

## Soil-Mediated Effects of Atmospherically Deposited Sulphur and Nitrogen [and Discussion]

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## Soil-mediated effects of atmospherically deposited sulphur and nitrogen

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The soil mediates both terrestrial and aquatic effects of sulphur (S) and nitrogen (N) deposition in a number of ways. Atmospherically deposited S in excess of biological requirements often accumulates by  $\text{SO}_4^{2-}$  adsorption onto Fe and Al oxides in highly weathered soils, causing the release of  $\text{OH}^-$ , which can neutralize incoming  $\text{H}^+$ , or an increase in cation exchange capacity. Atmospherically deposited N seldom exceeds biological requirements; when it does,  $\text{NO}_3^-$  is rapidly leached since no adsorption reactions analogous to those for sulphate exist. When the biological and adsorption capacities are exceeded, cation leaching is accelerated by the mobile  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  anions. The effects of this increased cation leaching must be assessed within the context of natural processes of cation removal such as leaching by internally produced carbonic, organic or (occasionally) nitric acid; natural atmospheric S inputs; and cation export by vegetation harvest. The proportion of individual cations available for leaching is regulated by soil exchange processes and biological demand, both of which tend to minimize the losses of those particular cations most tightly bound and, or, in shortest supply.

The ultimate effects of atmospheric S and N deposition will be highly site-specific in nature, depending on both inherent site characteristics and amounts and duration of atmospheric inputs. Thus, benefits of S or N deposition may outweigh negative effects in some sites, whereas the reverse may be true for other sites, making broad, global generalizations hazardous.

## INTRODUCTION

During the last decade, there has been considerable concern and debate over the effects of acid deposition on both terrestrial and aquatic ecosystems. In particular, the potential effects of acid deposition on acidification of soils and surface waters have been the subject of much research as well as speculation.

The hydrogen ion ( $\text{H}^+$ ) is ubiquitous in nature, however, and the sulphur (S) and nitrogen (N) associated with acid deposition are often of more consequence to important soil processes than is  $\text{H}^+$ . This is true not only because S and N inputs may supplement plant nutrient requirements but also because many of the effects attributed to  $\text{H}^+$  deposition (for example, base cation leaching from soils, or  $\text{Al}^{3+}$  transport to surface waters) are actually mediated by the  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  anions and can be either mitigated or exacerbated by soil chemical and biological reactions with associated S and N inputs.

This paper reviews some of the important processes regulating the transport and accumulation of atmospherically deposited S and N in soils and discusses the implications of these interactions for plant nutrient availability and terrestrial to aquatic elemental transport.

† Currently on leave to O.R.N.L.

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## EFFECTS OF S AND N DEPOSITION ON SOIL NUTRIENT AVAILABILITY

*Sulphur*

Because agricultural crop S requirements range from approximately 15–90 kg ha<sup>-1</sup> a<sup>-1</sup>, atmospheric deposition can be of substantial benefit to crop S nutrition (Terman 1978; Coleman 1966). Forests generally have much lower S requirements than crops because of their abilities to recycle nutrients and their generally lower tissue concentrations. Consequently, atmospheric deposition in polluted regions often exceeds forest S requirement (Turner *et al.* 1980; Johnson *et al.* 1982).

Excess S accumulates at SO<sub>4</sub><sup>2-</sup> in both plant tissue and soils (Turner *et al.* 1980; Johnson *et al.* 1982). The soil is a much larger sink for excess SO<sub>4</sub><sup>2-</sup> than vegetation, however. Adsorption on Fe or Al hydrous oxides is the predominant mechanism for soil SO<sub>4</sub><sup>2-</sup> retention (Harward & Reisenauer 1966), and soil SO<sub>4</sub><sup>2-</sup> adsorption is sometimes the dominant process in forest S cycling (Meiwes & Khanna 1981; Johnson *et al.* 1982).

