was no attempt to model differences between abiotic and biotic S transformations in the soil or to fractionate S into inorganic and organic constituents.

Hunt et al. (1986) model. In a somewhat analogous approach to Fuller et al. (1986a), Hunt et al. (1986) have developed a simulation model based on experimental additions of cellulose and $^{35}S\text{-}SO_4^{2-}$ to soil. Major differences in the model by Hunt et al. (1986) were that it was derived for a grassland soil and the actual role of microbial activity, including esterase production, was formulated explicitly in the model structure. Their model reflected the importance of fungal ester sulfates as labile storage forms under conditions of excess S. The differential roles of bacteria versus fungi were delineated in the model based on their chemical composition and elemental ratios. This model did not include formulations for studying the effects of sulfate adsorption or the role of leaching in S dynamics.

Limitations of current models on sulfur dynamics

Models of S dynamics in forest and grassland ecosystems have often been developed for different purposes and subsequently have had different emphases (Table 1). The role of hydrology has been a major focal point in ecosystem research of forested watersheds (Likens et al. 1977; Waring & Schlesinger 1985). The importance of the linkage between the biogeochemistry of forested catchments and surface water acidification has been clearly established (Church & Turner 1986). Hence, there has been considerable focus on examining the linkage of inorganic SO_4^{2-} dynamics to hydrological effects and the resultant role of S in acidification processes. The contribution of organic S in altering S flux has received less attention. In contrast, models of grassland ecosystem S dynamics have often considered explicitly the importance of microbial S transformations and biochemical linkages with other elements, especially N and C. These biological transformations play an important role in regulating S availability to grassland and agronomic systems where S deficiencies (Tabatabai 1984) are of more concern than in most forest ecosystems. In grassland models, the linkage of hydrological and S relationships has not been emphasized since most of these systems experience little net S export via leaching.

The importance of organic and inorganic S transformations in regulating soil S dynamics in various ecosystems will only be ascertained when factors such as temperature, moisture, plant uptake, pH and substrate type are incorporated into analytical and simulation models. For example, although it has been shown that SO_4^{2-} can be rapidly incorporated into organic S fractions (David & Mitchell 1986; Maynard et al. 1984; McLaren et al. 1985; Schindler et al. 1986; Swank et al. 1984; Strickland & Fitzgerald 1984), it has also been demonstrated that a fraction of the organic S is rapidly mineralized (David et al. 1983; Fitzgerald & Andrew 1984; Fitzgerald et al. 1984). If these immobilization and mineralization rates are nearly equal and sulfate adsorption is in equilibrium (Fuller et al. 1986), there is little net accumulation or loss of S from the soil. There is little information on these actual rates under field conditions and thus it is difficult to ascertain how either seasonal or longer term changes in soil conditions affect these processes.

It is difficult to parameterize and evaluate models which predict long term changes in sulfur constituents of ecosystems since there is a general absence of accurate measurements of these constituents and related parameters over extended periods (Hornberger et al. 1986). In studies examining the total flux of S within forest ecosystems it is generally assumed that the organic S pools are at steady state and thus SO_4^{2-} is acting as a conservative ion or is affected only by adsorption/desorption processes (Johnson 1984). Under conditions in which SO_4^{2-} adsorption/desorption reactions dominate S fluxes, as has been assumed for some forest ecosystems (Johnson et al. 1980), small deviations from this assumption would have little effect on estimating watershed S dynamics. However, when organic S transformations constitute a major portion of S flux, as has been suggested for some forest systems (David et al. 1984; Swank et al. 1984) and most grassland and agronomic systems (Bettany & Stewart 1983; Maynard et al. 1984; Hunt et al. 1986) any imbalance in S immobilization-mineralization reactions would have a substantial effect on the biogeochemical cycling of this element.

To further our understanding of factors regulating the biogeochemistry of S in terrestrial ecosystems it is important to ascertain the relative importances of all the major processes, including organic S transformation in addition to hydrology, SO_4^{2-} adsorption and/or solubility, and plant uptake processes and to compare these processes across a range of ecosystem types. The same process level formulations of organic and inorganic S transformations should be incorporated into both grassland and forest ecosystem models to ascertain the relative contributions of specific processes (e.g. biochemical versus geochemical) and various parameters such as hydrological regimes, land use patterns, and atmospheric sulfur inputs in regulating S biogeochemistry.

In addition, experimental manipulations of ecosystems, including S addition and exclusion, will be useful in refining and testing models of S dynamics and quantifying the linkage of S to the cycling of other elements.

