Sulfur Cycling, Retention, and Mobility in Soils: A Review

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Abstract

Sulfur inputs to forest ecosystems originate from mineral weathering, atmospheric deposition, and organic matter decomposition. In the soil, sulfur occurs in organic and inorganic forms and is cycled within and between those forms via mobilization, immobilization, mineralization, oxidation, and reduction processes. Organic sulfur compounds are largely immobile. Inorganic sulfur compounds are more mobile, and sulfate is the most mobile. However, adsorption onto soil limits or delays sulfate ion transport. Nonspecifically adsorbed sulfate ions are held only by electrostatic charges in the double diffuse layer, so they are not held as tightly as specifically adsorbed ions that are bonded to metal oxides in the Helmholtz layer. Sulfate adsorption and desorption are controlled predominantly by pH, sulfate concentrations, concentrations and types of other cations and anions in solution, and the character of the colloidal surfaces. Watershed hydrology and subsurface flow paths play important roles in determining the fate of sulfate in soils. Theories and models of sulfate transport from and retention within watersheds focus on contact times between ions and soil materials, macropore, mesopore, and micropore flow contributions to streamflow, and overall soil moisture conditions. Retention also is affected by deposition levels. As sulfur deposition to a watershed decreases, retention decreases; however, rates of decrease depend on whether the initial adsorption was completely irreversible, partially reversible, or completely reversible.

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Sulfur Sources and Forms

Sulfur (S) inputs to forest ecosystems originate from three major sources: mineral weathering, atmospheric deposition, and organic matter decomposition (Brady 1984). Soil minerals, such as iron, nickel, and copper sulfides, and gypsum ($CaSO_4$), weather and release sulfates and sulfides into soils (Moss 1978). Calcium carbonates also contain S at higher levels than many noncalcareous materials, so S is released during their weathering (Harward and Reisenauer 1966). In unpolluted natural situations, the primary source of S in forest ecosystems is parent material weathering (Hutchinson 1979); however, anthropogenic pollutants add considerable S to forests, particularly in the Eastern United States (NADP/NTN 1987). Human activities account for about 50 percent of current S inputs to the atmosphere (Kennedy 1986). Atmospheric sulfur dioxide (SO_2) is sorbed by soils and vegetation, and sulfate (SO_4^{2-}) aerosols are deposited via wet and dry deposition (Moss 1978, Christophersen and Wright 1980). Vegetative matter is decomposed by microorganisms, transforming organic S to other organic or inorganic forms (Tisdale and Nelson 1975); however, S released during organic matter decomposition is not considered a major source of S in terms of total S budgets because it is tightly cycled to meet plant needs (Reuss and Johnson 1986).

Sulfur can be grouped into two broad areas: organic and inorganic forms. Most of the total S pool in soils is composed of organic fractions (Williams 1967; Freney and Williams 1983; Mitchell and Fuller 1988), primarily due to leaf litter inputs (Pregitzer et al. 1992). Organic S in microorganisms constitutes less than 5 percent of total soil S, even in the microbially active zones (Mitchell and Fuller 1988; Strick and Nakas 1984). Transformations between major compartments of the S cycle (Fig. 1) result in a dynamic flux among organic and inorganic forms.

Organic Sulfur

Substantial research into organic S compounds has been done, but much about their precise characteristics remains unknown (Brady 1984; Hutchinson 1979; Mitchell and Fuller 1988). Organic S in soil organic matter occurs in two primary forms: ester sulfates, which have C-O-SO_3 linkages; and carbon-bonded S, which has direct C-S linkages. A few other organic forms also exist, but they are of comparatively minor importance. Ester sulfates include compounds such as choline sulfate, phenolic sulfates, and sulfated polysaccharides. Carbon-bonded S is comprised principally of amino acids such as methionine and cysteine, and sulpholipids (Neptune et al. 1975; Harwood and Nicholls 1979; Tabatabai and Bremner 1972). Classification of organic S into these two broad groups originated partially as a result of laboratory fractionation techniques described by Johnson and Nishita (1952), Freney et al. (1970), and Landers et al. (1983).
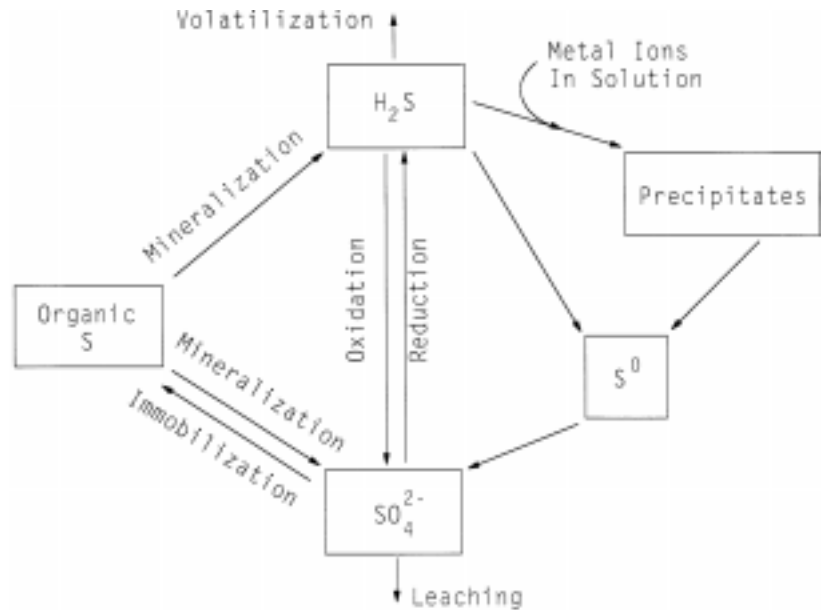

Figure 1.—Simplified schematic of sulfur cycle showing major components.

Ester sulfates originate predominantly from microbial biomass material (McLaren et al. 1985; David et al. 1984) and microbially formed materials (Fitzgerald 1978). Ester sulfate acts as readily available S stores when needed for plant and microbial nutrition (Fitzgerald 1978; Biederbeck 1978; Strickland et al. 1987), because it is mineralized faster than C-bonded S (Schindler et al. 1986; Biederbeck 1978; Hutchinson 1979). Soil microorganisms and plant roots can hydrolyze ester sulfates when S is needed to meet immediate nutritional demands (McGill and Cole 1981).

By contrast, most C-bonded S in soils is derived from litter and dead root inputs (David et al. 1984; Konova 1975), though some is present in microbial biomass (Konova 1975). Carbon-bonded S is broken down less easily and, therefore, is less labile and available to plants and microorganisms (Fitzgerald et al. 1982; Freney et al. 1971; Strick et al. 1982). Carbon-bonded S is particularly immobile if it is carried illuvially into mineral soil horizons (Konova 1975).

Inorganic Sulfur

Inorganic S occurs in several forms, the most common of which is dependent on the system in question. In the atmosphere, sulfur occurs primarily as gaseous SO_2 and aerosol sulfate (SO_4^{2-}). Coal burning emissions are the principal source of atmospheric oxidized S, with most of the S emitted as SO_2 (Kennedy 1986). Sulfur dioxide is oxidized at a conversion rate of about 0.1 percent per hour in the humid sunlit atmosphere to sulfite (SO_3) and then to sulfuric acid (H_2SO_4) (Bufalini 1971).

Other intermediary S forms, such as hydrogen sulfide (H_2S), are less stable, so they are present in lower, transient concentrations. More than 100 tons of H_2S are volatilized to the atmosphere annually from organic matter mineralization and biological SO_4^{2-} reduction; however, H_2S is oxidized to SO_2 very rapidly (Kennedy 1986).

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Within oxic soils and surface waters, most inorganic S occurs as SO_4^{2-}, which is the most mobile form of S in forest soils (Hutchinson 1979). In solution, SO_4^{2-} is associated with calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), ammonium (NH_4^+), hydrogen (H^+), or aluminum (Al^{3+}), depending upon the buffering character of the system. Sulfate also may be precipitated (primarily in arid climates), or adsorbed onto 1:1 clays and iron and aluminum hydrous oxides (Tisdale and Nelson 1975). Elemental S and sulfides are uncommon in well-drained forest soils because they are oxidized rapidly to SO_4^{2-}.

Sulfur Transformations

Immobilization, Mobilization, and Mineralization

The main transformations within the S cycle occur among immobilized, mobilized, and mineralized S compounds (Fig. 1). Immobilization, or the assimilation of S into microbial cells (Randlett et al. 1992), depends completely on microbial metabolism (Fitzgerald et al. 1983). Both aerobic and anaerobic microorganisms take part in organic S formation (Watwood et al. 1988b), though only 1 to 3 percent of microbial biomass is composed of S (Saggar et al. 1981a; Strick and Nakas 1984; Chapman 1987). The short life cycles of microorganisms, however, result in rapid turnover and S recycling (Smith and Paul 1990; McLaren et al. 1985). Microbial biomass has been described as the most active and readily available form of soil organic S (McLaren et al. 1985), and much of the mineralized S seen in short-term incubation experiments may originate from microbial biomass.