Soil SO<sub>4</sub><sup>2-</sup> adsorption also has important implications for the effects of atmospheric H<sub>2</sub>SO<sub>4</sub> inputs on soil leaching. It has been repeatedly shown that SO<sub>4</sub><sup>2-</sup> adsorption prevents cation leaching by H<sub>2</sub>SO<sub>4</sub> (Johnson & Cole 1977; Singh *et al.* 1980; Lee & Weber 1982; Richter *et al.* 1983). This is basically owing to the requirement for electrochemical neutrality in solution. That is, the reduction of anions in solution (in this case SO<sub>4</sub><sup>2-</sup>) owing to adsorption must be balanced by an equivalent reduction of cations by various processes including ion exchange, neutralization and precipitation.

Soil SO<sub>4</sub><sup>2-</sup> adsorption is positively correlated with Fe and Al oxide content but negatively correlated with organic matter content (Johnson & Todd 1984). Surface soils and organic-rich subsoils of Spodosols (podzols) are therefore inefficient SO<sub>4</sub><sup>2-</sup> adsorbers, even if enriched in Fe and Al hydrous oxides. Subsurface horizons of Ultisols, Oxisols, and certain suborders of Inceptisols and Entisols (Andepts, Psammets) are efficient SO<sub>4</sub><sup>2-</sup> adsorbers and often result in net ecosystem SO<sub>4</sub><sup>2-</sup> retention. However, the potential for retention of atmospherically deposited SO<sub>4</sub><sup>2-</sup> in subsoils may be reduced to the extent that water flows through soil macropores or laterally through surface soils. Further aspects of hydrological effects on elemental transport are discussed later.

One of the most important consequences of the SO<sub>4</sub><sup>2-</sup> adsorption process on soil-mediated effects of sulphur deposition is a delay and breakthrough phenomenon. If a soil is impacted with mobile, strong acid anion such as Cl<sup>-</sup>, the rate at which Cl<sup>-</sup> moves through the soil is controlled largely by the rate of water movement, and an input–output equilibrium is established rather rapidly. With sulphate, however, the breakthrough can be delayed by adsorption and sulphate-induced leaching may not be observed for years or even decades after impact. Eventually an equilibrium will be established, but the unwary investigator who fails to observe accelerated leaching rates from a plot that has been impacted for months or even years can easily be led to underestimate the long-term effect of S deposition on cation removal. It is also important to recognize that because the adsorption capacity is concentration-dependent, the time required to achieve equilibrium may not be materially shortened by an increase in the impact dosage. Finally, we must understand that the delay in accelerated leaching resulting from SO<sub>4</sub><sup>2-</sup> adsorption in the soil is not a ‘free lunch’; that is, to the extent the process is reversible, increased leaching will continue to occur during a desorption period, after impact is discontinued.

Recently, Fitzgerald *et al.* (1982) found  $\text{SO}_4^{2-}$  immobilization into ester- and carbon-bonded sulphur forms in a deciduous forest soil from Coweeta watershed, North Carolina. Their work conclusively showed that  $\text{SO}_4^{2-}$  incorporation into soil organic matter is significant and their assertion that this process must be considered in future attempts to study ecosystem S retention is well founded.

#### *Nitrogen*

Atmospheric N additions in most regions make only a minor contribution to agricultural production. Crop N requirements are high ( $100\text{--}300 \text{ kg ha}^{-1} \text{ a}^{-1}$ ) and routine fertilization rates usually greatly exceed atmospheric inputs. Many forests are N deficient, however, and atmosphere-derived N is usually rapidly immobilized by ecosystem biota. This retention precludes  $\text{NO}_3^-$  losses causing cation leaching and may even result in increased forest growth (Abrahamsen 1980). However, exceptions occur when N supplies are excessively enriched, whether by natural processes (for example, N fixation), fertilization, or atmospheric inputs. Van Miegroet & Cole (1984) noted high rates of  $\text{NO}_3^-$  and associated cation leaching in soils beneath red alder (*Alnus rubra*), an N-fixing species. Tamm & Popovic (1974) noted that repeated fertilization with N caused acidification of forest soils in Sweden. Van Breeman *et al.* (1982) found very large fluxes of ammonium sulphate in the throughfall of deciduous (*Quercus-Betula*) and coniferous (*Pinus sylvestris*) forests in the Netherlands and concluded that the large fluxes were the result of  $\text{NH}_3$  (volatilized from animal manures in nearby farms) and  $\text{SO}_2$  (from fossil fuel combustion) interception by forest canopies. The large inputs of  $\text{NH}_4^+$  to the soil caused high rates of nitrification, nitrate leaching, low soil solution pH (down to pH 2.8 at times), and  $\text{Al}^{3+}$  mobilization.

