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## Responses of Forest Ecosystems to Changing Sulfur Inputs

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### I. INTRODUCTION

There was little information on sulfur (S) cycling in forests compared with that of other nutrients (especially N) until the past two decades. Interest in S nutrition and cycling in forests was heightened with the discovery of deficiencies in some unpolluted regions (Kelly and Lambert, 1972; Humphreys et al., 1975; Turner et al., 1977, 1980) and excesses associated with acidic deposition in other regions of the world (Mewies and Khanna, 1981; Shriner and Henderson, 1978; Johnson et al., 1982, 1986b). Several reviews have been written about S cycling in forests, and the interested reader should refer to those papers for a general treatise on the subject (Turner and Lambert, 1980; Johnson, 1984; Mitchell et al., 1992a,b). It is our primary purpose to consider an important but often overlooked aspect of S cycling in forests—namely, the response to changing S inputs.

Several studies have addressed the effects of increased S inputs in forest soils and forest ecosystems (Johnson and Cole, 1977; Khanna and Beese, 1978; Singh et al., 1980; Lee and Weber, 1982; Khanna et al., 1986; Fernandez and Rustad, 1989), but few have considered the effects of decreased S inputs. Attention has recently begun to focus on the response of

acidified ecosystems to decreases in  $\text{SO}_4^{2-}$  inputs that have resulted from decreases in emissions from the combustion of fossil fuels.

Sulfur emissions reached a maximum in the contiguous United States around 1970 and subsequently have been steadily decreasing (Husar et al., 1991). These decreases should continue with the passage of various environmental regulations such as the amendment to the Clean Air Act (Public Law 101-549) passed by the United States Congress in 1991. These decreases in S emission have been reflected in decreases in  $\text{SO}_4^{2-}$  concentrations of surface waters in the northeast United States (Driscoll and Van Dreason, 1992; Likens et al., 1990), eastern Canada (Dillon and LaZerte, 1992; Kelso and Jeffries, 1988), and Europe (Allot et al., 1992). Such decreases have also been confirmed by experimental studies, including a roof exclusion experiment of a small catchment (800 m<sup>2</sup>) in southern Norway, which began in 1984. This exclusion caused a 50% decrease in  $\text{SO}_4^{2-}$  output after 3.5 years (Wright and Henriksen, 1990). A similar roof experiment was initiated in 1991 over a much larger (6500 m<sup>2</sup>) catchment in Sweden (Hultberg and Grennfelt, 1992). A variety of experimental manipulations including addition and exclusion of S in small catchments and forested plots are in progress in Europe and North America (Hultberg et al., 1992).

With increasing attention being focused on decreasing S inputs, considering the potential responses of forest S cycles to lowered S inputs is especially timely. Prior to such a consideration, however, a brief overview of S cycling in forests and some important ecosystem S retention mechanisms is in order.

## II. OVERVIEW OF SULFUR CYCLING IN FORESTS

The S cycle in forests can be represented as in Figure 1 (Johnson, 1984). As is the case for other nutrients, only a few of the fluxes shown in Figure 1 can be measured directly, and others must be calculated using various assumptions. Specifically, wet deposition, litterfall, and throughfall can be measured with relative ease, whereas measurement of dry deposition and leaching are made with considerably more difficulty and involve assumptions in order to scale up to an aerial (kg ha<sup>-1</sup>) level. Other fluxes, such as foliar leaching, uptake, requirement, and translocation, must be calculated from direct measurements, including the estimates of dry deposition, the latter of which may be subject to considerable error.

The traditional method of calculating uptake, requirement, foliar leaching, and translocation is as follows (Cole and Rapp, 1981):



$$\text{Uptake (U)} = \text{Nutrient return} + \text{nutrient increment} \\ \text{in perennial (woody) tissues (W)} \quad (3)$$

$$= \text{Litterfall (LF)} + \text{foliar leaching (FL)} \\ + \text{root turnover (RT)} + \text{W} \quad (4)$$

$$\text{Foliar leaching (FL)} = \text{Throughfall} + \text{stemflow} \\ - \text{total translocation (T)} \\ = \text{R} - \text{U} \quad (5)$$

Atmospheric deposition is a very important component of the S cycle. This is true not only in polluted areas, where atmospheric S deposition is very high, but also in areas of low S input. Probert and Asmosir (1983) argue that any S in soil parent material will have leached away before the soil is weathered enough to accumulate S in either organic or adsorbed forms. Thus, they argue, atmospheric S inputs are the major source of S for terrestrial ecosystems.

Only in recent years has the great importance of dry deposition of S been recognized. In the past, failure to account for dry deposition of S to forests has sometimes resulted in serious error propagation making flux estimates within the S cycle. If dry deposition is not measured or underestimated, foliar leaching is overestimated (Eq. 5), uptake is overestimated (Eq. 4), and translocation is underestimated. For instance, Shriner and Henderson (1978) measured S cycling parameters without accurate estimates of dry deposition on Walker Branch Watershed (WBW), Tennessee, and found that foliar leaching (termed "net removal" by the authors) was very large relative to other fluxes (Table 1). This led to a large value for calculated uptake, and a very rapid rate of foliar S turnover by leaching (4–5 times per year), leading the authors to suspect that there was a large input of dry-deposited S not included in these calculations. This was later confirmed by Lindberg et al. (1986), who made detailed measurements of wet and dry deposition of S at WBW and obtained lower estimates of foliar leaching. A corrected version of the S cycle for the chestnut oak forest type was then published (Johnson et al., 1982). This showed foliar leaching ( $2 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ) to be more than an order of magnitude lower and, consequently, uptake to be 65% lower ( $22 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ) than the values obtained by Shriner and Henderson (1978) ( $44.2 \text{ kg ha}^{-1} \text{ yr}^{-1}$  for foliar leaching and  $63.6 \text{ kg ha}^{-1} \text{ yr}^{-1}$  for uptake) (Table 1). Going back to the original data from Shriner and Henderson (1978) and inserting an assumed foliar leaching value of  $2 \text{ kg ha}^{-1} \text{ yr}^{-1}$  gives an uptake value similar to that obtained later by Johnson et al. (1982), but a much higher total deposition value ( $63.3$  versus  $26 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ) (Table 1). The latter may have been

**Table 1** Sulfur Fluxes on Walker Branch Watershed, Tennessee, Using Traditional Nutrient Cycling Methods and with Corrections by Dry Deposition

Flux	Walker Branch Watershed <sup>a</sup>		Chestnut Oak <sup>b</sup>
	Traditional	Corrected <sup>c</sup>	
Deposition	18.1	63.3 <sup>c</sup>	26
Foliar leaching	44.2	2.0 <sup>c</sup>	2
Litterfall	8.4	8.4	10
Root turnover	8.1	8.1	7
Wood increment	2.3	2.3	2.1
Uptake	63.6	18.5	22

<sup>a</sup>Data from Shriner and Henderson (1978).

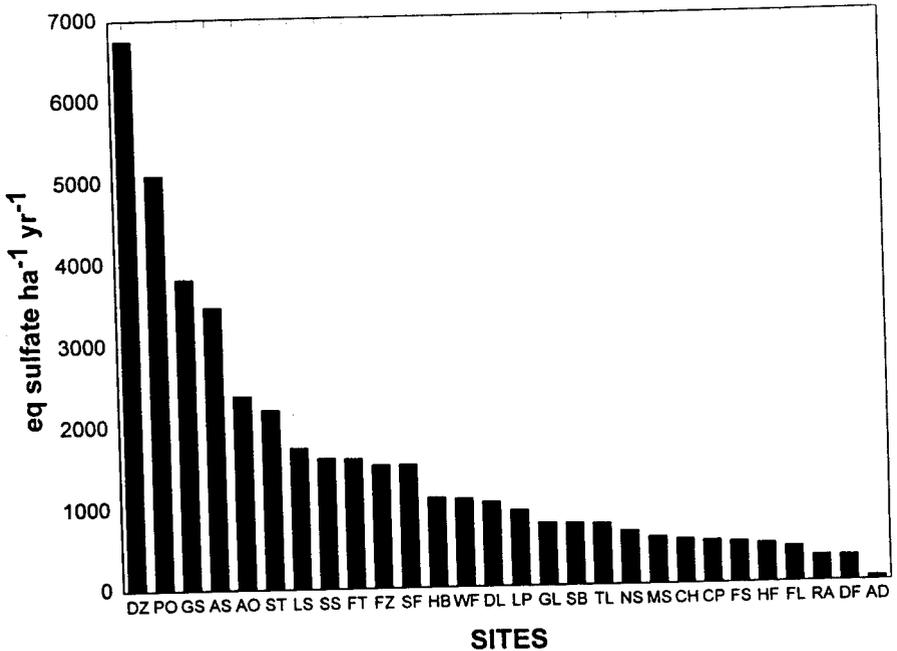
<sup>b</sup>Data from Johnson et al. (1982).

<sup>c</sup>Assuming a 2 kg ha<sup>-1</sup> yr<sup>-1</sup> for foliar leaching.

due to a reduction in local S emissions due to the closure of a local power plant in the interim.

A considerable amount of effort was expended during the era of acidic deposition studies in order to obtain accurate estimates of dry deposition of S because of the great uncertainties created by the underestimation of dry deposition (Garten et al., 1988; Lindberg et al., 1990). Very intensive, detailed measurements of S deposition, along with the analysis of forest S cycles, eventually revealed that simple measurements of throughfall and stemflow yield highly accurate estimates of total S deposition, as was originally suggested by Mayer and Ulrich (1974). This method involves either ignoring foliar leaching or subtracting a nominal amount (<1.0 kg ha<sup>-1</sup> yr<sup>-1</sup>) for it (Lindberg and Lovett, 1992). Thus, an inexpensive and convenient way to monitor changes in total S deposition on a long-term basis is readily available to anyone with bottles and funnels and the capability of analyzing SO<sub>4</sub><sup>2-</sup> accurately.