Immobilization occurs in organic and mineral soil layers (Fitzgerald et al. 1983), and immobilized S usually is incorporated into organic matter by covalent bonding (Strickland et al. 1987; Watwood et al. 1988b). Sulfate added to soil can be adsorbed quickly or transformed to low molecular weight organic S compounds, especially ester sulfates as fulvic acids (Saggar et al. 1981b), thereby resulting in rapid retention. Over time, some adsorbed SO_4^{2-} may be desorbed and incorporated into low molecular weight organic compounds, which later can be polymerized to larger insoluble organic compounds (Strickland et al. 1986a).

Watwood et al. (1986) described mobilization as the process by which large organic S molecules are reduced microbially to smaller S molecules—that is, depolymerization or removal of sulfonate groups from insoluble S molecules (Swank et al. 1985). Total mineralization is not a requisite for mobilization; though like mineralization, mobilization increases the mobility of organic S compounds. Strickland et al. (1984) used an expanded definition of mobilization, stating that mobilization is not necessarily dependent on microbial activity directly because many of the enzymes responsible for depolymerizing large S molecules are present extracellularly in the soil.

Mobilization is important because it controls S mineralization rates after soluble organic S (that is, low molecular weight) is exhausted. Depolymerization results in the solubilization of previously insoluble S matrices. Mobilization occurs even

when excess SO_4^{2-} is available from precipitation (Strickland et al. 1986b), and very rapid mobilization has been documented (Watwood et al. 1988b). Two possible mechanisms offered for rapid mobilization are direct oxidation of C-S linkages, and conversion of C-S linkages to ester sulfate linkages. Inorganic SO_4^{2-} then can be released through hydrolysis.

Sulfur mineralization goes beyond mobilization in that organic S forms are transformed to inorganic forms. Mineralization has been described as microbially driven decomposition (Brady 1984); however, mineralization of ester sulfates does not require direct microbial activity (McGill and Cole 1981), again, due to extracellular enzymes.

Organic matter decomposition rates vary with chemical makeup and complexities, and whether net S mineralization occurs depends upon the S supply and microbial demand. If more S is available to the system than needed to meet S requirements of sulfur-using microorganisms, mineralization will occur. If less S is available than needed, all S entering the system will become immobilized because microbial needs must be satisfied first. Consequently, in systems where S is limiting, a larger percentage of total S is found in microbial biomass than in systems where S is not limiting (Strick and Nakas 1984).

In sulfur-deficient soils, lower percentages of ester sulfate relative to C-bonded S usually exist compared to that in nondeficient-sulfur soils. Ester sulfate mineralization is greater in the former since ester sulfate is mineralized faster and rapidly provides a source of S (McGill and Cole 1981; Lee and Speir 1979). Analogously, in systems with excess SO_4^{2-}, most immobilized S occurs as ester sulfates (McGill and Cole 1981). In systems where SO_4^{2-} is minimally available, C-bonded S dominates (McGill and Cole 1981; Maynard et al. 1984), because its presence is related more to soil C levels than to S (Mitchell and Fuller 1988). However, soil surface properties also influence organic S pool characteristics. Kaolinitic clays may have lower ester sulfate levels than soils with high organic matter content, because the exposed sites on kaolinites provide fewer appropriate sites for formation of ester sulfate linkages (Watwood et al. 1986).

Ester sulfates are mineralized more easily than C-bonded S because they are not as likely to become bonded covalently to humic compounds as is C-bonded S (McGill and Cole 1981). Also, they occur principally with the fulvic acid component of humic compounds, which are more "active" or available and more labile (Saggar et al. 1981b) than humic acids with which C-bonded S is associated (Biederbeck 1978; Bettany et al. 1973; 1980). Hydriodic-reducible S compounds (that is, HI-reducible; ester sulfate + inorganic SO_4^{2-}) have been found in humic acids, but they are probably located on the exterior of the humic substance and are not an integral part of it (Bettany et al. 1980; Fitzgerald 1978). Less than 1.5 percent of the weight of humic acids is believed to be composed of S (Schnitzer and Khan 1972), with most thought to be C-bonded S (McGill and Cole 1981).

The driving forces behind microbial mineralization of ester sulfates and C-bonded S are inherently different. Ester sulfates are mineralized to satisfy microbial nutrition needs (for S). By contrast, C-bonded S mineralization is driven by the need to satisfy microbial energy needs (for C). Carbon-bonded S is mineralized only when microbes need C and significant amounts of S-rich substrate are available. If S-containing material is not available and C is needed, the microorganisms will mineralize other C material containing other elements. In turn, these other elements, such as nitrogen (N), are released (McGill and Cole 1981).

As mentioned previously, ester sulfate mineralization does not require microbial activity. Ester sulfate mineralization is controlled by the extracellular activity of sulfohydrolase enzymes (McGill and Cole 1981), such as sulfatase (Tabatabai and Bremner 1970), which can exist and remain active in the soil for extended periods (Dodgson et al. 1982). Plant roots also can hydrolyze ester sulfates. Such nonmicrobial mineralization has been defined as biochemical mineralization (McGill and Cole 1981). Fuller et al. (1986) suggested that ester sulfate is mineralized more rapidly in mineral horizons than in organic horizons due to the greater retention of these enzymes in mineral horizons. However, large supplies of C-bonded S (Fitzgerald 1978) and inorganic SO_4^{2-} (Cooper 1972) can suppress sulfohydrolase formation.

Mineralization of C-bonded S requires microbial activity, so it has been described as biological mineralization (McGill and Cole 1981). The evidence showing that C-bonded S requires microbial activity comes from the strong tie between microbial metabolism and C-bonded S formation, which is not demonstrated for ester sulfate (Schindler and Mitchell 1987). Carbon-bonded S mobilization and mineralization occurs as the C in the C bond is oxidized to carbon dioxide (CO_2). It is internal within microorganisms and is catabolic (McGill and Cole 1981).

While microorganisms may not be necessary for S transformations, they are responsible for the majority of the activity. Many soil microorganisms, including fungi, imperfect fungi, yeasts, and bacteria are involved.

Soil microorganism activity depends on substrate availability (Babiuk and Paul 1970), and substrate availability is controlled by above- and below-ground organic matter inputs (McGill and Cole 1981). Fresh litter provides a large and readily available pool of S and C in forest soils (Hutchinson 1979). Sulfur is needed for nutrition, while C-based substrates are needed for C and energy. Thus, if sufficient energy and S are available for immobilization, especially of higher molecular weight compounds, mobilization and mineralization will be depressed, and vice versa (Strickland and Fitzgerald 1984; Watwood et al. 1986). Increased mobilization and mineralization will follow, as more organic substrate becomes available for microbes involved with these two processes (Watwood et al. 1986). The degree to which the mobilized organic S molecules become further mineralized depends upon the system (Strickland and Fitzgerald 1984). Immobilization, mobilization, and mineralization occur simultaneously (Maynard et al. 1983,

Freney et al. 1971), but the timing of peak activity of each may be offset.

Factors Affecting Immobilization, Mobilization, and Mineralization

Sulfur transformations on a per-unit-weight basis are often greater in organic horizons because of the concentration of microbial activity, and transformation rates also tend to be greater in organic horizons (Strickland et al. 1987). However, total transformations actually may be greater in lower mineral horizons due to the greater mass of soil present (Strickland et al. 1987; Schindler et al. 1986).

Immobilization, as with all parts of the sulfur cycle, is affected by seasonally influenced environmental factors. Temperature, moisture, organic matter, atmospheric deposition inputs, and other factors influence immobilization rates (Randlett et al. 1992, Freney et al. 1971). Under favorable conditions, such as adequate organic C and N availability, immobilization of SO_4^{2-} to ester sulfate and C-bonded S can occur very quickly (Fitzgerald et al. 1982) because microbial activity is high (David et al. 1983; Schindler et al. 1986). Ester sulfate formation may reach equilibrium (that is, formation levels off over time) faster than C-bonded S (Fitzgerald et al. 1982), but in some soils, ester sulfate formation will continue for several weeks to months after SO_4^{2-} is incorporated into the soil (Freney et al. 1971; Schindler et al. 1986).