When a nitrogen-deficient ecosystem is impacted, a very simple conceptual model of the acidification effects of nitrogen input can be involved. The first effect is an increased rate of biomass production and an increase in the rate of uptake of basic cations from the soil. This cation uptake is in itself acidifying. If the input rates are moderate, most of the increased N input will be tied up in the increased biomass, and leaching of basic cations in association with  $\text{NO}_3^-$  will be small. If the biomass is harvested, acidification will largely result from the increase in base cation removal by harvest (for example, Alban (1982)). Further acidification may also result from cation demands of the regenerating forest. If the biomass is not harvested, the ecosystem will ultimately come to a new equilibrium. In the latter stage, the capital of both nitrogen and bases tied up in the biomass and litter components will have increased from pre-impact levels, along with an increase in annual cycling rates. Nitrogen outputs can now be expected to increase, perhaps eventually up to the level of input, and in well-drained systems this output will largely be in the form of  $\text{NO}_3^-$  leaching. Acidification will then occur to the extent that basic cations are leached in association with this  $\text{NO}_3^-$ .

#### *Base cations and aluminium*

##### *Atmospheric $\text{H}^+$ input against internal $\text{H}^+$ generation*

It is important to recognize that atmospheric  $\text{H}^+$  inputs are but increments to natural  $\text{H}^+$  production in soils via carbonic, organic, or nitric acid leaching, humus formation, and plant cation uptake (Reuss 1977; Ulrich 1980). Carbonic acid is an important natural leaching agent in many tropical and temperate forest soils (Nye & Greenland 1960; McColl & Cole 1968; Johnson *et al.* 1977). Organic acids are responsible for the formation of Spodosols, which occupy

both boreal and tropical–subtropical regions (Kononova 1966). These acids can produce high solution acidities, provide counter-anions for cation leaching and are responsible for the chelation and transport of Fe and Al from surface (A2 or albic) to subsurface (B2ir or spodic) horizons during the podzolization process (Kononova 1966). It is important to note, however, that soil acidification reduces the effectiveness of carbonic and organic acid leaching, because both are weak acids that protonate at low pH. Thus, acidification by these acids is ultimately self-limiting. As discussed previously, nitrification and nitrate leaching can be an important natural process that not only accelerates cation leaching but also causes significant soil acidification in N-fixing forests.

Soils can also be naturally acidified by base cation accumulation in forest biomass. Alban (1982) found that, because of above-ground Ca accumulation, mineral soils beneath *Populus tremuloides* and *Picea glauca* stands were more depleted of Ca and more acid (pH 5.3–5.6) than soils beneath adjacent *Pinus resinosa* and *P. banksiana* stands in Minnesota (pH  $\approx$  6.0).