The atmospheric inputs of S to forest ecosystems vary widely, with less than 60 eq ha<sup>-1</sup> yr<sup>-1</sup> of SO<sub>4</sub><sup>2-</sup> (1 kg S ha<sup>-1</sup> yr<sup>-1</sup>) in a Douglas fir site in Australia to over 5000 eq ha<sup>-1</sup> yr<sup>-1</sup> (80 kg S ha<sup>-1</sup> yr<sup>-1</sup>) polluted sites in central Europe such as in Poland (PO) and Czechoslovakia (DZ) (Fig. 2; Table 2). Examination of S inputs versus SO<sub>4</sub><sup>2-</sup> leaching losses from forest ecosystems shows that for many forest ecosystems there is generally little net retention or loss of this element on an annual basis (Fig. 3). There is a net accumulation of SO<sub>4</sub><sup>2-</sup> for some forest soils that has been attributed to sulfate adsorption processes that are a function of soil mineralogical



**Figure 2** Atmospheric inputs for forested sites throughout the world. See Table 2 for explanation of abbreviations, locations, vegetation, and sources of information. (Reprinted with permission from Kluwer Academic Publishers, The Netherlands.)

characteristics (Johnson and Todd, 1983; Rochelle et al., 1987; Harrison et al., 1989) or possible immobilization by soil microbial processes (Swank et al., 1984). In contrast, net losses of  $\text{SO}_4^{2-}$  may be caused by desorption of  $\text{SO}_4^{2-}$  adsorbed during an early period of higher S deposition (Mitchell et al., 1993). Further details on the processes regulating S loss or retention are discussed below.

One interesting and unique feature of S cycles is that a significant proportion of total S can be cycled and accumulated as  $\text{SO}_4^{2-}$ , within both vegetation and soils. The relative amount of  $\text{SO}_4^{2-}$  as a proportion of total S increases with S availability. In vegetation, most carbon-bonded S is associated with the amino acids cysteine, cystine, and methionine, which are in turn used for protein synthesis (Kelly and Lambert, 1972). Other forms of organic S in the biota include biotin, thiamine, glutathione, sulfolipids and ester sulfates, with the latter form not being found in trees (Frenay, 1967; Turner and Lambert, 1980). There is a very close relation-

**Table 2a** Sites of the Integrated Forest Study (IFS) Used in Analyzing Sulfur Budgets. Including Measurements of Atmospheric Deposition<sup>a</sup>. See Johnson and Lindberg (1991) for summary on these sites.

Abbreviation	Site location	Vegetation
DF	Thompson Forest, WA	<i>Pseudotsuga menziesii</i>
RA	Thompson Forest, WA	<i>Alnus rubra</i>
LP	Oak Ridge, TN	<i>Pinus taeda</i>
ST	Smoky Mountains, NC	<i>Picea rubens</i>
CP	Coweeta Hyd. Lab., NC	<i>Pinus strobus</i>
GL	BF Grant Forest, GA	<i>Pinus taeda</i>
FS	Gainesville, FL	<i>Pinus elliotii</i>
DL	Duke Forest, NC	<i>Pinus taeda</i>
TL	Turkey Lakes, Ontario	<i>Acer saccharum</i> , <i>Betula alleghaniensis</i>
HF	Huntington Forest, NY	<i>Acer saccharum</i> , <i>Fagus grandifolia</i>
WF	Whiteface MT., NY	<i>Picea rubens</i>
MS	Howland, ME	<i>Picea rubens</i>
NS	Nordmoen, Norway	<i>Picea abies</i>
FL <sup>a</sup>	Findley Lake, WA	<i>Abies amabilis</i> , <i>Tsuga heterophylla</i>
SS <sup>a</sup>	Smoky Mountains, NC	<i>Picea rubens</i>
SB <sup>a</sup>	Smoky Mountains, NC	<i>Fagus grandifolia</i>
CH <sup>a</sup>	Coweeta Hyd. Lab., NC	<i>Quercus</i> spp., <i>Carya</i> spp., <i>Acer</i> spp.

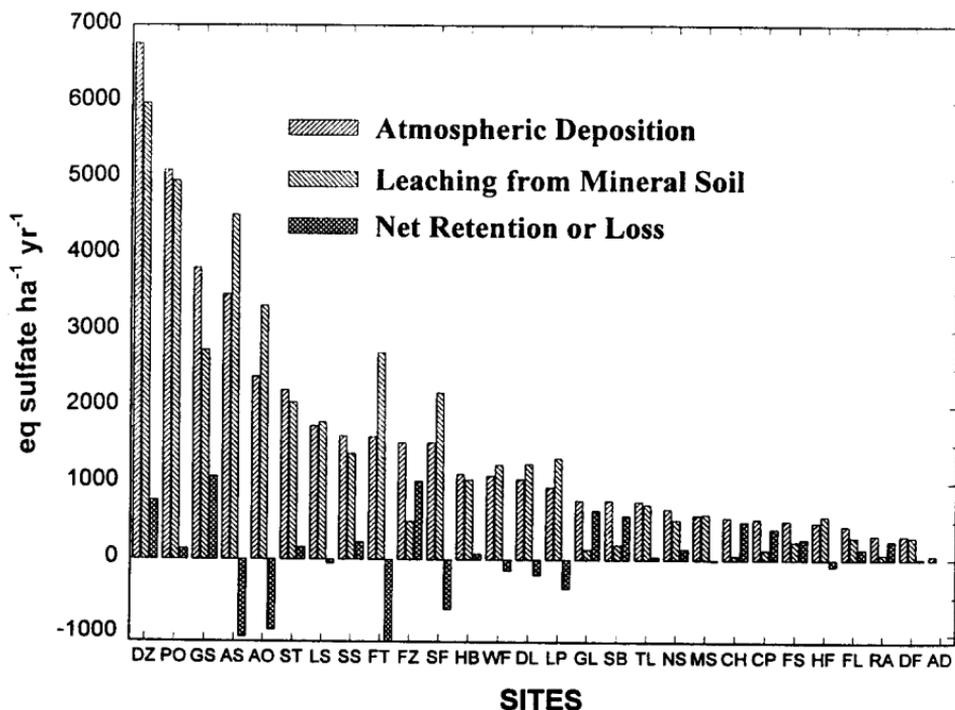
<sup>a</sup>Bulk deposition only sites.

ship between organic S and organic N in plant tissues due to their mutual involvement in protein synthesis. If N is limiting, even under conditions of relatively low S inputs,  $\text{SO}_4^{2-}$  may accumulate. Kelly and Lambert (1972) reported that the ratio of organic S to organic N in *Pinus radiata* foliage was a constant 0.03 on a molar basis (Kelly and Lambert, 1972; Turner et al., 1977; Turner and Lambert, 1980). Sulfur present in excess of that dictated by this ratio was present as  $\text{SO}_4^{2-}$ , extractable by dilute (0.01 M) HCl.

The potential importance of  $\text{SO}_4^{2-}$  in forest S cycles is illustrated in Figure 4, which depicts total S and  $\text{SO}_4^{2-}$  cycles for four forest ecosystems, two (chestnut oak [*Q. prinus*] and yellow poplar [*Liriodendron tulipifera*] mixed forest types) at Walker Branch Watershed, Tennessee, and two (red alder [*Alnus rubra*] and Douglas fir [*Pseudotsuga menziesii*]) at the Thompson site, Washington (Johnson et al., 1986b). At the more polluted

**Table 2b** Selected Non-IFS Forest Sites Used in Comparing Some Aspects of Sulfur Cycling

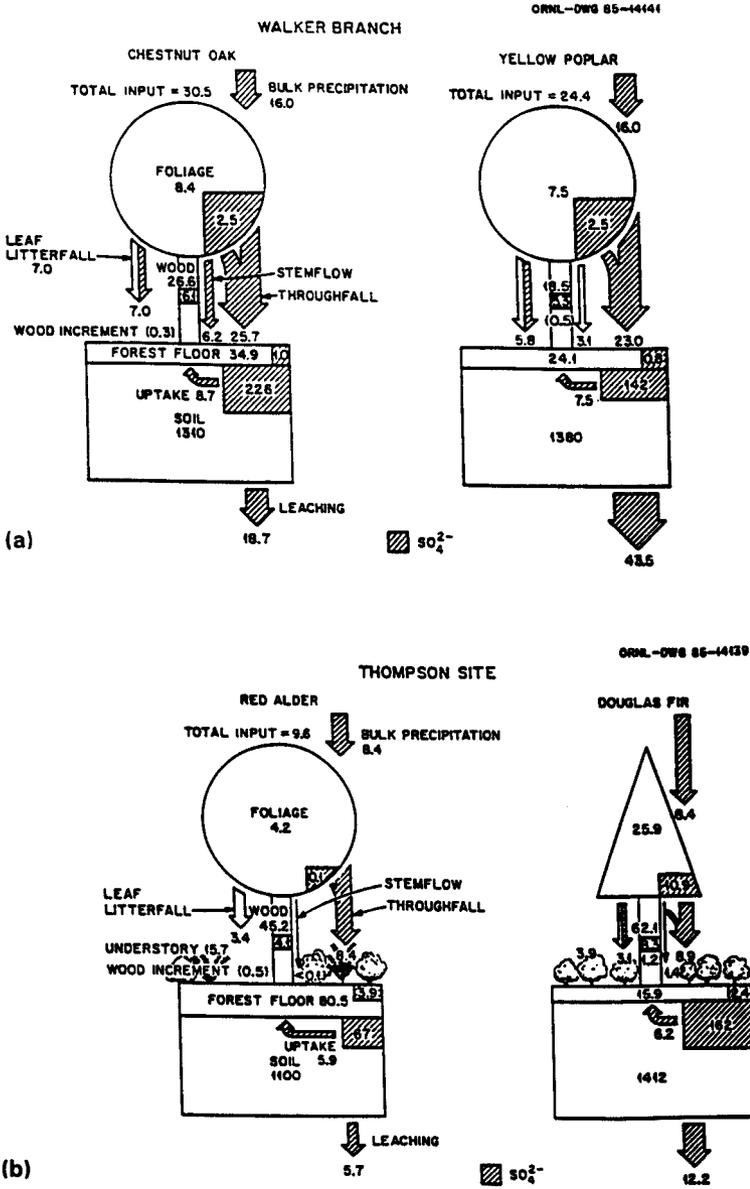
Name of site	Abbreviation	Location	Forest type	References
Vysoka Pec, Damaged Forest	DZ	Most, Czech.	<i>Quercus</i> spp. <i>Fagus</i>	Paces (1985)
Salacova Rural, Forest	FZ	Lhota, Czech.	<i>Picea</i>	Paces (1985)
Ardennes Oak	AO	Ardennes, France	<i>Quercus</i> spp.	Nys and Ranger (1988)
Ardennes Spruce	AS	Ardennes, France	<i>Picea abies</i>	Nys and Ranger (1988)
Ispina Mixed Oak	PO	Ispina, Poland	<i>Quercus robur</i>	Karkanis (1976)
Bago, NSW, Douglas-fir	AD	Australia	<i>Pseudotsuga menziesii</i>	Turner and Lambert (1980)
Solling, Beech	SF	West Germany	<i>Fagus sylvatica</i>	Meiwes and Khanna (1981)
Solling, Spruce	GS	West Germany	<i>Picea abies</i>	Meiwes and Khanna (1981)
Lake Gardsjon, Catchment	LS	Sweden	<i>Picea abies</i>	Hultberg (1985)
Hubbard Brook White Mts.	HB	New Hampshire, U.S.A.	<i>Pinus sylvestris</i> <i>Fagus grandifolia</i>	Likens et al. (1977, 1990), Mitchell et al. (1989)
Walker Branch (Fullerton soil)	FT	Tennessee, U.S.A.	<i>Acer</i> spp. <i>Quercus prinus</i> <i>Carya</i> spp.	Johnson et al. (1986), Lindberg et al. (1986)



**Figure 3** Net retention or loss of S in forest ecosystems. See Table 2 for explanation of abbreviations, locations, vegetation, and sources of information. (Reprinted with permission from Kluwer Academic Publishers, The Netherlands.)