In cold, wet regions, temperature conditions are not conducive to microbial activity during the winter when substrates are available (Williams 1967). Consequently, activity and, thus, immobilization and mineralization rates peak in autumn (after leaf fall) and early spring when substrate availability and soil moisture are high and temperatures are conducive to microbial activity (Randlett et al. 1992; Strickland et al. 1987). Swank et al. (1985) reported a slightly earlier peak for immobilization rates, August and September, with lowest rates in winter and late spring.

By contrast, Watwood et al. (1988b) observed that immobilization was only slightly seasonally dependent. The O1/O2 layer had the highest and approximately the same incorporation for May, August, and February. The rates were about 3 times as high as the A1, E2, and Bh horizons. Incorporation into organic S in the latter three horizons was about equal for all 3 months, though the rate in the A1 horizon during August was less than half of its rate during May and February. Mobilization in the litter layer for the same periods was greatest in May and least in February. Immobilization in the A1, E2, and Bh horizons was greatest in May, though the rates were only slightly lower in August and February.

Strickland et al. (1984) found mobilization strongly affected by temperature. At 5°C, mobilization was only one-fifth of its level at 20° or 30°C. They attributed this response to different enzymes achieving optimal activity levels at different temperatures. Sulfur mineralization increased markedly with increasing temperatures at 10°, 20°, and 30°C over a 64-day

incubation period (Williams 1967). It was significantly lower at 10°C than at higher temperatures.

Moisture extremes can affect mineralization and immobilization significantly. Organic matter mineralization may be inhibited near saturation by retarding S oxidation of reduced inorganic S. Likewise, mineralization can be retarded by very low soil moisture values that are below those necessary for microbial activity (Williams 1967). Methionine mineralization was affected sharply by moisture in A and B horizons in a North Carolina soil (Watwood et al. 1988a). Mineralization increased significantly from just above 0 percent to about 30 percent moisture, and then did not change significantly up to about 80 percent moisture. Methionine incorporation into organic matter also increased over the same moisture range, but fell off drastically above 50 percent moisture.

In the laboratory, rewetting of a soil retained dry for 4 to 5 months resulted in a rapid, but short-lived pulse of mineralization, though rates returned to predried levels relatively quickly (Williams 1967). Similar SO_4^{2-} releases have been reported immediately following soil drying (Hutchinson 1979).

Sulfur mineralization is tied closely to C and N levels in the soil (Williams 1967). Sulfur will become or remain immobilized if either the C:S or N:S ratios are too large (Tisdale and Nelson 1975), and conditions conducive to S mineralization often lead to N mineralization (Williams 1967). The N:S ratio in many soils is in the range of 8-12:1 (Anderson 1975). Carbon:sulfur ratios tend to be more variable (with respect to the C levels); they have been reported in the range from about 57-141:1 (Anderson 1975; Bettany et al. 1973; Neptune et al. 1975; Lowe 1969; Harward et al. 1962; Tabatabai and Bremner 1972).

Stotzky and Norman (1961) proposed that C:S ratios less than 900:1 are adequate for maximum microbial activity. This means that sufficient S is present to meet microbial needs and formation of organic S may not be necessary. However, smaller optimal ratios have been suggested by Barrow (1961). Indeed, C:S ratios in the literature are almost always within the 900:1 range; so the range may be too broad and/or other factors beside the C:S ratio must be considered when interpreting microbial activity.

Several studies have reported that SO_4^{2-} is released after liming. Williams (1967) showed that mineralization was stimulated after calcium carbonate was added to 17 Australian soils in the laboratory, and Ensminger (1954) and Neptune et al. (1975) found solution SO_4^{2-} releases after liming. Ellett and Hill (1929) also observed SO_4^{2-} increases in lysimeters after liming. The source of these releases may be attributable to enhanced mineralization by creating conditions favorable for oxidation and bacterial activity (Hutchinson 1979).

Caution should be used when extrapolating mineralization, mobilization, and immobilization rates determined from laboratory studies to the field. Laboratory methods typically involve mixing or shaking; consequently, laboratory S incorporation and transformations probably occur faster and perhaps to a greater extent than they would in the field (Schindler et al. 1986).

Sulfur Oxidation and Reduction

Microorganisms also mediate other parts of the sulfur cycle (Fig. 1), particularly S oxidation and reduction. Oxidation and reduction are key processes in S transformations because the occurrence of SO_4^{2-} depends on oxidation.

Completely mineralized S compounds can be transformed to SO_4^{2-} or H_2S by microbes. Hydrogen sulfide is a common product of mineralization. The reduction step from SO_4^{2-} to H_2S is microbially mediated, primarily by bacterial species in the genera *Desulfovibrio*, *Desulfotomaculum*, and *Desulfomas* (Brady 1984; Kennedy 1986) under anaerobic conditions (usually saturation). Reduction also can occur in anaerobic "microniches" (for example, within particles) that are present within a larger aerobic system (Jorgenson 1977). Hydrogen sulfide can be lost through volatilization, join with metal ions to form insoluble sulfide precipitates, or be oxidized to elemental S.

Sulfur oxidizing microorganisms are ubiquitous in most soils, so their numbers rarely limit oxidation (Janzen and Bettany 1987). Instead, oxidation is limited by substrate availability. Heterotrophic oxidizers, such as *Arthrobacter* and *Pseudomonas*, which carry out the majority of S oxidation (Vitolins and Swaby 1969; Janzen and Bettany 1987), require organic C to satisfy energy and C needs. Consequently, even if sufficient S and heterotrophic oxidizers are present, organic C is necessary to drive the biologically mediated oxidation reactions (Pepper and Miller 1978). In the absence of sufficient organic C, autotrophic microbes, including those in the genus *Thiobacillus,* become more important. They obtain their energy from inorganic S and their C from CO_2 (Tisdale and Nelson 1975).

Factors Affecting Oxidation and Reduction

The microorganisms responsible for S oxidation, like many microbes, are quite tolerant of soil acidity and low pH. In fact, oxidation can be substantial in acidic soils, often achieving maximum rates below pH 4 (Barton 1978). Oxidation by *Thiobacillus* has been reported from pH<2 to pH>9 (Brady 1984), so soil pH alone generally does not curtail oxidation significantly (Kennedy 1986).

Janzen and Bettany (1987) illustrated that oxidation depends more on the particle surface area of the S than on mass, because oxidation is a surface reaction and only S atoms at the exterior surface are oxidized. Thus, more SO_4^{2-} is produced from reduced S compounds (including elemental S) with larger surface areas than from compounds with smaller surface areas.

Sulfur oxidation usually increases with temperature within the range of those normally encountered under field conditions, meaning oxidation is greater during the summer than the

$$\left[\begin{array}{c} Fe\Big\langle\begin{array}{l} OH_2 \\ OH \end{array} \\ \\ Fe\Big\langle\begin{array}{l} OH_2 \\ OH \end{array} \end{array}\right]^{0} + 2H^{+} + SO_4^{2-} \rightleftharpoons \left[\begin{array}{c} Fe\Big\langle\begin{array}{l} OH_2 \\ OH_2 \end{array} \\ \\ Fe\Big\langle\begin{array}{l} OH_2 \\ OH_2 \end{array} \end{array}\right]^{2+} SO_4^{2-}$$
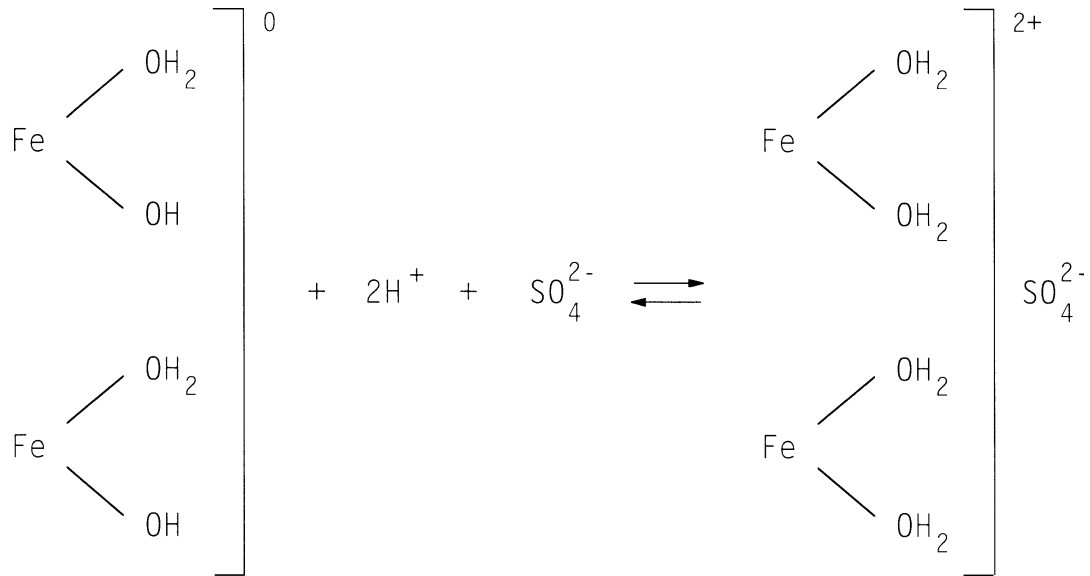
Figure 2.—Protonation of hydroxyl creates formation of net positive charges and results in nonspecific adsorption.

winter if all other factors are equal. Maximum oxidation occurs between 27 to 35°C, but even these levels may not be reached at the litter surface in forested ecosystems. Temperatures above 55 to 60°C destroy most soil microorganisms; however, such extreme conditions do not occur in forest soils (Tisdale and Nelson 1975).