#### *Effects of soil acidification on leaching*

Soil acidification, whether by natural processes or very high atmospheric inputs, has very important effects on the rate and nature of soil leaching processes. As base cations become scarce and  $H^+$  and  $Al^{3+}$  very abundant on exchange sites, the latter will become increasingly important cations, balancing the mobile anions in soil solution (Wiklander 1974; Reuss 1983). Thus, the rates of base cation leaching are reduced and the rate of  $H^+$  and  $Al^{3+}$  leaching increased as soils acidify. The rate at which base cations are accumulated or lost from soils is related to the lime potential ( $K_L$ ) of the solution entering that soil compared to the  $K_L$  of the soil itself (Reuss 1978, 1983). The lime potential,  $K_L = pH - \frac{1}{2}p(Ca^{2+} + Mg^{2+})$ , is determined by measuring the pH and  $Ca^{2+}$  and  $Mg^{2+}$  concentrations in a solution in equilibrium with the soil. It provides a good index of the soil's acidity. If the  $K_L$  of the incoming solution exceeds that of the soil, the incoming solution will increase the base saturation of the soil (assuming equilibrium), whereas the opposite is true of a solution with lower  $K_L$  than the soil. It is important to note that the ability of a solution to acidify or basify a soil is *not* solely a function of either solution or soil pH.

Soil acidification leads not only to lower leaching rates of base cations but also to reduced mobility of anions. As soils and soil solutions become more acid, the dissociation of carbonic and organic acids is reduced, thus resulting in a reduction of both mobile anions and internal  $H^+$  production. Increasing acidity also enhances anion adsorption (Hingston *et al.* 1967), which can be especially important to  $SO_4^{2-}$  mobility (Harward & Reisenauer 1966). As soils acidify, both the direct effects of lower pH and the build-up of Fe and Al hydrous oxides increase  $SO_4^{2-}$  adsorption, thereby reducing leaching rates of  $SO_4^{2-}$  and associated cations. The net effect of acidification is a reduction in total anion and total cation leaching as well as a shift toward increasing  $H^+$  and  $Al^{3+}$  concentrations.

#### *Interactions of atmospheric acid inputs with natural soil leaching and acidification processes*

In most forest systems that are not highly acidic, the dominant anion is either bicarbonate ( $HCO_3^-$ ) or organic. As the soil becomes more acid, the supply of  $HCO_3^-$  ion diminishes. At a pH of 4.3 and a  $CO_2$  partial pressure of 3.2% (100 times atmospheric), the  $HCO_3^-$  concentration is only  $10 \mu eq l^{-1}$ . The cation concentration of the soil solution then is limited to the available supply of other anions. Background concentrations of the strong acid  $Cl^-$  and



$\text{SO}_4^{2-}$  anions in these systems is typically a few tens of  $\mu\text{eq l}^{-1}$ , and these are supplemented by whatever organic acid anions may be stable under these conditions. The typical result is that soil solutions and leachates from naturally acid soils have low electrical conductivities and may not be particularly acid.

During the acidification process, base saturation is reduced. Most soil solutions will be dominated by basic cations until the base saturation is reduced to 10–15% or less (Reuss 1983), while at lower base saturation levels the dominant cations are Al species and  $\text{H}^+$ . In most systems undergoing acidification,  $\text{HCO}_3^-$  levels become very low, while base saturation is at a level where basic cations in solution predominate. Leaching rates are correspondingly reduced, tending to conserve the available base cation supply. The resulting solutions have low total dissolved ions and restrict the mobilization of  $\text{Al}^{3+}$  as the system shifts to  $\text{Al}^{3+}$  dominance.

Under the impact of sulphate the situation can be substantially changed. Precipitation will typically contain 60–100  $\mu\text{eq SO}_4^{2-} \text{ l}^{-1}$ . This source will be further increased by dry-deposition inputs and concentration by evapotranspiration so that  $\text{SO}_4^{2-}$  solutions in the 200–300  $\mu\text{eq l}^{-1}$  range may be typical after the system has achieved equilibrium with sulphate adsorption sites (for example, Richter *et al.* (1983); Seip (1980)). This increase in solution concentration is significant, particularly in soils where natural acidification has proceeded to the extent that  $\text{HCO}_3^-$  leaching has become unimportant. The logical consequences are an acceleration of base cations loss in systems where basic cations still predominate and an increase in  $\text{H}^+$  and Al species, particularly  $\text{Al}^{3+}$ , in solution as the shift from basic cations to  $\text{H}^+$  and  $\text{Al}^{3+}$  dominance proceeds.

