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Sulfur cycling in forests*

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Abstract. Sulfur is essential for the production of certain amino acids in plants. As amino acid sulfur is the major form of sulfur in trees, there is a strong relationship between organic S and organic N in tree tissue. Sulfur deficiencies occur in parts of southeastern Australia and northwestern North America, remote from pollutant inputs. Since bilogical S requirements of forests are modest ($< 5\ \mathrm{kg \cdot ha^{-1}\ yr^{-1}}$ for net vegetative increment), however, atmospheric S inputs in polluted regions ($10–80\ \mathrm{kg \cdot ha^{-1} \cdot yr^{-1}}$) often exceed not only the forest ecosystem S requirement but also its ability to biologically accumulate S. There is some increase in the SO_4^{2-} –S content of forest vegetation in response to elevated atmospheric S inputs, but this capacity is apparently easily saturated. Soil SO_4^{2-} adsorption is often the dominant feature of S cycling in polluted ecosystems and often accounts for net ecosytem S accumulations.

Introduction

Although sulfur (S) is an essential plant nutrient, only limited information is available on forest S nutrition and cycling as compared with that of N, P, K, Ca, and Mg. With the recent interest in air pollution effects (both SO_2 and acid deposition), increased attention has been paid to S cycling in forest ecosystems (Likens et al., 1977; Shriner and Henderson, 1978; Turner et al., 1980; Meiwes and Khanna, 1981; Johnson et al., 1982). Prior to this, forest sulfur nutrition research was limited largely to S-deficient regions of Australia (Kelly and Lambert, 1972; Humphreys et al., 1975) the northwestern United States (Youngberg and Dyrness, 1977; Turner et al., 1977), and east Africa (Hesse, 1957).

This paper reviews some basic features of S cycling in forests with special attention to the effects of elevated levels of atmospheric S input associated with air pollution.

Role of S in tree nutrition

Over 80% of S in tree tissue is thought to be used for the synthesis of the aminino acids cysteine, cystine, and methionine, which in turn are used for

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protein elaboration (Turner et al., 1977). Due to their mutual involvement in amino acid and protein synthesis, there is a close biochemical relationship between S and N (Kelly and Lambert, 1972). There are generally insignificant concentrations of inorganic nitrogen within conifer foliage, but sulfur can be present as both organic and inorganic (sulfate) compounds. The biochemical molar ratio of sulfur to nitrogen (based on protein and amino acids) in conifer foliage is 0.030 (Kelly and Lambert, 1972). This ratio was found to hold true for several deciduous forest species as well (Johnson et al., 1982). Sulfate sulfur is accumulated in excess of that sulfur required to balance the nitrogen in protein formation and is used as an indicator of foliage sulfur status (Kelly and Lambert, 1972).

A deficiency of sulfur may not reduce growth, but it does result in an accumulation in the foliage of non-sulfur-containing amino acids, especially arginine. These non-sulphur-containing amino acids are used by foliar fungal pathogens (for example, *Dilodia pinea, Dothistroma septospora*) as food sources, allowing very rapid growth of these organisms. These fungi are thus the secondary cause of deformity or defoliation arising from the primary stress induced by nutrient deficiency (Turner and Lambert, 1980).

Nissen and Benson (1961) noted the formation of large amounts of choline sulfate (an ester sulfate) in the roots of S-deficient sunflower, corn, and barley plants supplied with sulfate-^{35}S. They also noted that choline sulfate constituted 5 to 15% of total S in both roots and leaves of normal plants and suggested that choline sulfate, which is highly soluble in organic solvents, can be an important sulfur reservoir and a sulfur transport agent in plants. To the author's knowledge, no studies on the occurrence and amounts of choline sulfate in trees have been conducted, but since it hydrolyzes to SO_4^{2-} in 1 *N* HCl, the foliage sulfate extraction procedures of Kelly and Lambert (1972) (using 0.1 *N* HCl) probably extract choline sulfate as well as inorganic sulfate.

Soil sulfur reactions

In most cases, forest soil S is primarily organically bound (with certain exceptions noted later). Of the various soil organic S forms, organic sulfates and carbon-bonded S are most predominant (Bettany et al., 1980; David et al., 1982). These soil S pools are active in the soil S cycle and may represent a net sink for atmospherically deposited S in forest ecosystems (Fitzgerald et al., 1982; Swank et al., 1984). For detailed discussion of soil organic S transformations, see the companion papers by Mitchell, Fitzgerald, and Tabatabai.