Tennessee sites,  $\text{SO}_4^{2-}$  accounts for a somewhat greater proportion of total S in vegetation (25–30%) and soils (10–17%) than at the less polluted Washington sites (9–22% in vegetation and 6–11% in soils). Even more striking, however, is the much lower percentage of  $\text{SO}_4^{2-}$  in vegetation (9%) and soil (6%) in the N-fixing red alder stand than in the N-deficient Douglas fir stand (22% in vegetation and 11% in soil). This reflects incorporation of S into organic forms in the N-rich alder stand.

There has been some confusion in the literature as to the exact form of  $\text{SO}_4^{2-}$  in plant tissues. Some investigators found that the N:S ratio in tree tissues varied, especially following N fertilization (Turner et al., 1980; Kelly and Johnson, 1982; Mitchell et al., 1992a). Johnson et al. (1982) found that not all foliar  $\text{SO}_4^{2-}$  in some deciduous species could be extracted with water and suggested that some of this apparent  $\text{SO}_4^{2-}$  may be in organic forms (e.g., ester). However, Richter and Johnson (1983) found no difference between foliar  $\text{SO}_4^{2-}$  extracted by 0.01 M HCl and 0.01 M



**Figure 4** Sulfur cycles in a chestnut oak and yellow poplar forest type on Walker Branch Watershed, Tennessee (a) and a Douglas fir and red alder forest in Washington (b). (From Johnson et al., 1986b.)

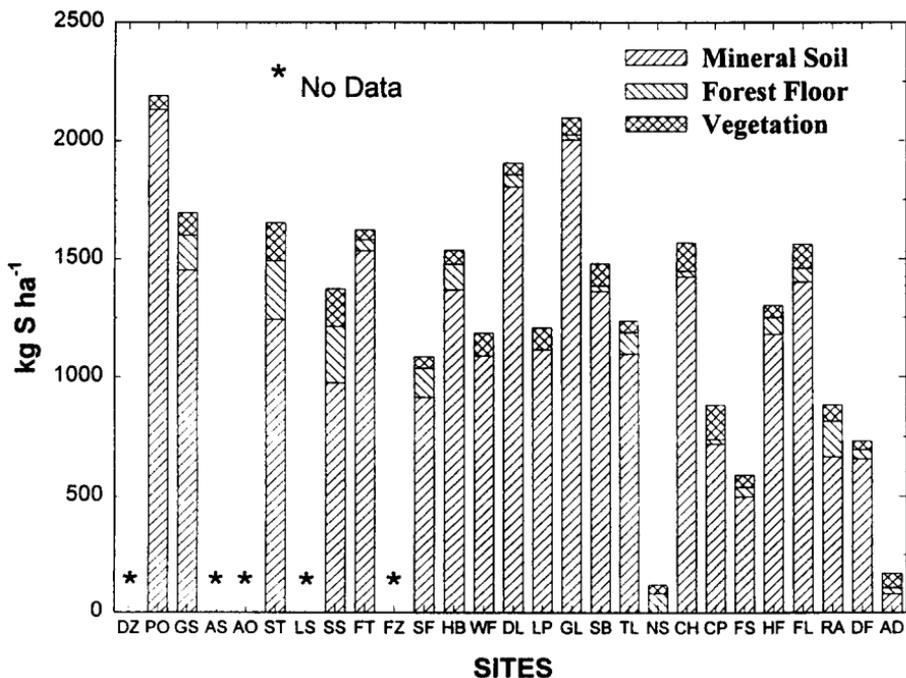
KCl in deciduous species, indicating that foliar  $\text{SO}_4^{2-}$  was indeed inorganic  $\text{SO}_4^{2-}$  rather than an organic (ester) sulfate, again indicating the absence of this form of organic S in trees.

It is interesting that a certain level of foliar  $\text{SO}_4^{2-}$  seems to be necessary for adequate S nutrition. Sulfur deficiency is known to occur at foliar  $\text{SO}_4^{2-}$  levels of 80  $\mu\text{g/g}$  (Turner and Lambert, 1980), suggesting that foliage  $\text{SO}_4^{2-}$  is not simply a reflection of excess S, but plays some important role in plant S nutrition. The most logical assumption for this role would be that foliar  $\text{SO}_4^{2-}$  acts as temporary storage; however, why this is not also the case for N is not known.

As is the case with many other nutrients, the soil is the major reservoir of S and site for S accumulation in forest ecosystems. Sulfur cycles in the four forest sites referred to above illustrate this (Fig. 4). In each case, the annual increment of S in vegetation is considerably less than deposition and leaching fluxes, indicating that sequestering by vegetation plays only a minor role in the retention (or loss) of S in these ecosystems. The same is true for a wide variety of forest ecosystems investigated as part of the Integrated Forest Study (Mitchell et al., 1992a) as well as for most other forest ecosystems throughout the world, except for a S-deficient Douglas fir stand in Australia (Mitchell et al., 1992b).

The distribution of S constituents among vegetation, forest floor, and mineral soil are given in Figure 5. The location of these sites and their vegetation composition is given in Table 2. Mineral soil S accounts for 80–97% of total ecosystem S in all sites but the Douglas fir stand in Australia, where vegetation contributes 37% of the total ecosystem content (Turner and Lambert, 1980). Regressing total ecosystem S content against total S input indicates that there is no direct relationship between these two parameters. However, the low input and low S content for the Australian site is noteworthy (Figs. 2 and 5). These data, however, may not be representative of forests on a global basis, because the vast majority of sites with information on S cycling are located in Europe and North America with no complete data from Asia, Africa, or South America (see Chapter 8, this volume) (Fig. 6).

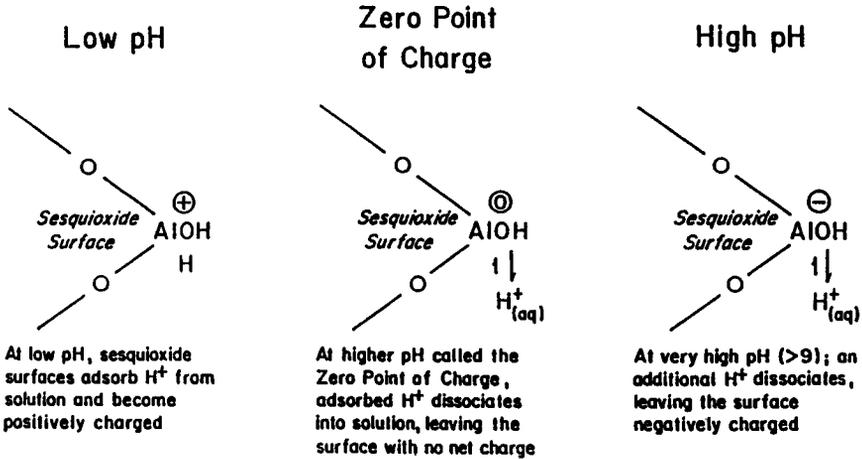
Significant accumulations in the forest floor seem equally unlikely as a major factor in S retention or release, given the relative magnitudes of forest floor S content and annual deposition and leaching fluxes for most sites. However, for sites such as the Douglas fir in Australia (AD) and red alder (RA) and Douglas fir (DF) in the northwest United States with relatively low inputs (i.e.,  $<15 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ) the uptake of S by vegetation and its return via litter may play important roles in regulating S flux (Mitchell et al., 1992a). Analyses of S cycles in the Integrated Forest Study



**Figure 5** Distribution of S constituents among vegetation, forest floor, and mineral. See Table 2 for explanation of abbreviations, locations, vegetation, and sources of information.

indicated that the forest floor did not serve a major role for S accumulation for any of the sites (Mitchell et al., 1992b).

The limited studies of volatile S losses from forest soils suggest that these fluxes are very small relative to those via leaching. For example, Andrea and Jaeschke (1992) estimated that in the wet tropics, average emissions ranged from 0.16 to 0.52 kg S ha<sup>-1</sup> yr<sup>-1</sup> and for vegetated land surfaces there was an average emission of 0.4 kg S ha<sup>-1</sup> yr<sup>-1</sup>. In contrast, SO<sub>4</sub><sup>2-</sup> leaching rates in forests are generally greater by up to two orders of magnitude, typically ranging from 5 to 60 kg S ha<sup>-1</sup> yr<sup>-1</sup> (Mitchell et al., 1992a). As mentioned previously, there is a paucity of data on tropical forests and it has been found for a few extreme cases that gaseous outputs may be as large as 10 to 20 kg S ha<sup>-1</sup> yr<sup>-1</sup>, mostly due to emissions from the vegetation (Mitchell et al., 1992a). In general, however, the soil is presumed to be the major site of S retention and release.



**Figure 6** Schematic representation of the effect of pH on surface charge of Al oxides.

The relative importance of inorganic  $\text{SO}_4^{2-}$  adsorption or organic S incorporation formation as mechanisms for S retention has been the subject of considerable research and debate over the last decade (Johnson and Todd, 1983; Johnson, 1984; Fitzgerald et al., 1982; Swank et al., 1984; Mitchell et al., 1992a). In most forest soils, organic S (mostly in the form of carbon-bonded S) and ester sulfates are the dominant pools (>90%) except in those soils with high sulfate adsorption capacity and/or high levels of S deposition where  $\text{SO}_4^{2-}$  concentrations may approach that of organic S. In general, the relative contribution of the ester sulfate pools as a portion of the total S constituents of soils increases with soil depth (Mitchell et al., 1992a). The organic and inorganic mechanisms of S retention and release in soils are reviewed in the following sections.