Soil texture and moisture content are interdependent in relation to S oxidation because texture influences aeration; thus, the effects of moisture and texture cannot be separated, and both are believed to affect oxidation rates. Oxidation is greatest near field capacity (Tisdale and Nelson 1975) because oxygen is required for oxidation by aerobic microorganisms (Janzen and Bettany 1987), and moisture is necessary for microbial activity. However, because soil texture controls the amount of moisture retained at field capacity, different textured soils have different oxidation rates. For example, clay soils contain more moisture and less air-filled porosity at field capacity than coarser-textured soils. In turn, oxidation rates in clay soils are lower. Oxygen diffusion into soil pores also may be lower in heavier textured soils at field capacity (Janzen and Bettany 1987). Textural effects may be most important only at or near field capacity. At 50-percent field capacity, Rehm and Caldwell (1969) did not find oxidation rate differences using several soils of different textures.

Sulfate Adsorption

Inorganic SO_4^{2-} in soil solution is termed soluble SO_4^{2-} and is highly mobile. However, SO_4^{2-} can be retained physically in the short- or long-term by adsorption. Adsorbed SO_4^{2-} sometimes is called insoluble SO_4^{2-} because it cannot be desorbed with just water (Fuller et al. 1985).

Anion adsorption can be nonspecific or specific. Nonspecific adsorption involves only electrostatic (Coulombic) attraction, while specific adsorption occurs by ligand exchange (Parfitt and Smart 1978). All anions are adsorbed nonspecifically, but only a few, including SO_4^{2-}, also are adsorbed specifically (Johnson et al. 1979b). Specific adsorption is believed to be the predominant mechanism of SO_4^{2-} adsorption (Neary et al. 1987).

In nonspecific adsorption, SO_4^{2-} is held within the double diffuse layer as a counter ion to positively charged surfaces on organic matter, layer silicates, or oxide- and hydrous oxide-dominated surfaces. These materials are amphoteric— they can have positive, negative, or zero charges—with the net charge being pH-dependent (Bohn et al. 1985). Positive charges are created on the surfaces by the presence of H^+ (Fig. 2). As pH decreases and H^+ becomes more available, more positively charged colloidal surfaces are created. In turn, the number of surfaces available for anion adsorption increases (Johnson and Cole 1980).

The functional groups involved with the protonation are hydroxyl ($_-OH$), carboxyl ($_-COOH$), phenolic ($_-C_6H_4OH$), and amine ($_-NH_2$) groups (Bohn et al. 1985). Because only electrostatic attraction is involved in nonspecific adsorption, desorption can be achieved relatively easily—either by increasing solution pH (Nodvin et al. 1986) or by exchange with other anions that have a greater or equal affinity for adsorption (Bohn et al. 1985).

Specific adsorption results in a greater adsorption capacity than would occur by nonspecific adsorption alone, and specifically adsorbed anions are held more tightly. Most specific adsorption occurs in soils with high levels of free iron and aluminum oxides and hydroxides (Rajan 1978; Fuller et al. 1985), though hydroxy-aluminum polymers bonded to clays and organic matter, and broken bonds on clays also provide surfaces for specific adsorption (Harward and Reisenauer 1966). Ligand exchange can occur when a net negative, positive, or zero charge exists (Bohn et al. 1985).

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$$\left[\mathrm{Al}\begin{array}{c}\diagup\mathrm{OH_2}\\[2pt]\diagdown\mathrm{OH_2}\end{array}\right]^{+} + \mathrm{SO_4^{2-}} \;\rightleftharpoons\; \left[\mathrm{Al}\begin{array}{c}\diagup\mathrm{OH_2}\\[2pt]\diagdown\mathrm{SO_4}\end{array}\right]^{-} + \mathrm{OH_2} \qquad (a)$$

or

$$\left[\mathrm{Al}\begin{array}{c}\diagup\mathrm{OH_2}\\[2pt]\diagdown\mathrm{OH^-}\end{array}\right]^{0} + \mathrm{SO_4^{2-}} \;\rightleftharpoons\; \left[\mathrm{Al}\begin{array}{c}\diagup\mathrm{OH_2}\\[2pt]\diagdown\mathrm{SO_4}\end{array}\right]^{-} + \mathrm{OH^-} \qquad (b)$$
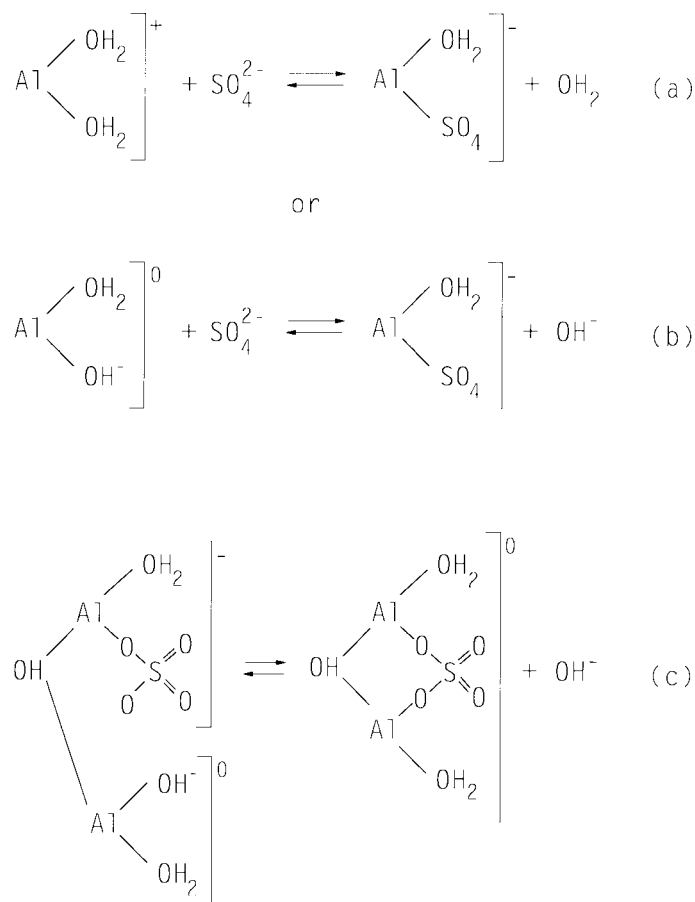
$$(c)$$

Figure 3.—Specific adsorption where (a) sulfate displaces water from net positive site, or (b) sulfate displaces hydroxyl from neutral site. Later (c) the adsorbed sulfate may displace another hydroxyl or water ligand from the adjoining metal resulting in a 6-member ring and neutralization (after Rajan 1978).

In specific adsorption, SO_4^{2-} bonds to the metal oxide within the inner Helmholtz layer by displacing an H_2O or OH^- molecule (Bohn et al. 1985) (Fig. 3) or occasionally other anions (Harrison et al. 1989). Whether H_2O or OH^- is displaced depends primarily upon the concentration of SO_4^{2-} in solution. At low concentrations, SO_4^{2-} usually is adsorbed on positive sites, displacing coordinated water (Fig. 3a). With greater SO_4^{2-} concentrations, SO_4^{2-} increasingly is adsorbed on neutral sites by displacing OH^- (Fig. 3b) (Rajan 1978). This concentration dependency results in the "activation" of new adsorption sites with increasing SO_4^{2-} concentrations (Chao et al. 1962a; 1962b). Specific adsorption effectively increases the negative charge on the adsorbing surfaces more than nonspecific adsorption, so nonspecifically adsorbed anions cannot desorb or displace those specifically adsorbed (Singh 1984d). Nonspecifically adsorbed anions held as counter ions in the double diffuse layer are displaced back into soil solution due to repulsion from the developed negative charges (Hingston et al. 1967). Conversely, the creation of higher pH and more negative charges from specific adsorption can result in cation adsorption increases (Marcano-Martinez and McBride 1989;

Couto et al. 1979). The net negative charge created can be neutralized further by the formation of a 6-member ring from displacement of another OH^- or water ligand from the adjoining metal (Fig. 3c) (Rajan 1978).