Soils rich in Fe and Al hydrous oxides often accumulate SO_4^{2-} by adsorption reactions (Chao et al., 1972; Harward and Reisenauer, 1965; Hingston et al., 1967); therefore, SO_4^{2-} adsorption can be an important component of forest S cycles, as will be shown later in this paper. Most recent work on soil

SO_4^{2-} adsorption, however, has emphasized the mitigative effect of adsorption on the leaching of cations by H_2SO_4 in precipitation (Johnson and Cole, 1977, Johnson et al., 1979, Singh et al., 1980; Lee and Weber, 1982). Cation-anion charge balance relationships dictate that H_2SO_4 leaching occurs only if SO_4^{2-} is mobile in the soil, a fact that has been repeatedly demonstrated in the empirical studies (cited above). The adsorption of sulfate ions results in the displacement of $-OH^{\circ}$ or $-OH_2^+$ ligands from Fe or Al-hydrous oxide surfaces. In the first ligand case, OH^- is released and neutralizes H^+; at the same time, a cation exchange site will be created by the adsorption of SO_4^{2-} (Rajan, 1978, Parfitt and Smart, 1978). In the second ligand case, only water is released and the site is transformed from a positive to a negative charge (i.e., from an anion to a cation exchange site). Rajan (1978) also proposed a reaction wherein two adjacent $-OH$ ligands are replaced by one SO_4^{2-}, leaving no net change in surface charge and the release of two OH^- ions. Parfitt and Smart (1978) found amorphous forms of Fe oxides to be most effective in adsorbing SO_4^{2-}. Hasan et al. (1970) found that volcanic soils are ineffective at SO_4^{2-} adsorption until they have weathered (i.e., hydrated) to some extent. Johnson and Todd (1983), however, found that crystalline Fe determined by chemical means (i.e., the citrate-dithionite method with a correction for oxalate-extractable Fe) was highly correlated with SO_4^{2-} adsorption in a variety of forest soils. The apparent conflict between these latter results and those of Parfitt and Smart (1978) was attributed in part to the presence of crystalline Fe forms that had varying SO_4^{2-} adsorption properties.

Several studies have documented the decidedly negative influence of organic matter on SO_4^{2-} adsorption, even in soils with high Fe + Al hydrous oxide contents (Couto et al., 1979; Johnson and Todd, 1983). This may be due to blockage of SO_4^{2-} adsorption sites by organic ligands or the influence of organic matter on the nature of Fe + Al oxides themselves (Schwertmann, 1966). In any event, the inhibitory effect of organic matter may account for the previously noted lack of SO_4^{2-} retention in surface soils (Williams and Steinbergs, 1964) and the more recently noted lack of adsorption in Spodosol B2ir horizons (Johnson and Todd, 1983), even when such soils are quite high in Fe + Al hydrous oxides.

The time required to reach a steady-state condition with respect to SO_4^{2-} flux in a SO_4^{2-}-adsorbing soil is related to soil depth and the slope of the adsorption isotherm. This is illustrated in Figure 1, where SO_4^{2-} adsorption isotherms for two fictions soils are plotted. Soil A (an Ultisol) is richer in Fe and Al oxides and adsorbs more SO_4^{2-} than soil B (a Spondosol). Let both soils be initially in equilibrium (i.e., no net SO_4^{2-} adsorption) with 40 μeq/l SO_4^{2-}. Concentrations are the raised to 300 μeq/l, each soil will adsorb additional SO_4^{2-} until a new steady-state is reached. For soil A, this requires an additional 2.2 meq · 100 g^{-1} of adsorption and for soil B only 1.0 meq · 100 g^{-1} of adsorption. Thus, a given depth of soil A will show net SO_4^{2-}

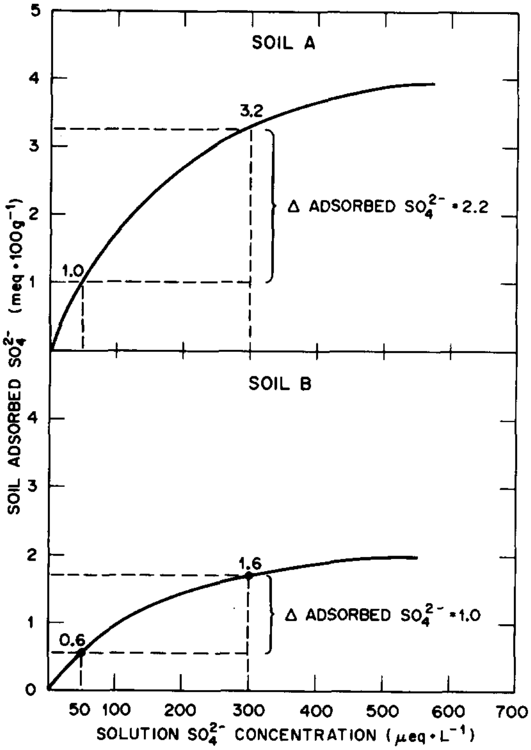

Figure 1. Idealized SO_4^{2-} adsorption isotherm for a soil with high adsorption capacity (soil A) and low adsorption capacity (soil B). Amounts of SO_4^{2-} adsorption required to re-equilibrate from 50 to 300 μeq • L^{-1} SO_4^{2-} are shown on the right.