### III. SOIL S RETENTION AND RELEASE MECHANISMS

#### A. Inorganic Processes

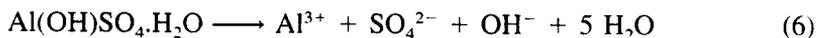
Two major soil inorganic  $\text{SO}_4^{2-}$  retention mechanisms have been identified as being important in forest soils: (1) adsorption and (2) precipitation. Most studies of  $\text{SO}_4^{2-}$  mobility indicate that adsorption is more important than precipitation (Singh, 1984c; Rajan, 1978; David et al., 1987; Fasth et al.,

1991; Khanna et al., 1986), but precipitation of aluminum (Al) sulfates has been found to play an important role in some soil systems where both  $\text{SO}_4^{2-}$  and Al concentrations are high (e.g., Khanna et al., 1987).

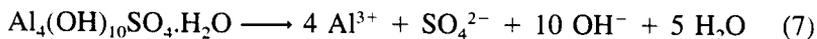
### 1. Sulfate Precipitation Reactions

Sulfate can be retained in soils by precipitation in many forms. Calcium sulfate ( $\text{CaSO}_4$ ) is the predominant form in arid soils, but in humid soils, the solubility product of  $\text{CaSO}_4$  ( $\log K = -4.62$ ) is seldom reached, and aluminum sulfates are predominant. Reuss and Johnson (1986) describe precipitation reactions of the three minerals and the possibilities for their control over  $\text{SO}_4^{2-}$  and Al concentrations in soil solution:

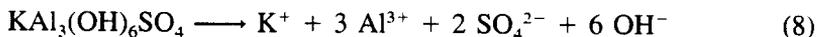
Jurbanite ( $\log K = -17.2$ ):



Basalunite ( $\log K = -117.5$ ):



Alunite ( $\log K = -85.4$ ):



Several investigators (Rajan, 1978; Singh, 1984c; Johnson et al., 1981, 1982; Fuller et al., 1987; Fasth et al., 1991) have concluded that sulfate adsorption rather than precipitation is the most important S retention mechanism in the soils that they studied. Others, however, have found evidence for a significant role for precipitation. Nilsson and Bergqvist (1983) investigated the possibilities for jurbanite and basaluminite control of  $\text{SO}_4^{2-}$  concentrations in soil solutions, groundwaters, and streamwaters from the Swedish coast. The authors concluded that  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  in lower B horizon soil solutions were near equilibrium with basaluminite, whereas  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  in upper B horizon and groundwater solutions were near equilibrium with jurbanite. Reuss and Johnson (1986), noting that  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  in both soil solutions and groundwaters often exceeded the solubility product for basaluminite, questioned whether basaluminite (or alunite, which is more soluble) could be controlling  $\text{SO}_4^{2-}$  concentrations. They did allow for the possibility that jurbanite controls  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$ , however.

Khanna et al. (1987) presented convincing evidence that jurbanite controlled soil solution  $\text{SO}_4^{2-}$  dynamics over a 13-year period (1969–1982) in beech and spruce stands at the Solling sites in Germany. They report notably increased soil solution  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  concentrations following an acidification pulse in 1975–1976, which was consistent with the dissolution

of jurbanite. Solubility diagrams also indicated jurbanite control of soil solution  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  in these sites.

The question of whether adsorption or precipitation is the major inorganic mechanism controlling  $\text{SO}_4^{2-}$  concentrations and S retention in soils has no single answer. In some cases,  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  concentrations are sufficiently high for precipitation, and such reactions may dominate  $\text{SO}_4^{2-}$  dynamics (e.g., Khanna et al., 1986). In other cases, soil solution  $\text{Al}^{3+}$  or  $\text{SO}_4^{2-}$  are not high enough for aluminum sulfate precipitation and  $\text{SO}_4^{2-}$  retention is consistent with adsorption models (e.g., Johnson et al., 1985).

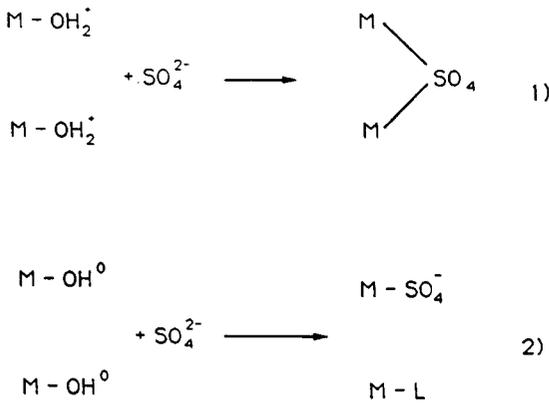
## 2. Sulfate Adsorption

Anion adsorption has been associated with hydrous oxides of Fe and Al and, to a lesser extent, kaolinite (Gebhardt and Coleman, 1974; Hingston et al., 1967; Rajan, 1978; Parfitt and Smart, 1978). There are two basic types of adsorption: (1) nonspecific adsorption, in which anions are held as counter-ions in the diffuse double layer next to a positively charged surface, and (2) specific adsorption, in which the anion displaces  $-\text{OH}$  or  $-\text{OH}_2$  groups from hydrous oxide surfaces (Hingston et al., 1967). Iron and Al hydrous oxides can take on a net positive, neutral, or negative charge depending upon the concentration of the potential determining ion (usually  $\text{H}^+$ ) (Hingston et al., 1967). At low pH (below the zero point of charge, or ZPC), surfaces become positively charged because of  $\text{H}^+$  adsorption, and surfaces take on either a neutral (at ZPC) or negative (above ZPC) charge as pH increases and  $\text{H}^+$  dissociates from the surface  $-\text{OH}$  or  $-\text{OH}_2$  ligands (Fig. 6). Thus, pH has a strong effect on anion adsorption, both because of the charge on adsorption surfaces and because of competition with  $\text{OH}^-$  for adsorption sites.

Rajan (1978) suggests two possible reactions for specific adsorption of sulfate: (1) a bi-dentate coordination when surfaces have a net positive charge (pH below ZPC) and (2) a mono-dentate coordination when surfaces are neutral (Fig. 7). No allowance is made for sulfate adsorption when surfaces have a net negative charge. Reaction one is favored when the surface has a positive charge (when pH is below ZPC) and reaction two is favored at neutral pH (when pH is at ZPC).

Specific adsorption of  $\text{SO}_4^{2-}$  (or any other anion) can result in the introduction of a net negative charge on the oxide surface, increasing cation exchange capacity and acidity (Hingston et al., 1967; Rajan, 1978; Parfitt and Smart, 1978; Coleman and Thomas, 1967).

Several soil chemical and physical factors affect sulfate adsorption capacity (see review by Harward and Reisenauer, 1966). As noted above,



**Figure 7** Suggested mechanism for sulfate adsorption on Fe or Al hydroxides. M = metal atom and L = ligand (usually  $\text{OH}^-$  or  $\text{OH}_2^+$ ). (Adapted from Rajan, 1978.)

pH has a strong effect on sulfate adsorption, and liming is known to cause displacement of adsorbed sulfate. Because adsorption of  $\text{SO}_4^{2-}$  is often accompanied by the displacement of  $\text{OH}^-$  and the creation of cation exchange sites, it can contribute to soil acidification. This acidity is manifested when pH is raised ( $\text{OH}^-$  concentration is increased)—for instance, during liming. The added lime needed to displace adsorbed sulfate has been termed the “acidity due to anions” (Mehlich, 1964). Mehlich (1964) noted that soils containing adsorbed  $\text{SO}_4^{2-}$  had higher lime requirements and lower pHs than those containing adsorbed  $\text{OH}^-$ .

The importance of pH in regulating  $\text{SO}_4^{2-}$  flux has been demonstrated in experimental forested watersheds. At the Hubbard Brook Experimental Forest (HBEF) and other sites in the northeastern United States, both clear-cutting and whole-tree harvesting exerts a major influence on soil solution and streamwater chemistry, including  $\text{SO}_4^{2-}$  concentration and flux (Likens et al., 1969, 1978; Hornbeck et al., 1986). After vegetation removal, nitrification and resultant nitrate leaching are accelerated and the soil is acidified. This pH depression causes significant increases in sulfate adsorption and lowers streamwater  $\text{SO}_4^{2-}$  concentrations and fluxes (Nodvin et al., 1986b; Fuller et al., 1987; Mitchell et al., 1989). It has also been found that, in general, there is an inverse relationship between leaching rates of nitrate and  $\text{SO}_4^{2-}$  in forest ecosystems (Mitchell et al., 1992b).

Aside from the effects of pH, the cationic composition of the soil or soil solution also has a marked influence on sulfate adsorption. Chao et al.

(1963) found that sulfate adsorption increased in the order of  $\text{Ca}^{2+} > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+$  in solution and  $\text{Al}^{3+} > \text{Ca}^{2+} > \text{K}^+$  on soil exchange sites. Chao et al. (1963) found that pH was a more important factor than cation composition, however.

Sulfate can be displaced by phosphate (Hingston et al., 1967; Mekar and Uehara, 1972), and phosphate is an effective extractant for soil  $\text{SO}_4^{2-}$  (Tabatabai, 1982). However,  $\text{SO}_4^{2-}$  is ineffective in displacing phosphate (see review by Harward and Reisenauer, 1966). Previous treatment of soils with phosphate reduces sulfate adsorption capacity (Ensminger, 1954). Thus, specific adsorption of  $\text{SO}_4^{2-}$  and phosphate is not true anion exchange, as is the case with cation exchange and with nonspecific anion adsorption.

Because adsorption sites are primarily Fe and Al hydrous oxides, the presence and nature of these constituents in soils may be correlated with sulfate adsorption capacity, especially among similar soils (Johnson and Todd, 1983; Harrison et al., 1989; MacDonald and Hart, 1990). Johnson and Todd (1983) found that the single soil property most closely correlated with sulfate adsorption in a variety of forest soils was  $\text{Fe}_c$  (difference between Fe extracted by citrate-dithionite and oxalate). This was somewhat surprising, in that  $\text{Fe}_c$  is supposed to provide an index of crystalline Fe oxides, whereas several investigators found that sulfate adsorption was most closely associated with the more amorphous forms of both Fe (Parfitt and Smart, 1978) and Al (Rajan, 1978). Similarly, Fuller et al. (1985) found that sulfate adsorption in forested Spodosols in the northeastern United States was correlated with crystalline Fe. In contrast, Johnson et al. (1986a), Harrison et al. (1989), and MacDonald and Hart (1990) showed correlations between sulfate adsorption and amorphous forms of Al and/or Fe rather than crystalline forms. Such results are more consistent with those patterns predicted from mechanistic studies (Parfitt and Smart, 1978; Rajan, 1978).