Quite clearly, the soil reactions described above can affect the transport of  $\text{H}^+$  and  $\text{Al}^{3+}$  to aquatic ecosystems. The mechanisms regulating terrestrial–aquatic transfer include both hydrological and chemical components. The next section of this paper reviews very briefly some of the proposed mechanisms of terrestrial–aquatic acid transfer and some of the controversies surrounding them.

#### TERRESTRIAL–AQUATIC TRANSPORT

Henriksen (1979) offered an empirical model of surface water acidification based on estimates of pre-acidification alkalinity using current  $\text{Ca}^{2+}$  concentrations. This model inherently assumes that acid deposition has no effect on  $\text{Ca}^{2+}$  concentrations. Because numerous studies have shown accelerated  $\text{Ca}^{2+}$  leaching in response to  $\text{H}_2\text{SO}_4$  input (Abrahamsen 1980; Abrahamsen & Stuanes 1980), even on barren rock (Abrahamsen *et al.* 1979), the assumption of a constant  $\text{Ca}^{2+}$  concentration in surface waters is highly dubious. Estimates of pre-acidification alkalinity, using this model, are likely to be too high, as are estimates of present day or future acidification. A later version of the model (Wright 1982), however, suggested the use of an ‘increase factor’ for Ca and Mg of 0.4 times  $\text{SO}_4$ , for non-marine components.

The suggested increase of ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) is only 40% of the increased  $\text{SO}_4^{2-}$  (that is, an increase in  $\text{H}^+$  and Al amounting to 60% of the increased  $\text{SO}_4^{2-}$ , neglecting  $\text{Na}^+$  and  $\text{K}^+$ ) and implies that either: (i) soils surrounding these waters must be extremely acid; or (ii) acid deposition fails to equilibrate with soils before entering aquatic systems. The latter could occur if a substantial portion of water enters aquatic systems via surface runoff or macropore flow. Thomas & Phillips (1979) provide an excellent review of this often-neglected phenomenon, which was recognized 100 years ago by Lawes *et al.* (1882) at the Rothamsted Experimental Station. Schaffer *et al.* (1979) found rapid transport of  $\text{NO}_3^-$  and  $\text{Cd}^{2+}$  to a depth of 120 cm via macropores in a Typic Hapludult in Pennsylvania. Tension lysimeters did not detect this

$\text{NO}_3^-$  and  $\text{Cd}^{2+}$  movement, and Schaffer *et al.* (1979) express scepticism about the ability of such lysimeters to monitor the chemical quality of water percolating through the soil profile.

Perhaps the most worrying aspect of the use of such an 'increase factor' in the Henricksen model is the question of transferability. One would expect the factor to be highly sensitive to the soil and hydrological conditions in the catchment area and thus highly variable among catchments.

Seip (1980) proposed a mechanism for surface water acidification that is consistent with the soil physical-chemical relations thought to regulate leaching. In essence, he proposed that the introduction of a mobile anion ( $\text{SO}_4^{2-}$  in this case, since it is mobile in many of the podzolized and highly organic soils in Norway) to an acid soil causes an elevation of soluble  $\text{H}^+$  and  $\text{Al}^{3+}$  concentrations. Thus, this introduction of the mobile anion, rather than  $\text{H}^+$  itself, is a critical factor in the terrestrial-aquatic transfer of  $\text{H}^+$  and  $\text{Al}^{3+}$ .