accumulation for a longer period than a given depth of soil B under the same input conditions. Conversely, if SO_4^{2-} adsorption is reversible, soil A will show a net export of SO_4^{2-} for a longer period than soil B if FO_4^{2-} inputs are reduced.

The availability of adsorbed SO_4^{2-} to plants is limited by its solubility in water or the 'intensity' of S nutrition (Hasan et al., 1970). If adsorbed SO_4^{2-} is not released rapidly enough to supply plant requirements, S deficiencies can develop even when total soil SO_4^{2-} pools are high. Conversely, if soil SO_4^{2-} is readily soluble, SO_4^{2-} leaching can cause S deficiencies due to low soil SO_4^{2-} (Humphreys et al., 1975). In the former case, S deficiencies can be corrected only by fertilization (which increases total adsorbed SO_4^{2-} and thereby increases SO_4^{2-} supplying intensity, Hasan et al. 1970) or by atmospheric inputs. In the case where soil SO_4^{2-} is readily soluble, fertilization is often ineffective because SO_4^{2-} leaches rapidly and plants must rely heavily on atmospheric S inputs, which are more continuous (Humphreys et al., 1975).

Recently, precipitation of SO_4^{2-} with Al (as basalunite, $Al_4OH_{10}SO_4$), alunite, $KAl_3OH(SO_4)_2$, or jurbanite, ($AlOHSO_4$) has been suggested as an important SO_4^{2-} retention mechanism in acid soils subject to high rates of SO_4^{2-} input (e.g., Meiwes et al., 1980, Nilsson and Bergkvist, 1983). Matzner and Ulrich (1981) note alternate net accumulations and releases of SO_4^{2-} and Al from soils at the Solling site in West Germany. The net releases of SO_4^{2-} and Al occur during acidification pulses (caused by nitrification) which cause the dissolution of jurbanite previously formed. This phenomenon is quite different from what one would expect if SO_4^{2-} adsorption controlled SO_4^{2-} leaching since acidification normally enhances SO_4^{2-} adsorption (reduces SO_4^{2-} leaching). However, Meiwes et al. (1980) and Khanna and Beese (1978) find SO_4^{2-} retention in laboratory studies of soils from Solling to be consistent with SO_4^{2-} adsorption mechanisms as well.

In practice, it may prove difficult to sort out the relative importance of adsorption vs precipitation reactions in controlling sulfate leaching in acid soils with high SO_4^{2-} inputs unless unusual phenomena such as the acidification pulse described by Matzner and Ulrich (1983) occur or are made to occur. Adsorption is likely most important in less acid soils, however, since Al concentrations in soil solutions of pH 4.5 or above will usually be too low to allow $Al-SO_4^{2-}$ precipitates to form.

General patterns in forest S cycling

There are various ways in which forest nutrient cycles can be depicted (e.g., Cole et al., 1978; Curlin 1970; Switzer and Nelson, 1972), but in general the relationships among nutrient pools and fluxes and the means of measuring them are basically the same. For the purpose of this discussion, a modification of the circle and arrow depiction of Cole et al. (1968) will be used (Figure 2).

Only a few of the fluxes depicted in Figure 2 (wet deposition, litterfall throughout, soil leaching) can be measured directly whereas others (dry deposition, foliar leaching, translocation, uptake, decomposition, adsorption, desorption) are either inferred from other, more direct measurements (wet deposition, litterfall, throughfall, root turnover, vegetation production, and nutrient pool sizes in vegetation components, litter, and soil) or they are simply left as unknowns (e.g., mineralization, immobilization, volatilization, weatherin). Details of methods used to characterize nutrient cycles are described elsewhere (Cole et al., 1978; Switzer and Nelson, 1972; Cole and Rapp, 1981), but a few points especially important S cycling should be elaborated here.