The role of organic matter in sulfate adsorption has also been a subject of debate and conflicting results. Some studies have indicated that organic matter interferes with sulfate adsorption (Couto et al., 1979; Johnson and Todd, 1983; Singh, 1980; Gobran and Nilsson, 1988), others have indicated that organic matter enhances sulfate adsorption (Haque and Walmsley, 1973; Fuller et al., 1985); and some have found that it has little effect (Singh, 1984b). The confusion may lie in the juxtaposition of two conflicting processes: (1) the indirect enhancement of sulfate adsorption by organic matter by maintaining Fe and Al oxides in more amorphous forms with higher adsorption capacities and (2) the competition for and blockage of adsorption sites by organic ligands. In the latter context, the results of Gobran and Nilsson (1988) are of special interest; they demon-

strated the decidedly negative effect of soil solution organic matter on sulfate adsorption in a Haplorthod, indicating strong competition of organic ligands for adsorption sites. They noted that laboratory-determined sulfate adsorption isopleths did not account for the effects of soil solution organic ligands and were of limited value for modeling or extrapolating to field conditions where concentrations of dissolved organic matter (DOM) may be quite high (e.g., surface horizons and Bh horizons of Spodosols).

The kinetics of sulfate adsorption and desorption have been explored by several investigators (Barrow and Shaw, 1977; Rajan, 1978; Johnson and Henderson, 1979; Singh, 1984d), but the most thorough studies have been done by Barrow and Shaw (1977) and Singh (1984d). In each case, the authors reported that sulfate adsorption occurred in two phases, an initial rapid one and a longer, slower one. The first phase occurs within 24 hours and can account for 60–85% of total adsorption (Singh, 1984d). Rajan (1978) reported that 95% of equilibrium sulfate adsorption was attained within 15 minutes in synthetic and natural allophane soils. The second phase of sulfate adsorption occurs over periods as long as 6 months, and although it typically accounts for less total sulfate adsorption than the first phase, it is accompanied by an increasing irreversibility of adsorbed sulfate (Sanders and Tinker, 1975; Barrow and Shaw, 1977; Singh, 1984d).

Of particular interest in terms of responses to lowered S emissions and hence lower  $\text{SO}_4^{2-}$  concentrations in soil solution is the reversibility of adsorbed sulfate. In some cases, a large fraction of adsorbed sulfate is retained against leaching with either water or dilute salt solutions containing nonspecifically adsorbing anions (Chao et al., 1962; Sanders and Tinker, 1975; Barrow and Shaw, 1977; Couto et al., 1979; Rajan, 1978; Johnson and Henderson, 1979; Singh, 1984c; Harrison et al., 1989). Several factors have been found to affect the reversibility of sulfate adsorption. As noted above, both pH and the contact time between soil solution and adsorbing soil prior to desorption has a major effect on the total amount desorbed. Rajan (1978) suggests that the often-observed hysteresis of sulfate adsorption–desorption isopleths is simply a reflection of pH changes (due to  $\text{OH}^-$  consumption or production) during the adsorption or desorption processes. This is an important point, as variations in pH have such a strong effect on sulfate adsorption.

We are aware of only one study that addressed the kinetics of sulfate desorption, that of Barrow and Shaw (1977). They found that most sulfate desorption was complete within 30 minutes at low solution to soil ratios; but at greater ratios, significant desorption continued to occur over the 60-hour measurement period. Unfortunately, it appears as if no research has been conducted on sulfate desorption over the longer periods that are more relevant to the issues of soil response to decreased S deposition. In this

context, it is interesting to examine the S budget for the yellow poplar stand in Figure 4. The apparent net loss of S (as  $\text{SO}_4^{2-}$ ) from this ecosystem—approximately  $20 \text{ kg ha}^{-1} \text{ yr}^{-1}$ —is greater than could be expected from either an underestimate of S deposition (a factor of approximately two) or an overestimate of water flux (also a factor of approximately two). Thus, it appears as if  $\text{SO}_4^{2-}$  is being desorbed from this system, perhaps as a result of the previously higher inputs of S to the Walker Branch Watershed, as discussed above. Alternatively, the excess S leaching could have originated from organic S pools; S mineralization rates on WBW are known to be very high (Johnson et al., 1982).

Similar conclusions were drawn by Mitchell et al. (1993) in analyzing the processes regulating the spatial and temporal patterns of  $\text{SO}_4^{2-}$  flux in a northern hardwood stand at the Huntington Forest in the Adirondack Mountains of New York. An increase in  $\text{SO}_4^{2-}$  flux with depth in the mineral soil and the lack of variability in solute concentration below the rooting zone all suggest that  $\text{SO}_4^{2-}$  stored during an early period of greater atmospheric inputs is now being desorbed. For this site the potential importance of organic S in effecting  $\text{SO}_4^{2-}$  leaching is shown by the important contribution of organic S mineralization in contributing to  $\text{SO}_4^{2-}$  leaching within the forest floor (David et al., 1987).

### 3. Modeling sulfate adsorption and desorption

All models of sulfate adsorption and desorption assume that adsorption is concentration-dependent. Thus, the capacity of soils to adsorb sulfate at any given time is a function of the slope of the sulfate adsorption isopleth and the position of the soil system on that isopleth at the time in question. The slope of the isopleth is a function of certain soil chemical properties (discussed above) and the position on the curve is a function of the history of S inputs.

Several equations have been used to model sulfate adsorption (see review by Singh, 1984d). The most commonly used are the Freundlich and the Langmuir equations:

$$\text{Freundlich: } X = A(\text{SO}_4^{2-})^b \quad (9)$$

where  $X$  = adsorbed sulfate on soil ( $\text{mol g}^{-1}$ )  
 $(\text{SO}_4^{2-})$  = solution sulfate activity ( $\text{mol l}^{-1}$ ) and  
 $A, b$  = constants.

$$\text{Langmuir: } X = \frac{(X_{\text{max}})(b)(\text{SO}_4^{2-})}{1 + (b)(\text{SO}_4^{2-})} \quad (10)$$

where  $X_{\max}$  = maximum sulfate that can be adsorbed on soil (a constant)  
and  
 $b$  = a constant.

Some studies have shown the Langmuir equation to provide the best depiction of laboratory-determined sulfate adsorption isopleths (e.g., Johnson and Cole, 1977), and some have shown the Freundlich to provide the best depiction (e.g., Khanna et al., 1986; Singh, 1984a).

Nodvin et al. (1986a) described a very different but very simple equation involving a partition coefficient, which best depicted the sulfate adsorption isopleth for a northern hardwood soil. They named their isopleth the "initial mass isotherm":

$$\text{IM: } \text{RE} = mX_i - b \quad (11)$$

RE = amount of sulfate removed from or released to solution (mmol/kg)

where

$m$  = partition coefficient (unitless)

$X_i$  = initial concentration of  $\text{SO}_4^{2-}$  in solution, expressed per unit soil (mmol/kg) and

$b$  = intercept (mmol/kg)

This formulation assumes that there is a total pool of reactive  $\text{SO}_4^{2-}$  that consists of readily soluble  $\text{SO}_4^{2-}$  in the soil (RSP) and that added in solution ( $X_i$ ):

$$\text{Total reactive sulfate} = \text{RSP} + X_i \quad (12)$$

The readily soluble sulfate pool in soil can be calculated from isopleth data as follows:

$$\text{RSP} = b/(1 - m) \quad (13)$$

In the case where  $\text{RSP} = 0$ , this reduces to a simple linear isopleth

$$\text{RE} = \text{Kd}(\text{Cf})$$

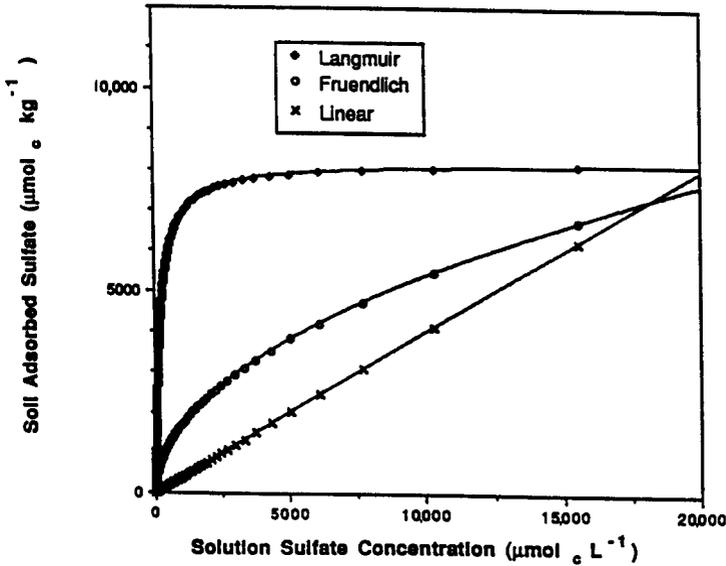
$\text{Kd}$  = distribution coefficient ( $\text{L kg}^{-1}$ )

where

$\text{Cf}$  = equilibrium solution concentration ( $\text{mmol L}^{-1}$ ) and

$$\text{Kd} = \frac{(m)(\text{volume of solution})}{(1-m)(\text{mass of soil})}$$

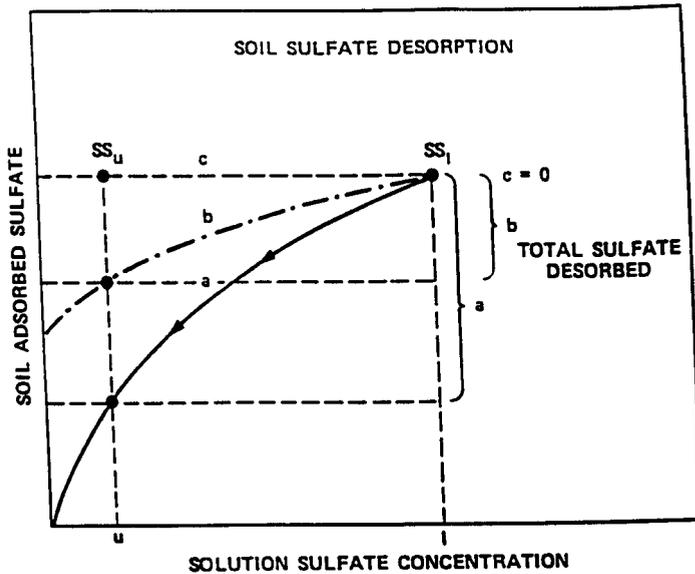
Figure 8 depicts three generic curves for the three types of isopleths. The Langmuir and Freundlich isopleths both show decreasing adsorption with increasing solution concentrations, whereas the linear isopleth does not. Only the Langmuir isopleth shows a maximum adsorption, and thus it is



**Figure 8** General shapes of Langmuir, Freundlich, and linear sulfate adsorption isopleths.

the most realistic at very high soil solution concentrations. However, typical soil solution concentrations seldom reach values that would produce maximum soil adsorbed sulfate, and thus both the Freundlich (Singh, 1984c) and linear (Nodvin et al., 1986b) isopleths have been found to best describe sulfate adsorption at lower concentrations.