The concentration dependency of SO_4^{2-} adsorption has been described mathematically in terms of several types of linear and nonlinear equations or isotherms. The Freundlich and Langmuir are the two most commonly used adsorption isotherms. The principal difference between the two is that the former does not have an adsorption maximum (Bohn et al. 1985). The Langmuir equation probably describes SO_4^{2-} adsorption better over large concentration ranges used in the laboratory or over long periods of SO_4^{2-} accumulation in the field, because a maximum adsorption capacity is expected for most if not all soils. However, the Freundlich equation may fit adsorption isotherms better over a limited solution concentration range (Singh 1984a; Weaver et al. 1985), because of the insensitivity of log-log plots (that is, the linear form of the Freudlich equation) and the greater curve-fitting flexibility from having two empirical constants (versus one for Langmuir) (Bohn et al. 1985).

The Langmuir isotherm is used commonly to illustrate general adsorption/desorption behavior (Reuss and Johnson 1986). The affinity for adsorption increases, but at a decreasing rate, until a maximum adsorption level is reached. A new steady state is attained at each new SO_4^{2-} concentration until the maximum is reached (Johnson and Cole 1980). Changes within the system can induce reversals in adsorption or desorption.

Adsorption can be completely irreversible, partially reversible, or completely reversible (Reuss and Johnson 1986; Harrison et al. 1989). Partial or complete reversibility means desorption can occur if the SO_4^{2-} concentration in soil solution decreases. If adsorption is totally reversible, the desorption and adsorption isotherms will be identical (that is, there is no hysteresis) (Fig. 4). Complete reversibility would be expected only if all adsorbed SO_4^{2-} was nonspecifically adsorbed. If specific adsorption has occurred, some SO_4^{2-} may remain irreversibly adsorbed, so that the desorption isotherm lies above the adsorption isotherm (Fig. 4). This process is partial reversibility. If no desorption occurs when solution concentrations decrease, adsorption is completely irreversible (Fig. 4) (Reuss and Johnson 1986). Complete irreversibility is extreme and has not been documented; however, Aylmore et al. (1967) reported what may be the closest case of nearly complete irreversible adsorption for iron and aluminum oxides described in the literature. Rajan (1978) observed atypical desorptive behavior. Desorption occurred on a hydrous alumina after an apparent adsorption maximum was reached, even though additional SO_4^{2-} was added to the system.

Occasionally when SO_4^{2-} is retained in soils, the experimental results indicate that adsorption was not the only retention mechanism acting. For example, if OH^- is displaced and released during specific adsorption, soil
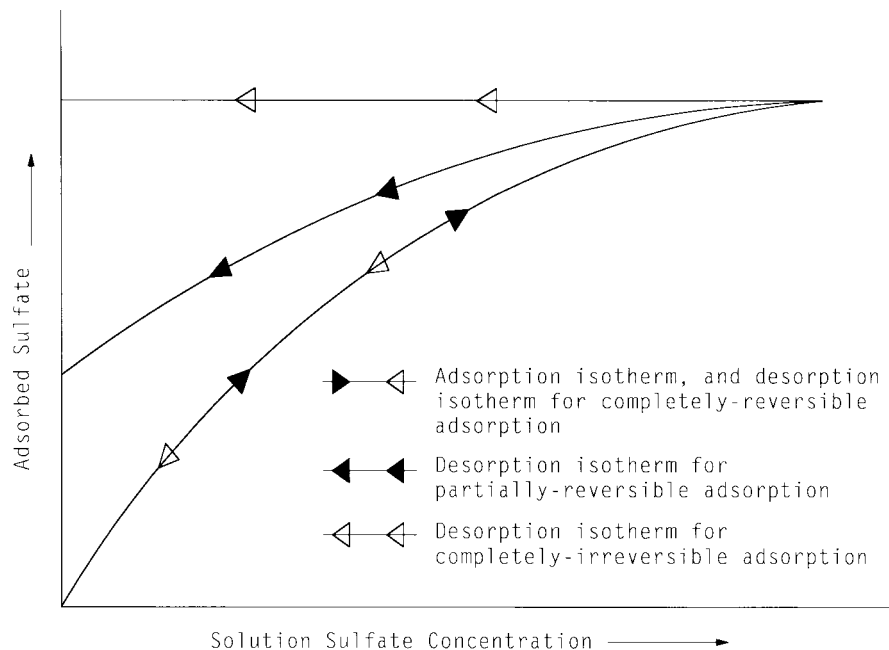
6

Figure 4.—Schematic representation of adsorption, completely reversible, partially reversible, and completely irreversible desorption isotherms (after Reuss and Johnson 1986).

solution pH should increase in a constant manner per unit of SO_4^{2-} adsorbed (Hingston et al. 1967). Such an increase is not always observed (Couto et al. 1979), and precipitation of some types of sulfate minerals has been suggested as a possible retention mechanism to explain this lack of pH change (Gebhardt and Coleman 1974). Additionally, precipitation of alunite and basaluminite also may be mistaken for specific adsorption, because OH^- is released during their formation causing solution pH to rise (Adams and Rawajfih 1977; Marcano-Martinez and McBride 1989).

Factors Affecting Sulfate Adsorption and Desorption

Anion adsorption is controlled predominantly by pH, anion concentration, the other cations and anions in solution, and the character of the colloidal surfaces present (Harward and Reisenauer 1966). However, because adsorption is not a simple exchange process, it is affected by many other physical, chemical, and biological factors (Singh 1984c). Consequently, laboratory estimates of adsorptive capacities are controlled by many factors, including the experimental procedures used. Thus, extrapolating laboratory results to the field requires caution and often field and laboratory findings are contradictory (Johnson et al. 1981).

In the laboratory, adsorption typically increases with decreasing pH induced by additions of acidic compounds (Harward and Reisenauer 1966; Couto et al. 1979; Kamprath et al. 1956). This pH effect has been attributed to neutralization of OH^- groups by H^+ (Mattson 1931; Chang and Thomas 1963), with the resulting H_2O then replaced by SO_4^{2-} (Mattson 1931). Protonation of soil colloids creates additional adsorption sites (Schofield and Samson 1954). However, Harrison et al. (1989) found increasing adsorption with increasing pH using soils of naturally different pH levels. They hypothesized that soil acidity differences derived during natural soil genesis may

react quite differently than short-term laboratory-induced pH changes. Lower pH levels also may retard the activity of microorganisms responsible for S immobilization, thereby, keeping more S as soluble SO_4^{2-} and allowing it to move through the soil until adsorbed (Fitzgerald et al. 1983).

Nodvin et al. (1986) reported a drop in adsorption after soil pH fell below 3.5. They attributed this difference to dissolution of aluminum and destruction of adsorption sites. Chao et al. (1964) found a similar decline below pH 4.0 with a soil subjected to various levels of aluminum oxide coatings. However, the same soil with iron oxide coatings continued adsorbing SO_4^{2-} below pH 4.0. Thus, adsorptive behavior at low pH levels may be tied closely to the character of the colloidal surfaces. In addition, SO_4^{2-} may precipitate out with hydroxy alumina (Neary et al. 1987), so distinguishing between retention due to adsorption or precipitation may be difficult or impossible. Precipitation probably only becomes important in soils at low pH since metals such as aluminum must be in solution before precipitation can occur (Rajan 1979).

Desorption, like adsorption, is pH dependent; however, the characteristics of desorption depend on the desorbing solution. As would be expected from SO_4^{2-} adsorption behavior, desorption by water increases with pH (Nodvin et al. 1986; Singh 1984d). Other desorbing solutions induce different behavior. Desorption by calcium dihydrogen phosphate [$Ca(H_2PO_4)$] was virtually unaffected by solution pH, whereas desorption by calcium nitrate [$Ca(NO_3)_2$] decreased slightly from pH 3 to pH 5, and then increased again to pH 7. At pH 7, desorption was just slightly greater than at pH 3 (Singh 1984d). Water is probably the best desorbing solution for evaluating most field situations, but other solutions may be appropriate to determine desorption behavior on sites where fertilizer, waste water, and other amendments have been applied.

$$\left[\begin{array}{c} \text{Al} \!-\! \text{OH}_2^{+\frac{1}{2}} \\[3em] \text{Al} \!-\! \text{OH}^{-\frac{1}{2}} \end{array}\right]^{0} + \text{CaSO}_4^{0} \longrightarrow \left[\begin{array}{c} \text{Al} \!-\! \text{O} \!-\! \text{SO}_3^{\frac{3}{2}} \\ \diagdown \\ \quad\text{Ca} \\ \diagup \\ \text{Al} \!-\! \text{OH}^{\frac{1}{2}} \end{array}\right]^{0} + \text{OH}_2$$

Figure 5.—"Cooperative adsorption" with Ca^{2+} and SO_4^{2-} ion pair (after Marcano-Martinez and McBride 1989).