Nutrient requirement (R) is normally defined as that amount of nutrient used to produce new plant tissue as foliage, bole and branch wood, and roots (Cole and Rapp, 1981). Part of this requirement may be met by translocation (T) of nutrients stored in older tissue to new tissue during growth, the rest being satisfied by uptake (U). Thus,

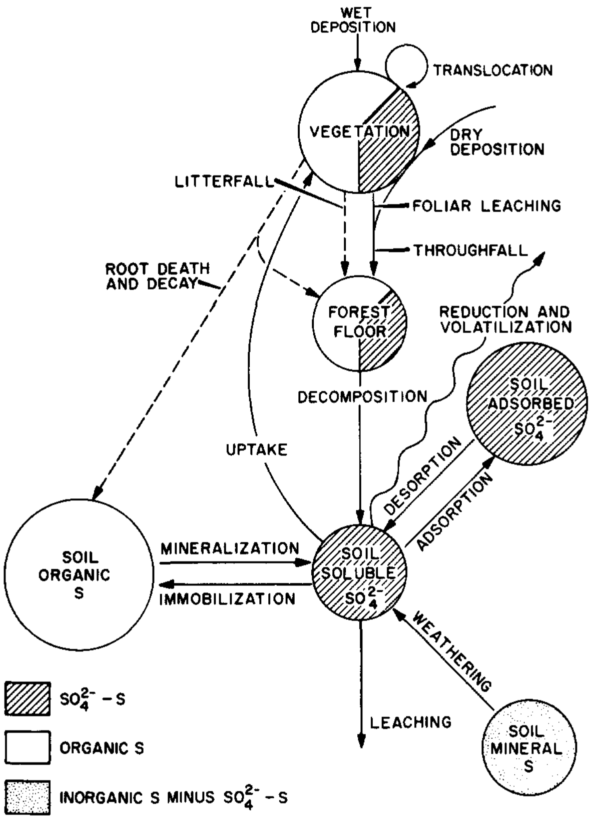

Figure 2. Schematic representation of the sulfur cycle in forests.

$$R = T + U$$

and $$U = R - T$$

(Cole and Rapp, 1981).

Neither T nor U are estimated directly; instead, uptake is assumed to be equal to that amount of nutrient used to produce perrenial (woody) tissue (ΔW) plus nutrient return via litterfall (LF) foliar leaching (L), and root turnover (RT):

$$U = \Delta W + LF + L + RT$$

(Cole and Rapp 1981).

Translocation is then calculated from estimates of R and U.

According to the available literature, the calculated forest uptake of S generally increases with increased atmospheric S deposition (as measured by

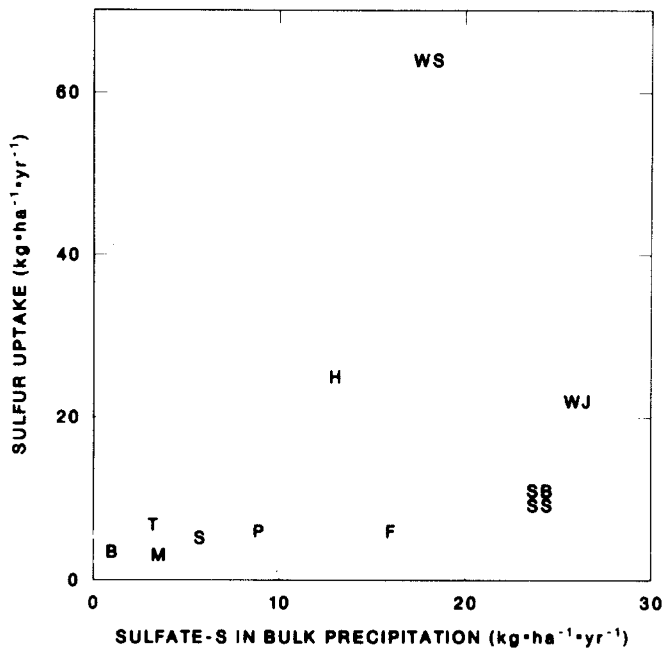

Figure 3. Sulfur (S) uptake vs SO_4^{2-}–S input in bulk precipitation at Bago, New South Wales, Australia (B) (Turner and Lambert, 1980); Thompson site, Washington USA (T), Turner et al., 1980); Mississippi, USA (M) (Switzer and Nelson, 1972); Central Sweden (S), (Bringmark, 1977); Pack Forest Washington, USA (P) (Stednick, 1982); Hubbard Brook, New Hampshire, USA (H) (Likens et al., 1977); Mediterranean France (F), (Rapp, 1973); Walker Branch Watershed, Tennessee, USA (WS), (Shriner and Henderson, 1978); beech (SB) and spruce (SS) stands at Solling, West Germany (Meiwes and Khanna, 1981); and a chestnut oak forest on Walker Branch Watershed, Tennessee (WJ) (Johnson et al., 1982).