This model is consistent with the soil chemical relations described by Wiklander (1974) and Reuss (1983) as well as the well-known 'salt effect' on soil pH (Yuan 1963), but there is some doubt as to whether it can account for the large declines in surface water pH frequently alluded to. For instance, Abrahamsen & Stuanes (1980) found only slight (6–10%) increases in  $\text{H}^+$  and  $\text{Al}^{3+}$  in effluents from heather and moorgrass lysimeters treated with pH 4.3 ( $31.5 \mu\text{mol l}^{-1} \text{SO}_4^{2-}$ ) simulated rain as opposed to pH 5.3 ( $9.3 \mu\text{mol l}^{-1} \text{SO}_4^{2-}$ ) control. Soils in these lysimeters were acid (water pH of 4.4–4.6 in the moorgrass and pH 4.0 in the heather) and high in exchangeable  $\text{Al}^{3+}$  (23–68  $\text{mmol kg}^{-1}$  in the moorgrass and 8–39  $\text{mmol kg}^{-1}$  in the heather). Also, Johnson (1981) applied Seip's model to naturally acid, unpolluted systems in southeastern Alaska and found only slight decreases in predicted pH with increasing  $\text{SO}_4^{2-}$  additions.

Factors affecting surface water acidification, including natural, cultural (that is, land-use changes, forest harvesting), and atmospheric deposition, are unclear. Given the great concern over aquatic effects of acid deposition, a comprehensive research effort into mechanisms of terrestrial-aquatic transfer (both hydrological and chemical) is badly needed, not only to clarify the roles of various factors in surface water acidification but also as a prelude to implementing effective mitigative techniques.

#### SUMMARY AND CONCLUSIONS

Atmospheric sulphur deposition can contribute beneficially to crop S requirements but frequently exceeds forest S requirements in polluted regions of the world. Sulphur in excess of biological needs accumulates as  $\text{SO}_4^{2-}$  in forests, with the soil being a major sink in many cases. Soil  $\text{SO}_4^{2-}$  adsorption reduces cation leaching by  $\text{H}_2\text{SO}_4$  and may result in the displacement of  $\text{OH}^-$ , raising the pH of solutions as they percolate through the soil. When an equilibrium is reached between adsorbed and solution  $\text{SO}_4^{2-}$  (a process that may take from months to decades, depending on inherent soil characteristics) cation leaching associated with  $\text{SO}_4^{2-}$  will be significantly accelerated. Because  $\text{SO}_4^{2-}$  adsorption is concentration-dependent, raising input concentrations results in further adsorption until a new equilibrium is reached. Conversely, lowering input concentrations will allow  $\text{SO}_4^{2-}$  to be released from adsorption sites if adsorption is reversible. This allows the potential leaching power of previously adsorbed  $\text{SO}_4^{2-}$  (and associated cations) to be ultimately realized. Clearly, the issue of the reversibility of soil  $\text{SO}_4^{2-}$  adsorption is critical to the long-term effects of atmospheric S inputs on soil cation leaching, especially in regard to delayed effects if atmospheric inputs are reduced.

Atmospheric nitrogen inputs are small relative to crop N requirements but may benefit the many N-deficient forests of North America and Scandinavia. Excessive N inputs, or N inputs to N-rich forests, results in net nitrification, a microbially mediated process by which nitric acid is introduced directly into the soil (rather than to the forest canopy, as is the atmospheric  $H^+$  input). Nitrification is a powerful acidifying process, as shown by studies of both naturally N-rich (for example, N-fixing forests) and artificially N-enriched (for example, fertilization, excessive atmospheric N inputs) forest ecosystems.

Soils are acidified naturally by the internal generation of carbonic, organic, and occasionally nitric acids; by vegetation uptake of base cations, and by humus formation. Soil acidification enhances anion adsorption and reduces the effectiveness of carbonic and organic acid leaching (since the latter are weak acids that protonate at low pH). Thus natural acidification by some processes (for example, carbonic and organic acid leaching) is ultimately self-limiting. Introduction of anions of strong acids may, if mobile in the soil, significantly accelerate natural leaching rates of base cations and, or,  $Al^{3+}$ .

The nature of the cations leaching with excess  $SO_4^{2-}$  and, or,  $NO_3^-$  in forest soils is dependent on well-known cation exchange processes, which dictate that very scarce or tightly bound cations are conserved while more abundant or loosely bound cations are leached. Forest systems may therefore show a net gain of one or more base cations, even when subject to very intense leaching (whether by atmospheric acid inputs or internal acid production). In very acid soils, all base cations may be conserved while  $Al^{3+}$  and  $H^+$  are leached.