Surface characteristics have a large influence on SO_4^{2-} adsorption. Shanley (1992) found no correlation between adsorbed SO_4^{2-} and iron and aluminum fractions, but typically both metals are strongly related to SO_4^{2-} adsorption. Consequently, sesquioxide clays have high anion adsorptive capacities (Donahue et al. 1977). Iron and aluminum occur in crystalline, amorphous, and organically complexed fractions (McKeague et al. 1971), with SO_4^{2-} adsorption most strongly associated with the crystalline fractions (Johnson and Todd 1983; Singh 1980). However, correlations between adsorption and the aluminum crystalline fraction may be weak because the extraction method that estimates crystalline aluminum is less specific than the method for crystalline iron (Johnson and Todd 1983; McKeague et al. 1971).

Chao et al. (1964) reported that aluminum oxide was more effective in adsorbing SO_4^{2-} compared to iron oxide, though adsorption on both became similar at solution pH 6. This convergence was attributed to a greater destruction of adsorption sites on aluminum than iron at this high pH. By contrast, Johnson and Todd (1983) and Singh (1984b) found iron to be a better adsorbing surface than aluminum. Singh's results may be somewhat inconclusive because he performed the extractions on the same samples, and the iron extractions may have removed some of the aluminum in the process.

Kaolinitic clays typically adsorb more SO_4^{2-} than montmorillonitic clays (Harward and Reisenauer 1966) because free iron and aluminum are more abundant on kaolinite, and montmorillonites have more negative charges resulting in anion repulsion (Harward and Reisenauer 1966; Singh 1980). Hydroxides bonded to the kaolinitic-associated metals are displaced by SO_4^{2-} (Donahue et al. 1977) as described previously.

Soil age or degree of weathering strongly influences SO_4^{2-} adsorption. In general, older, highly weathered soils are thought to have greater adsorptive capacities than younger, less weathered soils. The difference is attributed to a greater development of sesquioxide surfaces in older soils (Johnson and Henderson 1979).

Several investigators have observed that SO_4^{2-} adsorption in acid soils increased in the presence of added calcium or lime (Barrow 1972; Chao et al. 1963; Marsh et al. 1987; Marcano-Martinez and McBride 1989). In cases of relatively high calcium, specific adsorption processes and precipitation of gypsum alone could not explain the amount of increase observed. A mechanism of "cooperative adsorption" in which Ca^{2+} and SO_4^{2-} form an ion pair has been proposed as a possible mechanism (Marcano-Martinez and McBride 1989). Sulfate adsorption above predicted levels is achieved by Ca^{2+} adsorption onto negative OH^-, and the paired SO_4^{2-} ion displaces a neighboring water molecule (Fig. 5). This mechanism minimizes the formation of net negative charges at the oxide surface so cation exchange and SO_4^{2-} adsorption simultaneously increase.

Because adsorption is physically and chemically controlled and not microbially mediated (Watwood et al. 1988a), in the laboratory soil temperature and moisture have been found to affect SO_4^{2-} adsorption only minimally. For example, temperature had only a small influence on both a brown earth and iron podzol (Singh 1984c). Adsorption increases for both soils were less than 20 mg kg^{-1} over the range of 4° to 24°C. Temperature also had little effect under varying SO_4^{2-} solution concentrations. However, Courchesne and Hendershot (1990) reported that percentages of SO_4^{2-} adsorbed on two Spodosols increased with temperature, using 5°, 25°, and 40°C conditions.

In Singh's (1984c) experiment, soil moisture was related negatively to adsorption, though the decrease in adsorption at high moisture contents was much greater for the brown earth than for the iron podzol. Possible explanations for the response included dilution of the SO_4^{2-} in soil solution and reduction of SO_4^{2-} due to more anaerobic conditions. Adsorption of $^{35}SO_4^{2-}$ in soil samples collected from A and B horizons in North Carolina was not influenced by soil moisture between 0 and >60 percent moisture content (Watwood et al. 1988a).

Many studies have shown that organic matter can influence adsorption, though the results are not consistent. Chao et al. (1962a) and Haque and Walmsley (1973) reported that SO_4^{2-} adsorption was correlated positively to organic matter; while Couto et al. (1979), Singh (1980), Singh and Johnson (1986), and Johnson et al. (1980) reported a negative correlation; and Neary et al. (1987) reported no correlation. In addition, organic matter did not affect SO_4^{2-} adsorption in an iron podzol, while it negatively influenced it in a brown earth (Singh 1984b). In soils where a negative effect was observed, a number of mechanisms have been suggested. Organic coatings may block adsorption sites (Singh 1984b; Johnson et al. 1979b; 1980), or organic anions may compete with SO_4^{2-} for adsorption sites (Parfitt 1978; Marcano-Martinez and McBride 1989; Singh 1980)—even in soils that have very high iron and aluminum oxide contents (Johnson et al. 1979b; 1980). Organic matter also may retard iron and aluminum crystallization (Neary et al. 1987), which in turn reduces the number of available adsorption sites.

Sulfate adsorption may be affected significantly by the time of contact between the solid and solution phases (Singh 1984c). Many studies have shown that SO_4^{2-} adsorption increased and/or desorption became at least partially irreversible with increased contact time (Sanders and Tinker 1975; Barrow and Shaw 1977; Johnson et al. 1979a). The process of increased adsorption with contact time under field conditions has been termed "aging" (Johnson et al. 1979a). This is in contrast to the almost immediate and complete adsorption reported for other studies (Rajan 1978; Tripathi et al. 1975). Laboratory studies involve mixing, stirring, or shaking suspensions, thereby quickly exposing adsorption sites to the solution SO_4^{2-} ions. In the field, adsorption may require a longer time because SO_4^{2-} must migrate throughout the soil profile until available adsorption sites are found. Aging also has been shown to increase the formation of basaluminite precipitate in bentonite clay (Singh and Miles 1978).

In a series of laboratory analyses examining the effects of time on SO_4^{2-} desorption, Singh (1984d) reported that almost all desorption was complete in 30 minutes, though it increased slightly more over the 50-hour experimental period for the iron podzol than the brown earth. Soil/solution ratios of 1/10, 1/50, 1/100, and 1/200 all exhibited this pattern; however, desorption increased with decreasing soil solution ratios (that is, 1/200>1/100>1/50>1/10). This pattern of behavior was attributed to the dilution of the SO_4^{2-} in soil solution, which in turn influenced the kinetics of the desorption process. Rajan (1979) also reported complete

desorption in 30 minutes, and Barrow and Shaw (1977) observed nearly complete desorption within 30 minutes using a sulfur-deficient, high SO_4^{2-} adsorbing capacity soil.

Sulfur Retention and Movement

Sulfur retention in soils is the maintenance of S on site through several possible mechanisms. Retained S can move within the soil and undergo transformations, but it is not lost from the catchment either to ground water or surface water. The quantities of mobile and immobile fractions and the time that each remains mobile or immobile determine the degree of retention or movement that S will experience.

Immobilization and adsorption are considered the two primary S retention mechanisms in forests; however, a clear debate exists about which is most important (Randlett et al. 1992). Traditionally, SO_4^{2-} adsorption was considered the dominant mechanism (Johnson and Henderson 1979; Johnson et al. 1979b; Johnson et al. 1982; Johnson 1984; Shriner and Henderson 1978), and it is still considered so by many researchers today (Reuss and Johnson 1986). By contrast, other studies now suggest that immobilization is as or more important (David et al. 1982; Fitzgerald et al. 1983; Swank et al. 1984; Autry et al. 1990). This disparity may exist because S pool characteristics and processes are site-specific, so broad generalities are difficult to make. Very likely both mechanisms are important in most systems, though their time frames of importance may vary in different systems (Randlett et al. 1992). For example, in some soils initial retention of SO_4^{2-} may be by adsorption, followed later by a portion of that adsorbed pool being transformed to organic S constituents (Strickland et al. 1986a; Schindler et al. 1986), while in others SO_4^{2-} may be immobilized quickly through microbial assimilation (Saggar et al. 1981b).