bulk precipitation) (Figure 3). However, this relationship is confounded by several factors. Dry deposition of SO_2 to forest canopies may constitute very significant S inputs to forest ecosystems (Mayer and Ulrich, 1974). Shriner and Henderson (1978) in their initial characterization of S cycling on Walker Branch Watershed, Tennessee, noted a net removal (throughfall minus bulk precipitation input) of 44.4 kg • ha^{-1} • yr^{-1} as SO_4^{2-}–S. This value clearly exceeded any value possible from foliar leaching since the foliage contained only 10 kg ha of S. The authors were well aware of the probable influence of dry deposition, but felt they should calculate uptake in the traditional way, (as described above). Thus, as the authors note, estimated S uptake (64 kg • ha^{-1} • yr^{-1}) for Walker Branch was greater than requirement (21.8 kg • ha^{-1} • yr^{-1}) and probably greatly inflated by inadequate separation of dry deposition from foliar leaching in throughfall (WS in Figure 3). Johnson et al. (1982) later noted a net removal of SO_4^{2-}–S of only 2 kg • ha^{-1} • yr^{-1} for a chestnut oak forest on Walker Branch and thus calculated a much lower uptake value (22 kg • ha^{-1} • yr^{-1}, WJ in Figure 3) than Shriner and Henderson (1978). The differences in net removal were thought to result from changes in local SO_2 emission characterisitics as well as differences in methodology. Roughly half of the 26 kg • ha^{-1} • yr^{-1} of SO_4^{2-}–S measured by bulk precipitation by Johnson et al. (1982) was thought to be due to dry deposition.

Meiwes and Khanna (1981) also noted very large net removal values for SO_4^{2-} – in beech and spruce forests at Solling, West Germany. In that case, however, they estimated leaf leaching of SO_4^{2-}–S by independent means (2.2 and 1.8 kg • ha^{-1} • yr^{-1} of SO_4^{2-}–S for beech and spruce, respectively). These values were then used to calculate uptake (SB and SS for the beech and spruce stands, respectively, in Figure 3), and the remainder of the net removal was attributed to dry deposition. Thus, most of the throughfall flux at Solling was attributed to atmospheric input.

Perhaps a more realistic comparison of atmospheric S input vs biological S cycling is that of throughfall SO_4^{2-}–S vs litterfall S return. For this comparison, we can assume that most throughfall SO_4^{2-}–S flux (which includes both wet and dry deposition) is of atmospheric origin, whereas litterfall S return constitutes most of the biological S input to the forest floor. Throughfall flux overestimates input by that amount of SO_4^{2-} which is leached from foliage as a part of the biological S cycle. This overestimate, probably on the order of 1 to 3 kg • ha^{-1} yr^{-1} of S, is significant for sites with low S inputs but insignificant for sites with high S inputs. According to S-cycling studies by Turner et al. (1980), Meiwes and Khanna (1981), Stednick (1982), Switzer and Nelson (1972), and Johnson et al. (1982), neglecting leaf leaching would not greatly bias comparisons of atmospheric vs biological S inputs to the forest floor, especially in more polluted sites.

Plots of litterfall vs throughfall S fluxes among the sites listed in Figure 4 reveal lower litterfall S return at the low-input Bago and Mississippi sites (2.9 and 3.2 kg • ha^{-1} • yr^{-1} of SO_4^{2-}–S, respectively) than at the other sites. However, there is no indication that increasing atmospheric S inputs beyond 5 to 10 kg • ha^{-1} • yr^{-1} (as estimated by throughfall flux) causes increased S return via litterfall; indeed, litterfall S return is remarkably constant among the other sites (Figure 4).

The data in Figure 2 suggest that forests have little capacity to biologically accumulate the cycle excess S. Indeed, the net annual accumulation of S in forest biomass (i.e., in woody tissues) accounts for only a fraction (~ 10%) of that which cycles in forest ecosystems (Shriner and Henderson, 1978; Turner et al., 1980; Johnson et al., 1982), as is the case for most nutrients in forest ecosystems. Thus, forest requirement for S from sources external to the biological S cycle (i.e., from the mineral soil or the atmosphere) are quite modest.' Humphreys et al. (1975) suggested that atmospheric S inputs as low as 1 kg • ha^{-1} • yr^{-1} may be sufficient to supply forest S needs in Australian *Pinus radiata* stands.