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References

Almer B., W. Dickson , C. Ekstrom & E. Hornstrom (1978) Sulfur pollution and the aquatic ecosystem. In: J.O. Nriagu (Ed) Sulfur in the Environment. Part II. Ecological Impacts (pp 271–311). John Wiley and Sons, New York

Bettany, J.R. & J.W.B.Stewart (1983) Dynamics of organic sulphur in semi-arid agroecosystems. In: A.I. More (Ed) Sulphur-82: Proceedings of the International Conference. Vol II (pp 767–785). British Sulphur Corporation, London

Biederbeck, V.O. (1978) Soil organic sulfur and fertility. In: M. Schnitzer & S.U. Khan (Eds) Soil Organic Matter (pp 273–310). Elsevier Sci Publ, New York

Chen, C.W., S.A. Gherini, R.J.M. Hudson, & J.D. Dean (1983) The integrated lake-watershed acidification study. Vol I. Model principles and application procedures. EPRI Report EA-3221, Vol I. Res Proj 1109–5

Christophersen, N. & R.F. Wright (1981) Sulfate budget and a model for sulfate concentration at Birkenes, a small forested catchment in southernmost Norway. Water Resources Research 17: 337–389

Christophersen, N., L.H. Dymbe, M. Johannssen & H.M. Seip (1984) A model for sulphate in streamwater at Storgama, Southern Norway. Ecological Modelling 21: 35–61

Christophersen, N., H.M. Seip & R.F. Wright (1982) A model for streamwater chemistry at Birkenes, Norway. Water Resources Research 18: 977–997

Church, M.R. & R.S. Turner (Eds)(1986) Factors affecting the long-term response of surface waters to acidic deposition: state-of-the-science. U.S. Environmental Protection Agency Report, Corvallis, Oregon

Connell, W.E. & W.H. Patrick Jr (1968) Sulfate reduction in soil: effects of redox potential and pH. Science 59: 86–87

Connell, W.E. & W.H. Patrick Jr (1969) Reduction of sulfate to sulfide in waterlogged soil. Soil Science Society of America Proceedings 33: 711–714

Coughenour, M.B. (1981) Relationship of SO_2 dry deposition to a grassland sulfur cycle. Ecological Modelling 13: 1–16

Coughenour, M.B., W.J. Parton, W.K. Lauenroth, J.L. Dodd & R.G. Woodmansee (1980) Simulation of a grassland sulfur-cycle. Ecological Modelling 9: 179–213

Cosby, B.J., G.M. Hornberger & J.N. Galloway (1985a) Modeling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. Water Resources Research 21: 51–63

Cosby, B.J., G.M. Hornberger, J.N. Galloway & R.F. Wright (1985b) Time scales of catchment acidification. Environmental Science and Technology 19: 1144–1149

Cosby, B.J., R.F. Wright, G.M. Hornberger & J.N. Galloway (1985c) Modeling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. Water Resources Research 21: 1591–1601

Cosby, B,J,, G.M. Hornberger, R.F. Wright & J.N. Galloway (1986) Modeling the effects of acid deposition: control of long term sulfate dynamics by soil sulfate adsorption. Water Resources Research 22: 1283–1291

Cuhel, R.L., C.D. Taylor & H.W. Jannasch (1981) Assimilatory sulfur metabolism in marine microorganisms: sulfur metabolism, protein synthesis and growth of *Pseudomonas halodurans* and *Alteromonas luteoviolaceus* during unperturbed batch growth. Arch Microbiol 130: 8–13

David, M.B., S.C. Schindler, M.J. Mitchell & J.E. Strick (1983) Importance of organic and inorganic sulfur to mineralization processes in a forest soil. Soil Biology and Biochemistry 15: 671–677

David, M.B., M.J. Mitchell & S.C. Schindler (1984) Dynamics of organic and inorganic sulfur constituents in hardwood forest soils. In: E.L. Stone (ed) Forest Soils and Treatment Impacts (pp 221–345). Proceedings of the Sixth North American Soils Conference. The University of Tennessee, Knoxville, Tenn

David, M.B. & M.J. Mitchell (1985) Sulfur constituents and cycling in waters, seston, and sediments of an oligotrophic lake. Limnology and Oceanography 30: 1196–1207

David, M.B. & M.J. Mitchell (1987) Transformation of organic and inorganic sulfur: importance to sulfate flux in an Adirondack Forest Soil. Journal Air Pollution Control Federation 37: 39–44