The complexities of the debate are heightened by the inability to make generalizations about the dominant form of S in various soil horizons. In some studies, immobilization has been associated primarily with upper soil horizons, in which high levels of organic matter are present (David et al. 1982; David et al. 1983; Hutchinson 1979; Schindler and Mitchell 1987), and adsorption with deeper mineral horizons (Johnson and Cole 1977; Chao et al. 1963; Harward and Reisenauer 1966; Schindler and Mitchell 1987). Conversely, other research has shown that organic S fractions can be substantial in deeper mineral soil horizons as well as in organic layers (Mitchell et al. 1986; David et al. 1983; David et al. 1987; Autry et al. 1990; Schindler et al. 1986; Swank et al. 1984), and SO_4^{2-} adsorption can be significant in surface horizons (Johnson and Henderson 1979), even shortly after incorporation in the soil (Strickland et al. 1986a).

David and Mitchell (1987), Schindler and Mitchell (1987), and MacDonald et al. (1992) suggested that retention by adsorption and immobilization are limited-term sinks for S, although they did not define the length of "limited term". Cosby et al. (1986) proposed that retention times may be years, decades, or even centuries depending upon the system. Retention times may be quite short on watersheds where SO_4^{2-} outputs equal or exceed inputs (MacDonald et al.

1992; Cosby et al. 1986), or they may be fairly long in systems where the current amount of SO_4^{2-} adsorbed is much less than the adsorptive capacity (Cosby et al. 1986).

Watersheds that have significant capacity to retain SO_4^{2-} are termed delayed response systems, because stream acidification will not occur soon. Watersheds that have reached SO_4^{2-} adsorption capacities are termed direct response systems. In these catchments, stream acidification has begun or will begin soon, depending upon the buffering capacity of the soil (Lynch and Corbett 1989).

Contact time between SO_4^{2-} and the soil affects retention/mobility and has been proposed as the most important factor controlling SO_4^{2-} leaching to surface waters (Vance and David 1992). Short contact times are believed to be a requisite to the presence of storm-associated SO_4^{2-} (Schnabel et al. 1991). Generally, longer contact times result in less SO_4^{2-} available for leaching, due to adsorption and/or transformation to less mobile organic forms. This aging effect seems intuitive; however, Randlett et al. (1992) showed that soluble SO_4^{2-} concentrations increased more than adsorbed SO_4^{2-} after an 8-day incubation period in upper horizons of Spodosols. Thus, the influence of desorption and transformations are significant enough in some soils to negate the effects of potentially greater retention through increased contact time. Ultimately the net flux of S depends upon the net exchanges within the cycle (Schindler et al. 1986).

Watershed hydrology and flow paths play an important role in determining the fate of SO_4^{2-} in any ecosystem (Schnabel et al. 1991; Johnson and Henderson 1979). Sulfate leaching is influenced by factors that control the rates and patterns of water movement and by those that affect ionic movement and exchange (Harward and Reisenauer 1966).

In many watersheds, SO_4^{2-} concentration peaks correspond to peak discharge. For example, Johnson and Henderson (1979) observed SO_4^{2-} concentrations during stormflow that were 4 to 5 times higher than baseflow conditions on the Walker Branch Watershed in Tennessee. Drawing from soil SO_4^{2-} extraction results, they hypothesized that these high concentrations were due to the substantial soluble SO_4^{2-} pools in surface horizons on the watershed. The soluble pool may originate from SO_4^{2-} that was not adsorbed, or it may have been generated from mineralization (Johnson et al. 1982; Randlett et al. 1992; Singh and Johnson 1986). Johnson and Henderson (1979) believed the soluble SO_4^{2-} was contributed by variable source areas (Hewlett and Hibbert 1967) during storm events. Thus, streamflow during storms is generated primarily through the organic and upper mineral horizons of streamside areas (Shanley 1992), and these areas simultaneously contribute the majority of the storm-associated SO_4^{2-} to streams. Fuller et al. (1985), Neary et al. (1987), Johnson and Henderson (1979), Singh and Johnson (1986), and Shanley (1992) also found soluble SO_4^{2-} to be the dominant inorganic SO_4^{2-} fraction present in organic and upper mineral soil horizons and concurred that it was the major source of episodic SO_4^{2-} in streams.

Christophersen and Wright (1981) drew upon the work of Johnson and Henderson (1979) and proposed a two reservoir model to explain SO_4^{2-} transport to streams (that is, the Birkenes model). Catchments are separated into 1) the upper horizons that primarily contribute stormflow and some "old soil water" (Christophersen et al. 1982) and associated ions to streams by macropore flow, and 2) the deeper soil or rock layers that contribute flow and associated ions during baseflow (Christophersen and Wright 1981). The latter presumably occurs by micropore flow or from ground water. Micropore flow is slower, and the potential for retaining SO_4^{2-} in the soil subsequently increases (Stam et al. 1992). Within the upper reservoir, subsurface stormflow is in contact with only the humus and uppermost mineral horizons. They suggested that all of the SO_4^{2-} in the upper reservoir originates from atmospheric deposition, and that it remains soluble.

Neither of these assumptions probably is true, and in fact Christophersen and Wright (1981) acknowledged that their model was too simple to predict SO_4^{2-} in stream water from a Norwegian watershed for many long-term periods. Some predictions were high, whereas others were low. The exclusion of organic S transformations and oxidation/reduction reactions from the model was a major reason suggested for poor fit by the model. Despite the difficulties, they suggested the model provides a good basic structure to explain SO_4^{2-}/flow relationships. The presence of multiple storage areas for soluble SO_4^{2-} means the watershed does not have to be entirely hydrologically active for SO_4^{2-} to be contributed to surface waters (Lynch and Corbett 1989), though larger concentrations of SO_4^{2-} tend to be delivered to stream systems during larger runoff events due to more expansive variable source area contributions (Christophersen and Wright 1981).

Lynch and Corbett (1989) used the Birkenes model as a basis for explaining SO_4^{2-} losses from a watershed in central Pennsylvania. They observed greater export of SO_4^{2-} during a February to May period than that which was deposited in wet deposition for that period. They hypothesized that soluble SO_4^{2-} stored in the upper horizons during dry periods created a significant reservoir that was flushed out as the soils rewetted. In dry periods, subsurface flow during small storms was insufficient to transport significant concentrations of soluble SO_4^{2-} to streams. Sulfate that reached the streams during small storms came from very limited riparian areas. Soil rewetting resulted in progressive remobilization of soluble SO_4^{2-}, starting in the areas closest to the stream and moving upslope. As with the Birkenes model, SO_4^{2-} concentrations during baseflow were attributed to deeper soil or bedrock horizons where soil moisture was sufficient for lateral or upward movement. Most SO_4^{2-} in baseflow was attributed to weathering, ground water, or direct atmospheric deposition onto the stream surface (Lynch and Corbett 1989; Christophersen and Wright 1981).

The Birkenes model, as well as other SO_4^{2-} behavior models, are overly simplistic (Mitchell and Fuller 1988). However, the Birkenes model does provide a plausible hydrologic

explanation for describing stormflow generation and episodic chemistry that is consistent with the accepted variable source area concept and principles of macropore flow. Thus, although it may not function perfectly mathematically, the model conceptually merges hydrology and chemistry.

Both S retention and movement have been demonstrated in the laboratory. However, results often may have only limited applicability to field conditions. Relatively easy and rapid SO_4^{2-} leaching has been shown in the laboratory. However, these studies use soil cores or similar methods that artificially force movement downward and compact soils thereby lessening the distribution of macropores (Harward and Reisenauer 1966). Resulting leaching losses, thus, often are controlled primarily by the amount of percolate applied (Korentajer et al. 1984; Chao et al. 1962c; Kinjo et al. 1971). Even the previous simplistic discussions of hydrologic controls suggest that lateral movement (especially downslope) occurs, and more realistic studies of movement/retention must allow lateral movement.

Toward this end, David and Mitchell (1987) applied 10 mCi of carrier-free sodium sulfate ($Na_2{}^{35}SO_4$) to two 0.5-m^2 plots in September 1983. Soil leachate was collected using ceramic cup suction lysimeters in the O, B, and C horizons on each plot (6 per plot). No rain fell on the plot for the first week, but 10.24 cm of precipitation fell over the next 5 weeks. One day after application, most of the activity recovered was in the O horizon; however, some isotope was collected in the B horizon on one plot and in the C horizon on the other, indicating movement into deeper horizons did occur. All of the lysimeters had detectable activities from week 1 to 6 with the exception of one C-horizon lysimeter. The plot in which both C-horizon lysimeters contained radioactivity from week 1-6 had a boulder that was believed to have directed water and ^{35}S downward to a greater degree than on the other plot.