Reuss and Johnson (1986) considered the potential effects of differing degrees of reversibility of sulfate adsorption on recovery of soils and soil solutions using the Langmuir model. For the purposes of illustration, a square wave input pulse was considered with three reversibility scenarios: (1) complete reversibility with no hysteresis, (2) partial reversibility, and (3) complete reversibility (Figure 9). If sulfate adsorption is completely reversible with no hysteresis (scenario *a* in Fig. 9), there is theoretically no difference in the response slope of soil solution to increases or decreases in  $\text{SO}_4^{2-}$  input (scenario *a* in Fig. 10), and no residual CEC or acidity due to anions remaining in the soil. The soil has, theoretically, been acidified to the amount equivalent to the  $\text{SO}_4^{2-}$  lost on desorption. With partial reversibility (scenario *b* in Fig. 9), soil solution response is more rapid (Fig. 10), and some residual CEC and acidity due to anions remains within the soil. With no reversibility (all adsorbed  $\text{SO}_4^{2-}$  is permanently retained;

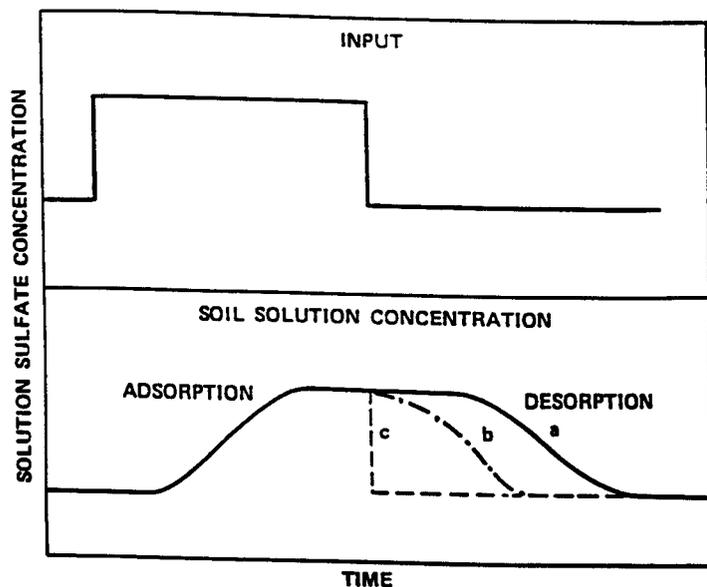


**Figure 9** Schematic representation of different degrees of reversibility of sulfate adsorption: (a) completely reversible (no hysteresis); (b) partially reversible; (c) irreversible. (From Reuss and Johnson, 1986. Reprinted with permission from Springer-Verlag, New York, New York.)

scenario *c* in Fig. 9), soil solution recovery is instantaneous, and all CEC and acidity due to adsorbed sulfate remains within the soil.

#### IV. ORGANIC S RETENTION MECHANISMS

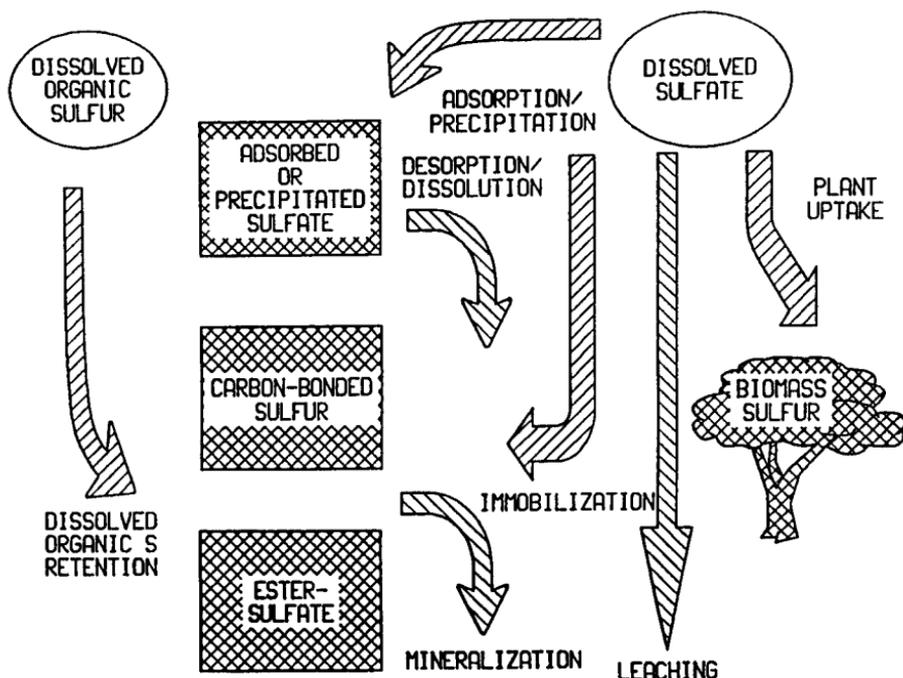
Organic S accumulates in soil if immobilization plus organic S inputs is greater than mineralization and/or dissolved organic S constituents show a net retention in soil as shown conceptually in Figure 11. It is obvious that over extended periods, there is a net accumulation of organic S in soil, resulting in the formation in this large pool of organic S. For example, Mitchell et al. (1989) estimated within a northern hardwood forest at the Hubbard Brook Experimental Forest that the net retention of dissolved organic S since the period of most recent glaciation, which occurred about 10,000 years ago, could account for the present organic S concentration. The importance of dissolved organic S being retained in soils has also been proposed for other soils (Schoenau and Böttner, 1987)



**Figure 10** Theoretical response of soil solution sulfate concentration to a square wave pulse input and different degrees of reversibility as in Figure 7. (From Reuss and Johnson, 1986. Reprinted with permission from Springer-Verlag, New York, New York.)

The use of the radioisotope of sulfur  $^{35}\text{S}$  has been used extensively to study the dynamics of organic S. Laboratory (Strickland et al., 1986b; Schindler and Mitchell, 1987; Dhamala et al., 1990) and field studies (Strickland et al., 1986a; David et al., 1987) have both shown that there is a rapid conversion of  $^{35}\text{S}$ -  $\text{SO}_4$  to both ester sulfates and carbon-bonded S. However, these pools may be highly labile and there may also be a rapid mineralization of this newly formed organic S back to inorganic sulfate. The ester sulfate pools appear to be particularly labile, but depending on the actual chemical species, carbon-bonded S may also be rapidly mineralized (Strickland et al., 1984).

When interpreting rates of sulfur incorporation using  $^{35}\text{S}$  techniques, it is important to clearly define whether gross or net rates are being estimated. If gross rates are used to estimate the potential for  $\text{SO}_4^{2-}$  incorporation and retention into organic pools and the reverse mineralization reaction is not evaluated concomitantly, then these estimates would overestimate the actual net incorporation of inorganic  $\text{SO}_4^{2-}$  into organic pools. Such estimates may be useful for estimating the potential for organic S



**Figure 11** Schematic diagram of mechanisms for S retention in a forest ecosystem.

formation over short periods (i.e., days or weeks), but they do not give the actual rate of organic S accumulation over longer periods (i.e., greater than one year). The more extended periods are most important in considering the long-term reversibility of sulfur retention in soils.

Fuller et al. (1986a), incorporating laboratory data into a simulation model of S fluxes among inorganic and organic pools including adsorption-desorption as well as immobilization-mineralization reactions, found that residence time was much shorter in adsorbed pools than in either carbon-bonded or ester sulfate pools. In addition, within the mineral soil, ester sulfates had significantly greater turnover rates than the total pool of carbon-bonded S.

Stable isotopes of sulfur have begun to be used more commonly to examine S transformations and fluxes directly in the field. Sulfur isotope ratios are expressed in the standard  $^{34}\text{S}$  notation:

$$^{34}\text{S}(\text{‰}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000 \quad (14)$$

where  $R_{\text{sample}}$  and  $R_{\text{standard}}$  refer to the  $^{34}\text{S}/^{32}\text{S}$  abundance ratio of the sample and the Canyon Diablo meteorite standard, respectively. Natural abundances of  $^{34}\text{S}$  range from  $-40$  to  $+40\%$  (Ehleringer and Rundel, 1988). Stable isotope abundances have been especially useful in ascertaining the contribution of anthropogenic sources (i.e., combustion of fossil fuels) to atmospheric inputs of S if the source of fossil fuel has a  $^{34}\text{S}$  signature that is distinctive from natural levels (Krouse et al., 1991). Analysis of  $^{34}\text{S}$  in forested watersheds has also been used to evaluate which processes are regulating  $\text{SO}_4^{2-}$  flux in solutions (Stam et al., 1992), although in some cases it appears that isotopic discrimination processes may be affecting the distribution of S isotopes among different ecosystem components (Fuller et al., 1986b; Heslein et al., 1988). An analysis of  $^{34}\text{S}$  values of precipitation and streamwaters at Bear Brook Watershed in Maine (BBWM) suggested that inorganic  $\text{SO}_4^{2-}$  dynamics was primarily responsible in regulating seasonal changes of  $\text{SO}_4^{2-}$  in surface waters at this site (Stam et al., 1992).

A major problem in estimating S turnover in soil organic pools, especially carbon-bonded S, is the assumption of pool homogeneity. It has been established that only a small fraction of the organic S pool is biologically active, with less than 5% of the S represented by microbial biomass (Nakas, 1986). Similarly, it is generally assumed for agronomic soils that only 1–3% of the organic S is converted to inorganic  $\text{SO}_4^{2-}$  annually (Freyne and Williams, 1983).

More studies have been done on the transformations of organic S in grassland soils than in forest soils. McGill and Cole (1981) proposed a model that separates biochemical and biological mineralization processes for S in soil systems, and portions of this model have been incorporated into more complex conceptual (Maynard et al., 1984) and simulation (Hunt et al., 1986) models. In general, these models (which incorporate organic S) have been utilized only for grasslands whereas models of  $\text{SO}_4^{2-}$  dynamics in forest soils have focused on adsorption-desorption processes (Mitchell and Fuller, 1988).