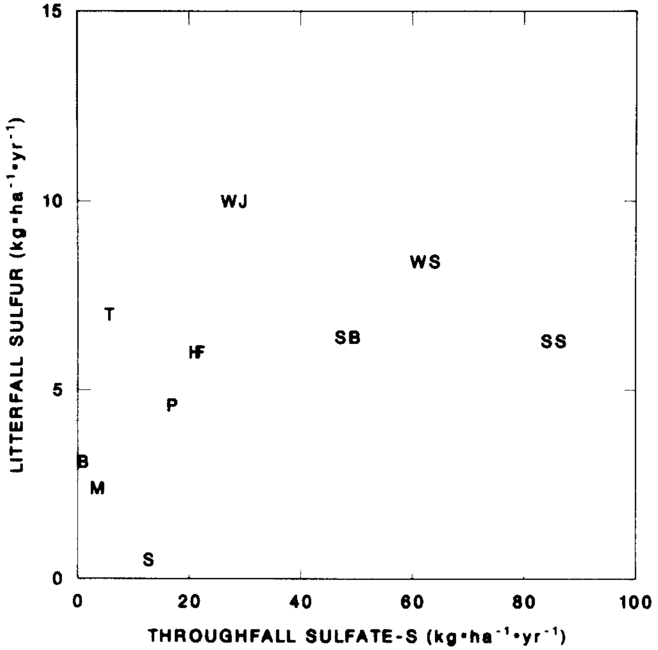

Figure 4. Sulfur (S) fluxes in litterfall and throughfall for various forest ecosystems (see Figure 3 for legend).

Despite relatively low biological S requirements, several of the forest ecosystems listed in Figure 3 appear to be accumulating S, that is SO_3^{2-}–S inputs measured as throughfall flux exceed leaching outputs (Figure 5). As noted by Haines (1983), the 'apparent' net SO_4^{2-} accumulation in these ecosystems could in theory be due to a number of factors, including tree uptake, incorporation into soil organic matter, soil SO_4^{2-} adsorption or precipitation with Al, organic S leaching, and reduction and volatilization of H_2S, dimethyl sulfide, or other gaseous S compounds. The latter two processes constitute unmeasured losses and might lead to a balanced S budget.

As noted previously tree uptake is unlikely to be of sufficient magnitude to account for differences in SO_4^{2-} inputs and outputs. Incorporation of SO_4^{2-} into organic matter may constitute a net SO_4^{2-} sink (Swank et al., 1984; Mitchell et al., this volume; Fitzgerald, this volume). Measurements of S losses by volatilization and organic S leaching are rare, but available measurements suggest that whereas these fluxes are not necessarily insignificant, they would generally be too low to account for SO_4^{2-} input-output imbalances (Haines, 1983; Adams, 1980; Mitchell et al., this volume; David et al., in press).

Several factors suggest that SO_4^{2-} adsorption (and, in some cases, coprecipitation with Al complexes) account for a large portion of apparent

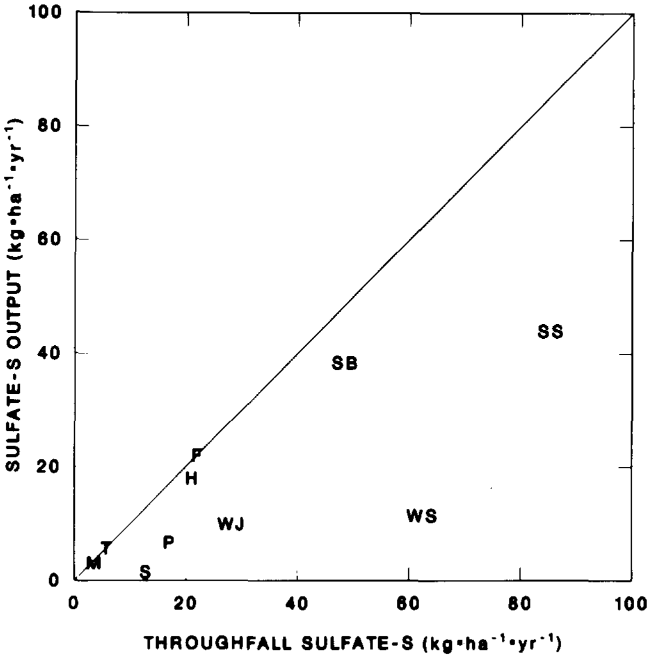

Figure 5. Sulfate–S outputs and inputs (via throughfall) in various forest ecosystems (see Figure 3 for legend). The line indicates inputs equal outputs; points falling below the line indicate net ecosystem accumulation, whereas points falling above the line indicate net ecosystem loss.