After the study was complete, soil excavation indicated that most of the ^{35}S retained was in the organic horizons in both plots, primarily as organic S. Carbon-bonded S and ester sulfate activities were similar in the Oe horizons, but ester sulfate accounted for almost 100 percent of the organic ^{35}S in all other horizons. In both plots, E-horizon activities were low, while those in the Bh horizon were approximately equal to activities in the organic layers. Sulfate activities were significantly lower than organic S in all horizons, with soluble SO_4^{2-} generally most dominant in the organic and E horizons, and insoluble SO_4^{2-} most important in the B horizons. Seventy and 99 percent of the applied activities were accounted for in the soil in the two plots after 6 weeks. No isotope was found more than 1 m laterally away from either plot.

The isotope that David and Mitchell (1987) applied was dissolved in several liters of water, but precipitation was not involved in the application as would occur with SO_4^{2-} in wet deposition. Dahl et al. (1979) included rainfall as a factor in their application of $^{35}SO_4^{2-}$ to plots on barren rock and soil-covered heather plots in Norway. They observed

virtually no adsorption or other type of retention within the plots over a period of about 5 hours. However, water movement was fairly rapid and they speculated that adsorption might have occurred if the water carrying the ^{35}S had a longer residence time. Anion exclusion in small pores was given as a possible explanation for minimal interaction with the plot materials. Sulfate ions are fairly large compared to many other types of ions in solution, so they may not easily enter narrow pores present in these soil-poor systems. The rock surfaces were believed to have net negative charges on their exposed surfaces, causing SO_4^{2-} repulsion rather than adsorption.

Edwards (1994) applied 25 mCi of $^{35}SO_4^{2-}$ during a rain event to a plot on a forested watershed in the central Appalachians and monitored movement for 55 weeks. Initial isotope movement was rapid and extensive, and movement continued throughout the year. Dominant pathways of movement were linked to soil moisture. However, even though the watershed soils had no net sulfate retention capacity, less than 1 percent of the applied isotope was recovered in soil leachate and watershed exports. Some retention on the watershed was due to vegetative uptakes and microbial immobilization. Retention of soluble $^{35}SO_4^{2-}$ was attributed to "physical retention" in which SO_4^{2-} remained on site simply because insufficient soil moisture was available to transport the ions far.

Dahl et al. (1980) applied $^{35}SO_4^{2-}$ evenly over a snowpack on a 264-m^2 miniwatershed in April 1978 and over a 75-m^2 miniwatershed that was 49 percent covered by soil and heather in June 1978. On the snow-covered catchment, about 50 percent of the ^{35}S was recovered. Nearly 90 percent of that recovered was collected in the first 30 percent of runoff from the watershed. Thus, they concluded that SO_4^{2-} deposited in snowpacks either as wet or dry deposition is washed to surface waters fairly easily during the first snowmelts.

Almost 40 percent of the tracer was recovered from the summer-application plot during the first 4 months after application (Dahl et al. 1980). Most of the ^{35}S was recovered during the initial 20 days, probably because rainfall for that period was higher than usual. The 60 percent of the isotope retained in the watershed was present in both soils and vegetation during November/December sampling. Soil depth on this catchment averaged 17 cm, and soil did not cover the entire surface area of the catchment, so greater retention might have occurred if the soil volume had been larger.

In a waste-water spray irrigation study on a loamy sand in Washington, Johnson et al. (1979a) reported that more than one-third of the SO_4^{2-} applied was retained in the top 10-cm layer (that is, the A horizon). Retention was greater than that predicted from laboratory studies on the same soil and was attributed to longer contact time with the soil in the field.
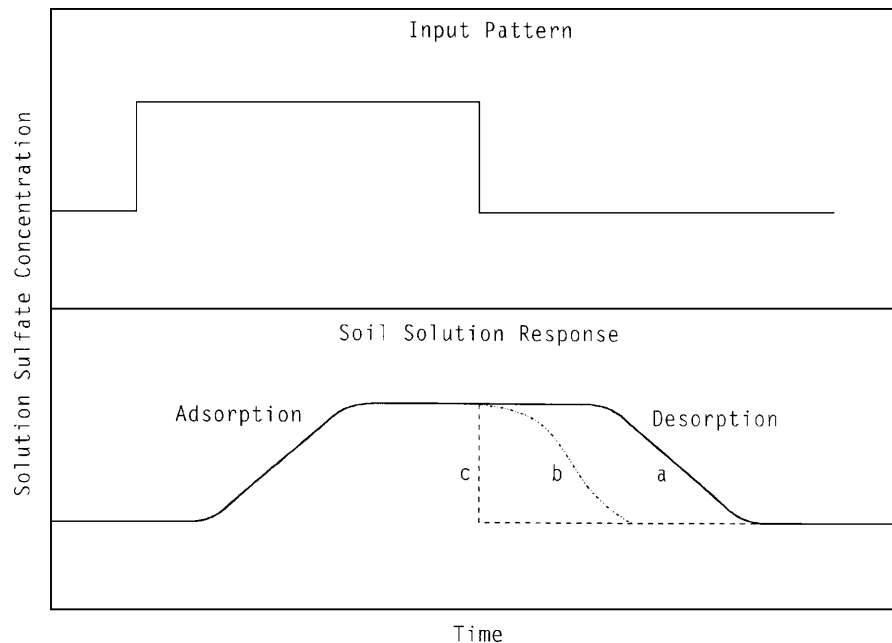
Figure 6.—Relationship between sulfate input changes and sulfate concentrations in soil solution over time with (a) completely reversible adsorption, (b) partially reversible adsorption, and (c) completely irreversible adsorption (after Reuss and Johnson 1986).

Relationship Between Deposition Changes and Retention

Rates of ecosystem responses to S deposition changes, and particularly SO_4^{2-} deposition, depend on the shape of the adsorption/desorption isotherms. Thus, the reductions in S emissions and corresponding reductions in deposition expected from the Clean Air Act amendments should result in changes in soil SO_4^{2-} adsorption. If completely irreversible adsorption occurrs during years with elevated deposition, a reduction in SO_4^{2-} exports and associated cation leaching would occur immediately (Fig. 6). Conversely, if either partial or completely reversible adsorption occurrs, SO_4^{2-} exports during desorption will exceed inputs as new steady state levels are achieved. Thus, a lag will exist between the beginning of lower deposition and the time when soil leachate and surface waters achieve that new steady state (Reuss and Johnson 1986).

Such a lag was documented in Norway when a roof was constructed over a catchment to exclude ambient deposition.

Deposition was controlled at lower levels for several years. Three years later, SO_4^{2-} levels in stream water were still high and had not reached equilibrium with the lowered deposition (Wright et al. 1988).

Although adsorption isotherms provide information about the type of adsorption/desorption behavior that might be expected from soils, they do not incorporate many precipitation or biologically mediated transformation processes. Consequently, precise prediction of lag times is considered impossible. However, the time needed for a watershed to show a response to decreased deposition is usually shorter in watersheds that have been exposed to high SO_4^{2-} deposition than for those that have been exposed to low deposition. In addition, it takes significantly more time to reach a steady state after SO_4^{2-} deposition is reduced than the time needed to achieve steady-state conditions after deposition increases (Cosby et al. 1986).

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Sulfur inputs to forests originate from mineral weathering, atmospheric deposition, and organic matter decomposition. In the soil, sulfur occurs in organic and inorganic forms and is cycled within and between those forms via mobilization, immobilization, mineralization, oxidation, and reduction processes. Organic sulfur compounds are largely immobile. Inorganic sulfur compounds are more mobile, and sulfate is the most mobile. Adsorption onto soil limits or delays sulfate ion transport. Nonspecifically adsorbed sulfate ions are held by electrostatic charges, so they are not held as tightly as specifically adsorbed ions. Sulfate adsorption and desorption are controlled predominantly by pH, sulfate concentrations, concentrations and types of other cations and anions in solution, and the character of the colloidal surfaces. Subsurface flow paths play important roles in determining the fate of sulfate in soils. Theories and models of sulfate transport from and retention within watersheds focus on contact times between ions and soil materials, macropore, mesopore, and micropore flow contributions to streamflow, overall soil moisture conditions and deposition levels.
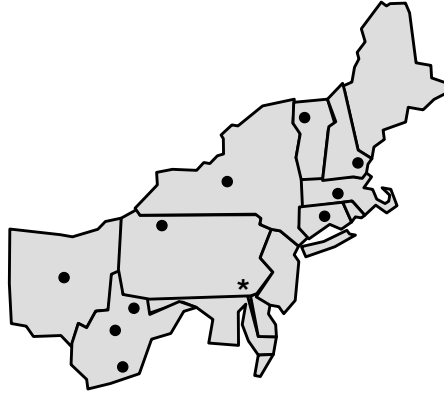
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