Most measurements of  $\text{SO}_4^{2-}$  incorporation under field conditions have focused on evaluating changes in soil water or surface water chemistry and using mass balance calculations to quantify the contribution of soil sulfate adsorption. A few studies have made direct measurements of changes in soil pools. At Hubbard Brook Experimental Forest (HBEF), Mitchell et al. (1989) combined measurements of soil solution chemistry, stream chemistry, and changes in soil S constituents to establish that the reduction of  $\text{SO}_4^{2-}$  in solution could be attributed to adsorption of  $\text{SO}_4^{2-}$ , especially in the upper B horizon. David et al. (1990), using buried mineral soil bags installed at Bear Brook (BBMW) in experimental plots treated

with sulfuric and/or nitric acid, was able to establish that adsorbed sulfate significantly increase as a function of  $\text{SO}_4^{2-}$  loading. Moreover, this approach showed promise in detecting smaller changes in organic S pools than could be detected using more traditional soil sampling procedures. Small changes in these large organic S pools may be significant in evaluating S storage over extended periods (i.e., >5 years). At BBWM, HBEF, and the Adirondack Mountains, a series of studies have been recently initiated using buried mineral soil bags that are evaluating changes in S pools under various additions of N and S.

## **V. SIMULATION MODELING OF SULFATE RETENTION AND RELEASE IN TWO FOREST ECOSYSTEMS**

The effects of increased and decreased S inputs on N, P, K, Ca, Mg, and S cycling; soil S retention; and soil acidification/alkalization were simulated for two forest ecosystems—a red spruce system in the Great Smoky Mountains, North Carolina, and a mixed hardwood forest at Coweeta Hydrologic Laboratory in the southern Appalachians of North Carolina—using the Nutrient Cycling Model (NuCM). Following is a brief description of the model; see Liu et al. (1991) for more detail.

### **A. The NuCM Model**

NuCM was developed as part of the Electric Power Research Institute's Integrated Forest Study (Liu et al., 1991; Johnson and Lindberg, 1991). The NuCM model incorporates state-of-the-art understanding of the biogeochemical and transport processes controlling nutrient cycles. The available nutrients in soil strata and vegetation pools and the fluxes between them are explicitly tracked and provided as model output. The model can be used to simulate the response of forests to atmospheric deposition and to various management practices (e.g., application of fertilizers). Factors are included in the model that allow the user to easily increase or decrease atmospheric deposition loads. The forested ecosystem is represented as a series of vegetation and soil components. The model provides for both an overstory and understory, each of which can be divided into canopy, bole, and roots.

Tree growth in the model is a function of user-defined developmental stage and the availability of nutrients and moisture. Translocation of nutrients prior to senescence is included. The understory is simulated in a similar manner to the overstory, except that its "incident precipitation" is the overstory's throughfall and its biomass nutrient concentrations are al-

lowed to be different. For both the overstory and the understory, variable tissue nutrient concentrations are allowed to accommodate multiple species and availability of nutrients.

Using mass balance and transport formulations, the model tracks 16 solution-phase components, including the major cations and anions (analytical totals), ANC (acid-neutralizing capacity), an organic acid analogue, and total Al (Liu et al., 1991). The model routes precipitation through the canopy and soil layers and simulates evapotranspiration, deep seepage, and lateral flow. The soil includes multiple layers (up to ten), and each layer can have different physical and chemical characteristics. The nutrient pools associated with soil solution, the ion-exchange complex, minerals, and soil organic matter are all tracked explicitly. The processes that govern interactions among these pools include decay, nitrification, anion adsorption, cation exchange, and mineral weathering. Litter decay is represented as a series reaction with first-order dependencies on the reactant concentrations and C/N ratios. The decay products include nutrients and organic matter—both solid (e.g., humus) and solution phase (e.g., organic acids). The nutrients produced enter the solution phase, where they are available for uptake by vegetation or the exchange complex, and for transport from the forest floor by percolation and/or lateral flow.

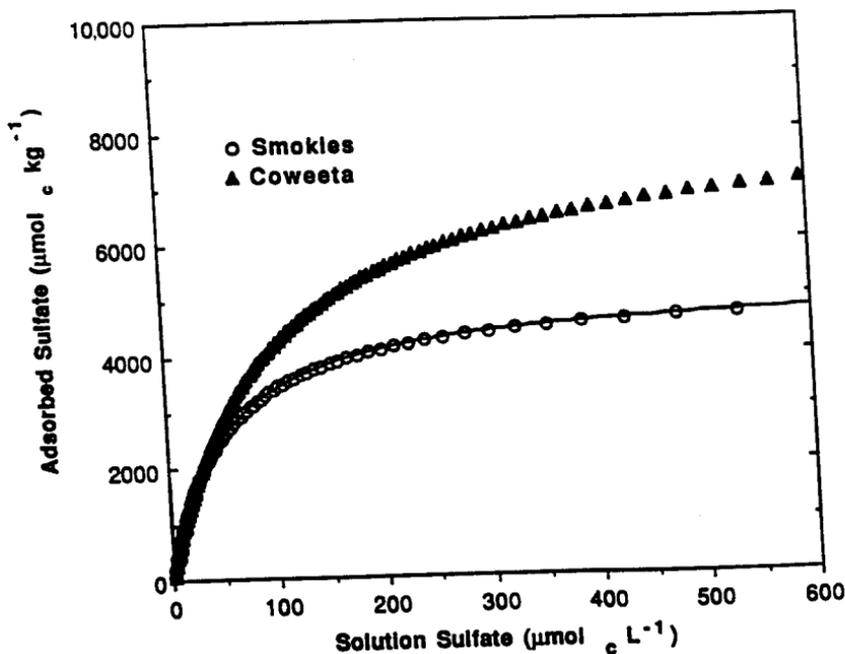
The model simulates the noncompetitive adsorption of sulfate, phosphate, and organic acid. Sulfate adsorption can be simulated in NuCM using either linear or Langmuir (saturation) adsorption isopleths; Langmuir equations were used for these simulations. Figure 12 shows the isopleths input for the Smokies and Coweeta sites.

Cation exchange is represented by the Gapon equation. Mineral weathering reactions are normally slow and are described in the model using rate expressions with dependencies on the mass of mineral present and solution-phase hydrogen-ion concentration taken to a fractional power.

Model input is based on measurable parameters. The model uses such data to compute selectivity coefficients for each soil layer simulated. Model output options include nutrient pool sizes, fluxes between components, the relative contribution or loss by process, and soil solution and adsorbed concentrations versus time. Long-term nutrient loss or accumulation can be tracked by following annual pool and flux charts.

## B. Simulation Results

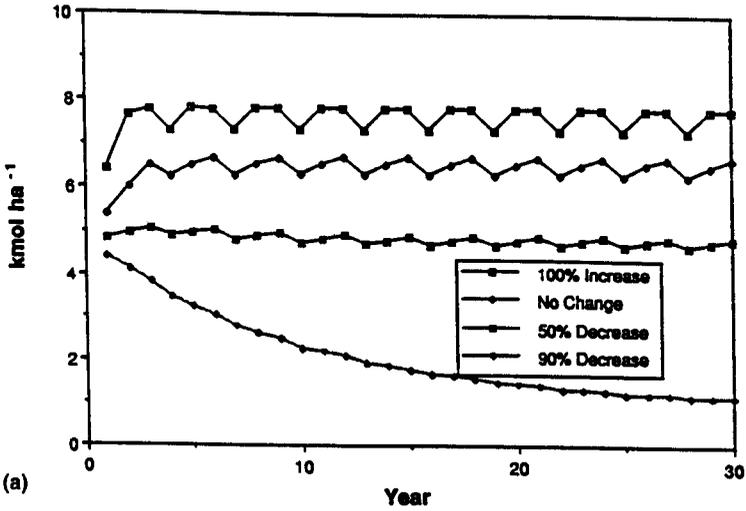
Thirty-year simulations were run that included current (no change) S inputs, 100% increase, 50% reduction, and 90% reduction for both the Smokies and Coweeta sites. Simulated soil  $\text{SO}_4^{2-}$  leaching and soil-adsorbed  $\text{SO}_4^{2-}$  for each site are summarized in Figures 13 and 14.



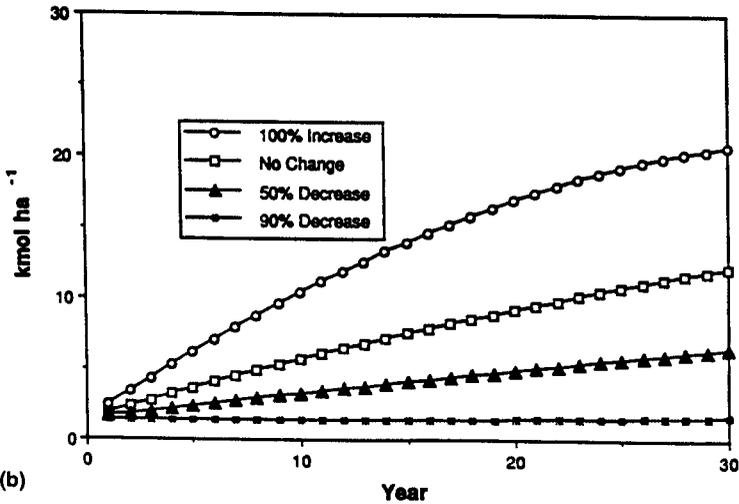
**Figure 12** Sulfate adsorption isopleths (Langmuir) used for simulations for the Coweeta and Smokies red spruce sites.

The effects of soil  $\text{SO}_4^{2-}$  adsorption characteristics (Fig. 13) on response times to changes in atmospheric S loading are very clear. Sulfate leaching at the Smokies site increased or decreased with changes in S deposition almost immediately, and there was little or no net retention or loss of S from the system during most of the simulations (Fig. 13a). Soil  $\text{SO}_4^{2-}$  reached a steady-state condition rapidly under all but the 90% decrease scenario, where it declined slowly (Fig. 14a). On the other hand, the Coweeta site accumulated S throughout all scenarios except for the 90% decrease, where it was approximately at steady state (Figs. 13b and 14b). At Coweeta, the rates of increase in  $\text{SO}_4^{2-}$  leaching and soil  $\text{SO}_4^{2-}$  increased with increasing deposition but showed no signs of leveling off except in the 90% decrease scenario, which was approximately in steady state to begin with (Figs. 13b and 14b). Sulfur continued to accumulate in the soil throughout the 100% increase, no change, and 50% decrease scenarios (Fig. 13b).