Davis, J.A., R.O. James & J.O. Leckie (1978) Surface ionization and complexation at the oxide/water interface. I. Computation of electrical double layer properties in simple electrolytes. J Colloid Interface Sci 63: 480–499

Dodgson, K.S., C.F. White & J.W. Fitzgerald (1982) Sulfatases of Microbial Origin. Vol I. CRC Press, Boca Raton, Florida

Drablos, D. & A. Tollan (Eds)(1980) Ecological impact of acid precipitation. Proceedings of an International Conference, Sandefjord, Norway. SNSF Project, Norway

Driscoll, C.T. & W.D. Schecher (1985) Nature and rates of aluminum removal in acidic surface waters. In: Comparative Interregional Analysis of Aluminum Biogeochemistry in Forest Watersheds Exposed to Acidic Deposition (pp 107–128). EPRI Prog Report 2365-01, Palo Alto, Ca

Fitzgerald, J.W. (1978) Naturally occurring organosulfur compounds in soil. In: J.O. Nriagu (Ed) Sulfur in the Environment. Part II. Ecological Impacts (pp 391–443). John Wiley and Sons, New York

Fitzgerald, J.W. & T.L. Andrew (1984) Mineralization of methionine sulphur in soils and forest floor layers. Soil Biology and Biochemistry 16: 565–570

Fitzgerald, J.W., T.L. Andrew & W.T. Swank (1984) Availability of carbon-bonded sulfur for mineralization in forest soils. Canadian Journal of Forest Research 14: 839–843

Fitzgerald, J.W., T.C. Strickland & W.T. Swank (1982) Matabolic fate of inorganic sulphate in soil samples from undisturbed and managed forest ecosystems. Soil Biology and Biochemistry 14: 529–536

Freney, J.R. (1958) Determination of water-soluble sulfate in soils. Soil Science 86: 241–244

Freney, J.R. (1961) Some observations on the nature of organic sulphur compounds in soil. Australian Journal of Agricultural Research 12: 424–432

Freney, J.R. (1967) Sulfur-containing organics. In: A.D. McLaren & G.H. Peterson (Eds) Soil Biochemistry (pp 229–259). Marcel Dekker, New York

Freney, J.R., G.E. Melville & C.H. Williams (1970) The determination of carbon bonded sulfur in soil. Soil Science 109: 310–318

Freney, J.R. & C.H. Williams (1983) The sulphur cycle in soil. In: M.V. Ivanov & J.R. Freney (Eds) The Global Biogeochemical Sulphur Cycle (pp 129–201). SCOPE 19. John Wiley and Sons, Chichester

Fuller, R.D., M.B. David & C.T. Driscoll (1985) Sulfate adsorption relationships in some forested Spodosols of the northeastern U.S. Soil Science Society of America Journal 49: 1034–1040

Fuller, R.D., C.T. Driscoll, S.C. Schindler & M.J. Mitchell (1986a) A simulation model of sulfur transformations in forested Spodosols. Biogeochemistry 2: 313–328

Fuller, R.D., C.T. Driscoll, G.B. Lawrence & S.C. Nodvin (1986b) Processes regulating sulfate flux after whole-tree harvesting. Nature 325: 707–710

Gherini, S.A., L. Mok, R.J.M. Hudson, G.F. Davis, C.W. Chen & R.A. Goldstein (1985) The ILWAS model: formulation and application. Water, Air and Soil Pollution 26: 425–459

Haines, B. (1983) Forest ecosystem SO_4-S input-output discrepancies and acid rain: Are they related? Oikos 41: 139-143

Harward, M.E. & H.M. Reisenauer (1966) Movement and reactions of inorganic soil sulfur. Soil Science 101: 326–335

Heasley, J.E., W.K. Lauenroth & T.P. Yorks (1984) Simulation of SO_2 on a Grassland In: W.K. Lauenroth & E.R. Preston (Eds) the Effects of SO_2 on a Grassland (pp 161–184) Springer-Verlag, New York

Hornberger, G.M., B.J. Cosby & J.N.Galloway (1986) Modeling the effects of acid deposition: uncertainty and spatial variability in estimation of long-term sulfate dynamics in a region. Water Resources Research 22: 1293–1302

Hunt, W.B., J.W.B. Stewart & C.V. Cole (1986) Concepts of sulfur, carbon, and nitrogen transformations in soil: evaluation by simulation modeling. Biogeochemistry 2: 163–177

Hunt, W.B. & W.J. Parton (1986) The role of modeling in research on microfloral and faunal interactions in natural and agroecosystems. In: M.J. Mitchell & J.P. Nakas (Eds) Microfloral and faunal interactions in natural and agro-ecosystems (pp 443–494) Martinus-Nijhoff Publishers, Dordrecht