net SO_4^{2-} accumulation (where it occurs) in forest ecosystems. First, there are good correlations between soil SO_4^{2-} adsorption properties and apparent SO_4^{2-} accumulation in the system (Johnson et al., 1979; Johnson and Todd, 1983; Richter et al., 1983; Meiwes et al., 1980). Second, where lysimeter budgets are available for estimating fluxes through various soil horizons, net SO_4^{2-} accumulation (i.e., input > output) usually occurs primarily in Fe- and Al-oxide rich subsurface horizons (except in Spodosols, where organic matter blocks adsorption) rather than in organic matter-rich surface horizons (Johnson et al., 1979, 1982; Stednick, 1982; Meiwes et al., 1980). Finally, artificial additions of SO_4^{2-} often result in net SO_4^{2-} retention in soils, even when SO_4^{2-} budgets with ambient inputs were in steady-state (Johnson and Cole, 1977; Lee and Weber, 1982; Singh et al., 1980), a finding consistent with the concentration-dependent nature of soil SO_4^{2-} adsorption and precipitation reactions (Figure 1; Chao et al., 1974; Harward and Reisenauer, 1966; Nilsson and Bergkvist, 1983).

Organic vs inorganic cycling of S

Several investigators have shown that forest S cycles may have large inorganic (SO_4^{2-}) components. Hesse (1957) first noted that a considerable portion of

Table 1. Distribution and fluxes of total S and SO_4^{2-}–S in several forest ecosystems

	Bago, NSW[a]		Thompson, WA[b]		Walker Branch, TN[d]		Solling, W. Germany[c]			
Forest type	Douglas-fir		Douglas-fir		Chestnut oak		Beech		Spruce	
	SO_4^{2-}–S	Total S	SO_4^{2-}–S	Total S	SO_4^{2-}–S	Total S	SO_4^{2-}–S	Total S	SO_4^{2-}–S	Total S
				Ecosystem contents (kg ha)						
Foliage	1.3	16	11	18	6	12	4[e]	8	20[e]	40
Branch	10.1	47	0.5	4	1	15	–	10	–	14
Bole			7	29	2	19	–	30	–	42
Σ Aboveground	11.4	63	18.5	41	9	57	–	60	–	83
Litter	1	27	3	26	7	51	–	122	–	147
Soil	5	80	110	880	1730	4830	321	915	952	1453
Total ecosystem	19	170	131.5	947	1746	4938	–	1097	–	1683
				Ecosystem fluxes ($kg \cdot ha^{-1} \cdot yr^{-1}$)						
Precipitation	1.0	–	3.2	–	26	–	24	–	24	
Crownwash	0.9	–	2.5		2		24.4		61.3	
Litterfall	1.2	3.1	5.2	7.0	7	10	–	6.4	–	6.3
Total input to forest floor	3.1	6.1	10.9	12.7	35	38	–	54.8	–	91.6
Uptake[f]		3.5		6.8		15		10.1		9.6
Leaching		?	5.7	–	7	–	35		44	
Net Accumulation[g]		?	0		+ 21		+ 13.4		+41.3	

[a] From Turner and Lambert (1980).
[b] From Turner et al. (1980).
[c] From Johnson et al. (1982).
[d] From Meiwes and Khanna (1981).
[e] Calculated from N:S ratio (Meiwes and Khanna, 1981).
[f] Aboveground portion only.
[g] (Precipitation + crownwash) – Leaching. Assumes crownwash flux is due to dry deposition.

S cycled as SO_4^{2-} in forests of east Africa and that SO_4^{2-} adsorption in subsoils was a dominant feature of the S cycle in these ecosystems. Similar patterns were later noted by Turner and Lambert (1980) Turner et al. (1980), Meiwes and Khanna (1981) and Johnson et al. (1982) for forests in Australia, western Washington, West Germany, and eastern Tennessee, respectively. Results of these studies are summarized in Table 1.