Johnson and Reuss (1984) note that "because sulfate adsorption is concentration-dependent, the time required to achieve equilibrium may not

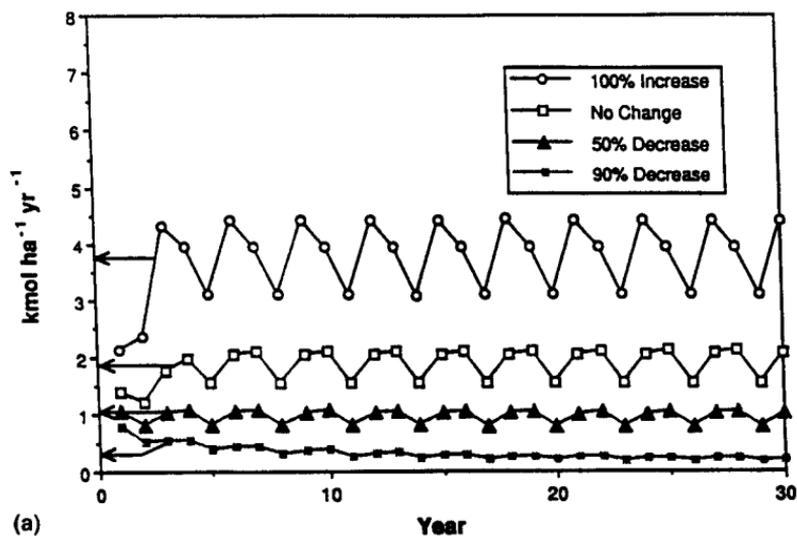


(a)

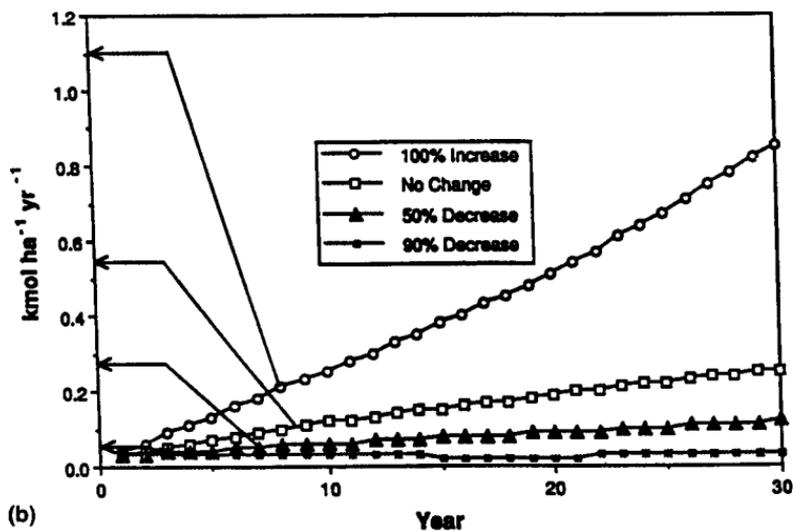


(b)

Figure 13 Simulated adsorbed sulfate in the Smokies (a) and Coweeta (b) sites.



(a)



(b)

**Figure 14** Simulated soil solution sulfate concentrations in the Smokies (a) and Coweeta (b) sites.

be materially shortened by an increase in the impact dosage." The results of these simulations would tend to support this contention. However, the time required to achieve steady state (equilibrium) is not entirely independent of the impact dosage, in that the latter may affect the amount of soil-adsorbed sulfate. Soil-solution  $\text{SO}_4^{2-}$  concentration becomes increasingly responsive to changes in soil adsorbed sulfate as the latter increases, as can be seen from the slope (first derivative) of the adsorption isopleth. Solving the Langmuir equation (Eq. 10) for  $(\text{SO}_4^{2-})$  and taking the first derivative yields:

$$d(\text{SO}_4^{2-})/dX = X_{\text{max}}/[b(X_{\text{max}} - X)^2], \quad \text{for } X < X_{\text{max}} \quad (14)$$

Thus, the responsiveness of soil-solution  $\text{SO}_4^{2-}$  to increases in soil-adsorbed sulfate (and, therefore, to increased sulfate inputs to the system) increases as the soil becomes "saturated" with  $\text{SO}_4^{2-}$ ; i.e., as  $X$  increases and approaches  $X_{\text{max}}$ ,  $d(\text{SO}_4^{2-})/dX$  increases. This can be seen in Figure 8 where as the curve of soil-adsorbed sulfate versus solution- $\text{SO}_4^{2-}$  concentration flattens out. In practice, however, soils subjected to atmospheric S inputs are far below saturation and typically within the region where the adsorption isopleth is still increasing sharply, and the statement of Johnson and Reuss (1984) is valid under those conditions.

These simulations indicate the great importance of the nature of sulfate-adsorption isopleths in determining the response of soils to changes in S inputs. Other S retention factors were either not built in to the model (precipitation) or were unimportant in the simulations (net changes in storage in soil organic matter and vegetation were negligible in all cases). Thus, these simulations in effect show the theoretical responses of these systems to changing S inputs due to soil adsorption-desorption alone. Whether the predicted responses are accurate or not remains to be tested with long-term monitoring, manipulations, or both (bearing in mind that short-term manipulative studies may produce little change at Coweeta, even with large increases in input).

## VI. OTHER MODELS

Mitchell and Fuller (1988) reviewed a wide range of models of both forest and grassland systems and outlined how sulfur processes were formulated in various applications (Table 3). For those models that have been applied to forest ecosystems, the major focus with respect to sulfur retention has been on sulfate adsorption-desorption processes with no attention being paid to organic sulfur dynamics. It has also been assumed that the sorption processes are completely reversible. There has been some attempt to do

**Table 3** Comparison of the Treatments of Sulfur Dynamics in Forest and Grassland Ecosystem Models

Model (Reference)	General model type	Inorganic S dynamics	Organic S dynamics	Hydrology
McGill and Cole, 1981	Conceptual (general soil)	Two-phase (solid and soluble)	Linked to C and N dynamics	Not considered
Bettany and Stewart, 1983; Maynard et al., 1984	Conceptual (grasslands)	Adsorbed and occluded sulfate. Precipitated sulfide, elemental S, labile organic S	Extension of McGill and Cole (1981) and inclusion of microbial S, labile organic S, stable organic S, plant uptake	Not considered
David et al. 1984	Conceptual (forest soils)	Adsorbed sulfate, sulfate in solution	Carbon-bonded S, ester sulfate in solution and solid phases, mineralization and 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 and 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 and 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, which could include both organic and inorganic S transformation	See inorganic S	Linked to hydrology sub-model
Trickle-Down Schnoor et al., 1984	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

Table 3 Continued

Model (Reference)	General model type	Inorganic S dynamics	Organic S dynamics	Hydrology
Coughenour et al., 1980	Simulation (grassland)	Sulfate adsorption by Freundlich isotherm	Uptake of sulfate by Michaelis-Menton; 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., 1986a	Simulation (Spodosols)	Sulfate adsorption by kinetic formulation	Transformation rates of sulfate between ester sulfates and carbon-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 effecting formation of carbon-bonded S and ester sulfates	Not considered

Source: Mitchell and Fuller, 1988.

historical reconstructions using models and it has been shown in some simulations using Model of Acidification of Groundwater in Catchments (MAGIC) (e.g., Jenkins et al., 1990; Wright et al., 1986) that acidification processes, including sulfate adsorption-desorption, appear to be reversible.

As part of the National Acid Precipitation Assessment Program, there was an extensive evaluation of a set of models that predict surface water chemistry as part of the Direct/Delayed Response Project for three regions (Northeast, Mid-Appalachian, and Southern Blue Ridge) in the United States (Thornton et al., 1990). This research focused on the utilization of three models: Enhanced Trickle Down (ETD) (Lee and Schnoor, 1988), Integrated Lake-Watershed Acidification Study (ILWAS) (Gherini et al., 1985) and MAGIC (Cosby et al., 1985). In the review of the application of these models for predicting future changes in surface water chemistry, it was concluded by Thornton et al. (1990) that any irreversible adsorption of  $\text{SO}_4^{2-}$  could alter predictions on the rate of recovery of forested watersheds from acidification.

## VII. SUMMARY AND CONCLUSIONS

There was little information on S cycling in forests compared to other nutrients (especially N) until the past two decades, when interest in S nutrition and cycling in forests was heightened with the discovery of deficiencies in some unpolluted regions and excesses associated with air pollution in other regions. Several studies have addressed the effects of increased S inputs in forest soils and forest ecosystems, but few have considered the effects of decreased S inputs, which are now occurring as S emissions decline in many polluted regions. These decreases in S emission have been reflected in decreases in  $\text{SO}_4^{2-}$  concentrations of surface waters in the northeast United States, eastern Canada, and Europe; however, there are no data as to effects on soils or forest ecosystems.

One interesting and unique feature of S cycles is that a significant proportion of total S can be cycled and accumulated as  $\text{SO}_4^{2-}$ , within both vegetation and soils. The relative amount of  $\text{SO}_4^{2-}$  as a proportion of total S increases with S availability. In vegetation, most carbon-bonded S is associated with the amino acids cysteine, cystine, and methionine, which are in turn used for protein synthesis, and thus there is a very close relationship between organic S and organic N in plant tissues. As is the case with many other nutrients, the soil is the major reservoir of S and site for S accumulation in forest ecosystems. Mineral soil S accounts for >80% of total ecosystem S in all but the most S-deficient systems. In most forest soils, organic S—mostly in the form of carbon-bonded S and ester

sulfates—makes up the dominant pools (>90%), except in those soils with high sulfate adsorption capacity and/or high levels of S deposition where  $\text{SO}_4^{2-}$  concentrations may approach that of organic S. In soils, S can accumulate by incorporation into organic matter, precipitation, and adsorption, mostly as adsorbed  $\text{SO}_4^{2-}$ . In cases in which S deposition is high, the capacity for organic S incorporation is often exceeded, and precipitation and adsorption reactions predominate. Precipitation reactions tend to be important when soil solution  $\text{SO}_4^{2-}$  concentrations are very high, whereas adsorption predominates in most moderately polluted systems. The degree to which soils can accumulate  $\text{SO}_4^{2-}$  is a function of Fe and Al hydrous oxide content and the concentration of  $\text{SO}_4^{2-}$  in soil solution. Soil  $\text{SO}_4^{2-}$  adsorption can be modeled by adsorption isotherms of the Langmuir, Freundlich, or linear type.

A major remaining gap in our understanding of S cycling in forests is the response to the reduced S deposition that is currently under way. The degree and duration of  $\text{SO}_4^{2-}$  release from organic matter, precipitates, and adsorption sites under lower deposition will have profound impacts upon the effectiveness of S emission controls on both terrestrial and aquatic ecosystems. We know little about the potential release of S from organic matter under reduced S availability. Models are available that can predict the release of  $\text{SO}_4^{2-}$  from precipitates and adsorption sites; however, none of the current models incorporate the significant hysteresis always noted in the adsorption–desorption of  $\text{SO}_4^{2-}$  from soil adsorption sites.

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