Hutchinson, T.C. & M. Havas (Eds)(1980) Effects of Acid Precipitation on Terrestrial Ecosystems. Plenum Press, New York

Innis, G.S. (Ed)(1978) Grassland Simulation Model. Springer-Verlag, New York

Johnson, D.W. (1984) Sulfur cycling in forests. Biogeochemistry 1: 29–43

Johnson, D.W. & D.W. Cole (1980) Anion mobility in soils: relevance to nutrient transport from terrestrial ecosystems. Environ Int 3: 79–90

Johnson, D.W., G.S. Henderson, D.D. Huff, S.E. Lindberg, D.D.Richter, D.S. Shriner, D.E. Todd & J. Turner (1982a) Cycling of organic and inorganic sulfur in a chestnut oak forest. Oecologia 54: 141–148

Johnson, D.W., J.W. Hornbeck, J.M. Kelly, W.T. Swank & D.E. Todd (1980) Regional pattern of soil sulfate accumulation: relevance to ecosystem sulfur budgets. In: D.S. Shriner, C.R. Richmond & S.E. Lindberg (Eds) Atmospheric sulfur deposition, Environmental Impact and Health Effects (pp 507–519) Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan

Johnson, D.W. & D.E. Todd (1983) Relationships among iron, aluminum, carbon, and sulfate in a variety of forest soils. Soil Science Society of America Journal 47: 792–800

Johnson, D.W., J. Turner & J.M. Kelly (1982b) The effects of acid rain on forest nutrient status. Water Resources Research 18: 449–461

Landers, D.H., M.B. David & M.J. Mitchell (1983) Analysis of organic and inorganic sulfur constituents in sediments, soils and water. International Journal of Analytical Chemistry 14: 245–256

Likens, G.E., F.H. Bormann, R.S. Pierce, J.S. Eaton & N.M. Johnson (1977) Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York

Linthurst, R.A. (Ed)(1984) Direct and Indirect Effects of Acidic Deposition on Vegetation. Acid Precipitation Series, Vol V. Butterworth Publ., Boston

Lowe, L.E. & R.M. Bustin (1985) Distribution of sulphur forms in six facies of peats of the Fraser River delta. Canadian Journal of Soil Science 65: 531–541

Lowe, L.E. & W.A. DeLong (1963) Carbon bonded sulphur in selected Quebec soils. Canadian Journal of Soil Science 43: 151–155

Maynard, D.G., J.W.B. Stewart & J.R. Bettany (1984) Sulfur cycling in grassland and parkland soils. Biogeochemistry 1: 97–111

McGill, W.B. & C.V. Cole (1981) Comparative aspects of cycling or oganic C, N, S and P through soil organic matter. Geoderma 26: 267–286

McGill, W.B., H.W. Hunt, R.G. Woodmansee & J.O. Reuss (1981) PHOENIX, a model of the dynamics of carbon and nitrogen in grassland soils. Ecol Bull (Stockholm) 33: 49–115

McLaren, R.G., J.I. Keer & R.S. Swift (1985) Sulphur transformation in soils using sulphur labelling. Soil Biology and Biochemistry 17: 73–79

Meiwes, K.J. & P.K. Khanna (1981) Distribution and cycling of sulphur in the vegetation of two forest ecosystems in a acid rain environment. Plant and Soil 60: 369–375

Millard, P., G.S. Sharp & N.M. Scott (1985) The effect of sulphur deficiency on the uptake and incorporation of nitrogen in ryegrass. Journal of Agricultural Science, Cambridge 105: 501–504

Mitchell, M.J., M.B. David, D.G. Maynard & S.A. Telang (1986) Sulfur constituents in soils and streams of a watershed in the Rocky Mountains of Alberta. Canadian Journal of Forest Research 16: 315–320

Murphy, M.D., J.C. Brogan & D.G. Noonan (1983) Sulphur fertilization of pasture improved cattle performance. Sulphur in Agriculture 7: 2–6

Nakas, J.P. (1986) The role of microflora in terrestrial sulfur cycling. In: M.J. Mitchell & J.P. Nakas (Eds) Microfloral and Faunal Interactions in Natural and Agro-Ecosystems (pp 285–316) Martinus-Nijhoff Publishers, Dodrecht

Nodvin, S.C., C.T. Driscoll & G.E. Likens (1986) The effect of pH on sulfate adsorption by a forest soil. Soil Science 142: 69–75