The ultimate effects of atmospheric S and N deposition will depend on the amount and duration of inputs and the characteristics of the site impacted. In some cases, beneficial effects of nutrient additions may outweigh the negative effects of nutrient losses (for example, S against  $H^+$  deposition to croplands), whereas, in other cases, negative effects may outweigh benefits (for example, excessive N inputs to N-rich forest ecosystems). While there is a good theoretical basis for generalizations about processes of soil leaching and acidification, broad generalizations as to the effects of atmospheric S and N deposition *in toto* are hazardous and probably misleading, because site characteristics as well as inputs vary enormously, even within relatively small distances.

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*Discussion*

K. A. BROWN (*Central Electricity Research Laboratories, Kelvin Avenue, Leatherhead, Surrey, U.K.*). I would like to ask Dr Johnson what proportion of the sulphate in the Walker Branch soil was reversibly, as opposed to irreversibly, adsorbed, and what is the basis of his distinction between these forms?

D. W. JOHNSON. For practical purposes, we define reversibly adsorbed sulphate as that which is recoverable with water and irreversibly adsorbed sulphate as that which is recoverable with phosphate (0.032 M NaH<sub>2</sub>PO<sub>4</sub>) but not with water. On Walker Branch, nearly all the sulphate in surface (A) horizons is reversibly adsorbed (approximately 360 kg SO<sub>4</sub><sup>2-</sup>-S ha<sup>-1</sup>, to a depth of 40 cm) whereas nearly all B horizon sulphate is irreversibly adsorbed (approximately 1280 kg SO<sub>4</sub><sup>2-</sup>-S ha<sup>-1</sup> to a depth of 180 cm). This corresponds to the distribution of free iron oxide in these horizons.

D. V. CRAWFORD (*Nottingham University School of Agriculture, Sutton Bonington, Loughborough, Leicestershire, U.K.*). Dr Johnson referred to the significant storage of sulphate-S by sorption in A and B horizons of certain profiles containing hydrated iron and aluminium oxides. Could he indicate how the quantities (kg ha<sup>-1</sup>) of sulphur stored in this way in these profiles compares with the annual input of sulphur? How do these quantities relate to the sulphur reserves stored in the profile as organic-S compounds?

D. W. JOHNSON. The amount of sulphate stored in soils varies considerably, as one might expect, with iron and aluminium oxide content, organic matter content (which inhibits sulphate adsorption), and amount in input. Thus, soil sulphate pools can equal as little as eight times annual sulphur input in a spodosol with poor adsorption properties at Hubbard Brook, New Hampshire, or as much as eighty times annual input in an andosol at LaSelva, Costa Rica (Johnson *et al.* 1980).

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SIR JAMES BEAMENT, F.R.S. (*Department of Applied Biology, Cambridge University, Pembroke Street, Cambridge, CB2 3DX, U.K.*). Speakers have referred to the absence of Lumbricidae from soils where trees are unhealthy, and to consequent lack of mixing of soil. Are ants, Collembola and other essential fauna and decomposers of healthy soil absent? We need to know which is cause and which effect: are the higher plants damaged because of changes in the soil, and what is causing changes to the soil fauna?

There is a need to distinguish between the effect of a short-term episode of low pH, which may have serious effect on a biological system, and the effect that such an episode may have on the physicochemical system of soil. Can the soil system smooth out and perhaps compensate for such an episode when average conditions prevail?

D. W. JOHNSON. I will leave it to others to comment on biological effects of acid episodes and will comment on chemical effects. We have noted large variations in soil solution pH and conductivity within rain events (with continuous monitoring equipment; see Cole & Johnson, *Water Resour. Res.* **13**, 313–317, 1977). Such excursions most definitely affect the chemistry of drainage water, but I think it doubtful that they affect the chemical properties of the soil itself. Soil chemical properties will normally change only over a long period, reflecting an integration of many short-term changes in soil leaching rates.