There are very large differences in atmospheric input among these sites (as noted also in Figures 3–5). Considering only bulk precipitation, inputs of SO_4–S range from 1.0 kg • ha^{-1} • yr^{-1} at the Bago, NSW, to 26 kg • ha^{-1} • yr^{-1} at the Walker Branch site (Table 1). Clearly, however, there is a very large dry deposition component at the Solling site, as noted previously, in that net removal (bulk throughfall minus bulk precipitation) exceeds foliar S content by 3 times in the beech and by 1.5 times in the spruce stand. The actual magnitude of dry deposition is much greater in the spruce stand due to its perennial canopy and its greater leaf area. Meiwes and Khanna (1981) attributed only 1.8 and 2.2 kg • ha^{-1} • yr^{-1} of the 21.4 and 61.3 kg • ha^{-1} • yr^{-1} net removal of SO_4^{2-}–S in throughfall to leaf leaching (i.e., to internal S cycling) in the beech and spruce stands, respectively. These estimates are of similar magnitude to crownwash values for the Bago, Thompson, and Walker Branch sites. However, this similarity does not necessarily imply a lack of dry deposition in the latter cases. Lindberg et al. (1979) estimated that dry deposition of both SO_2 and particulate SO_4^{2-} accounted for approximately 50% of total S input to this Walker Branch site, for example. Dry deposition has not been estimated at the Bago or Thompson sites, but it is interesting to note that attributing crownwash to dry deposition at the Thompson site (which is downwind from a smelter) gives a total input of 5.7 kg • ha^{-1} • yr^{-1} of SO_4^{2-}–S, which exactly balances output.

In comparing the Douglas-fir stands at Bago and the Thompson site, Turner and Lambert (1980) noted greater proportions of S cycling as SO_4^{2-} at the Thompson site. For example, SO_4^{2-}–S accounted for 61% of the foliar S, 74% of the litterfall S return, and 86% of the total S input to the forest floor at the Thompson site. At Bago, SO_4^{2-}–S accounted for 8% of total S in foliage, 38% of total S in litterfall, and 51% total of S input to the forest floor (Table 1). These differences are clearly associated with greater soil S availability at the Thompson site (soil soluble SO_4^{2-}–S is equal to 110 kg/ha vs 5 kg/ha at Bago; Table 1), which may in part be a reflection of different atmospheric S inputs.

Comparisons of SO_4–S cycling among the other sites listed in Table 1 are confounded by species differences (in addition to soils and atmospheric input differences), but it is interesting to note that foliar SO_4^{2-}–S does not exceed 50% of total S. This suggest that these forests have reached their limit to sequester and biologically cycle excess S with current atmospheric S inputs. This hypothesis could be tested by further S applications to the Walker Branch and Solling sites.

Although the biological capacity to retain excess S is apparently limited, the Walker Branch and Solling sites appear to be accumulating SO_4^{2-} (inputs $>$ outputs; Table 1). At the Walker Branch site, Fe oxides are primarily responsible for SO_4^{2-} adsorption (Johnson and Todd, 1983), whereas at the Solling site, polymer aluminum-hydroxy-aquo complexes (PAHAC, which occupy both interlattice and exchange sites of clay micelles) are primarily responsible for SO_4^{2-} adsorption (Meiwes and Khanna 1981). Co-precipitation of SO_4^{2-} with PAHAC and jurbanite are also though to occur in deeper soil horizons, as noted previously (Meiwes and Khanna, 1981; Matzner and Ulrich, 1981).

As a result of the accumulations, soil SO_4–S constitutes a relatively large percentage of both soil total S and ecosystem S content at the Walker Branch and Solling to sites. Soil SO_4–S accounts for 36, 35, and 66% of soil total S and 35, 29, and 57% of ecosystem total S at the Walker Branch, Solling beech, and Solling spruce sites, respectively. In contrast, soil SO_4^{2-}–S accounts for only 6 and 12.5% of soil total S and 3 and 12% of total ecosystem S at the Bago and Thompson sites, respectively. Clearly the generalization that inorganic S is an unimportant component of soil S (Williams and Steinberg, 1964) is invalid for forest ecosystems where atmospheric S inputs greatly exceed biological demands. Quite to the contrary, adsorption and precipitation of SO_4^{2-}–S in soils may be the dominant feature of S cycling in these ecosystems. Thus, as atmospheric S inputs become excessive, forest S cycles become dominated by chemical rather than biochemical processes.

Summary and conclusions

Sulfur deficiencies in forests are rare, occurring primarily in areas remote from pollutant inputs (such as southeastern Australia and northwestern United States). Forest S requirements are modest relative to atmospheric inputs in polluted regions, where dry deposition of S may be a considerable proportion of total input. Excess S accumulates and cycles as SO_4^{2-} in forest vegetation, but the biological capacity of forest ecosystems to sequester excess S is apparently easily reached under conditions of elevated atmospheric S inputs. Soil SO_4^{2-} adsorption is frequently the dominant process of S cycling in highly polluted forests, and soil adsorbed SO_4^{2-} may account for a large fraction of total soil S and total ecosystem S in such cases.

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