Prenzel, S. (1983) A mechanism for storage and retrieval of acid in acid soils. In: B. Ulrich & J. Pankrath (Eds) Effects of Accumulation of Air Pollutants in Forest Ecosystems (p 157–170) D Reidel, Dordrecht

Rennenberg, H. (1984) The fate of excess sulfur in higher plants. Annual Review of Plant Physiology 35: 121–153

Reuss, J.O. & D.W. Johnson (1985) Effect of soil processes on the acidification of water by acid deposition. Journal of Environmental Quality 12: 26–31

Reuss, J.O. & D.W. Johnson (1986) Acid Deposition and the Acidification of Soils and Waters. Springer-Verlag, New York

Richter, D.D., D.W. Johnson & D.E. Todd (1983) Atmospheric sulfur deposition, neutralization, and ion leaching in two deciduous forest ecosystems. Journal of environmental Quality 12: 263–270

Rochelle, B.P., M.R. Church & M.B. David (1986) Sulfur retention at intensively studied sites in the U.S. and Canada. Water Air and Soil Pollution 33: 18–83

Schecher, W.D. & C.T. Driscoll (1987) An evaluation of uncertainty associated with aluminum equilibrium calculations. Water Resources Research 23: 525–534

Schindler, S.C. (1984) Sulfur transformations and movement in an Adirondack Forest soil. MS Thesis, S.U.N.Y. College of Environmental Science and Forestry, Syracuse, New York

Schindler, S.C., M.J. Mitchell, T.J. Scott, R.D. Fuller & C.T. Driscoll (1986) Incorporation of ^{35}S-sulfate into inorganic and organic constituents of two forest soils. Soil Science Society of America 50: 457–462

Schnoor, J.L., W.D. Palmer Jr & G.E. Glass (1984) Modeling impacts of acid precipitation for northeastern Minnesota. In: J.L. Schnoor (Ed) Modeling of Total Acid Precipitation Impacts (pp 155–173) Butterworth Publ., Boston

Seip, H.M., R. Seip, P.J. Dillon & E.D. Grosbois (1985) Model of sulphate concentration in a small stream in the Harp Lake catchment, Ontario. Canadian Journal of Fisheries and Aquatic Sciences 42: 927–937

Strick, J.E. & J.P. Nakas (1984) Calibration of a microbial sulfur technique for use in forest soils. Soil Biology and Biochemistry 16: 289–291

Strickland, T.C. & J.W. Fitzgerald (1984) Formation and mineralization of organic sulfur in forest soils. Biogeochemistry 1: 79–95

Strickland, T.C., J.W. Fitzgerald & W.T. Swank (1984) Mobilization of recently formed forest soil organic sulfur. Canadian Journal of Forest Research 14: 63–67

Swank, W.T., J.W. Fitzgerald & J.T. Ash (1984) Microbial transformation of sulfate in forest soils. Science 223: 182–184

Tabatabai, M.A. (1982) Sulfur. In: A.L. Page, R.H. Miller & D.R. Keeney (Eds) Methods of soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd edn (pp 501–538) American Society of Agronomy, Inc., Madison

Tabatabai, M.A. (1984) Importance of sulphur in crop production. Biogeochemistry 1: 45–62

Tabatabai, M.A. & J.M. Bremner (1972) Forms of sulfur, and carbon, nitrogen and sulfur relationships in Iowa soils. Soil Science 114: 380–386

Turner, J. & M.J. Lambert (1980) Sulfur nutrition in forests. In: D.S. Shriner, C.R. Richmond & S.E. Lindberg (Eds) Atmospheric Sulfur Deposition: Environmental Impact and Health Effects (pp 321–334) Ann Arbor Science, Ann Arbor, Michigan

Van Veen, J.A. & E.A. Paul (1981) Organic carbon dynamics in grassland soils. 1. Background information and computer simulation. Canadian Journal of Soil Science 61: 185–201

Waring, R.H. & W.H. Schlesinger (1985) Forest Ecosystems, Concepts and Management. Academic Press, Inc., Orlando, Florida

Westall, J.C., J.L. Zachary & F.M.M. Morel (1985) MINEQL. A computer program for the calculation of chemical equilibrium composition of aqueous systems. Water Quality Laboratory, Department of Civil Engineering, Massachusetts Institute of Technology. Technical Note No 18

Wright, R.F. (1984) Norwegian models for surface water chemistry: an overview. In: J.L. Schnoor (Ed) Modeling of Total Acid Precipitation Impacts (pp 73–87) Butterworth Publishers, Boston