# CHAPTER 7

# *Pedosphere and Biosphere*

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## 7.1 PEDOSPHERE

### 7.1.1 Forms of sulphur in soil

In soils, most of the S occurs as organic forms. However, there are a few special exceptions to this statement. Inorganic sulphate can dominate in saline and acid sulphate soils. Generally the inorganic pool of soluble and adsorbed sulphates (in well-drained soils) and sulphides (in poorly drained anaerobic soils) account for less than 10% of the total sulphur. The sulphur cycle in soil has been extensively reviewed by Freney and Williams (1983) and will only be described briefly to provide a framework for discussion of the isotope data.

#### 7.1.1.1 *Inorganic sulphur*

In most well-drained soils, the dominant form of inorganic sulphur is sulphate with a negligible percentage of compounds of lower oxidation state present (cf. reviews by Biederbeck, 1978; Bettany and Stewart, 1983; Freney and Williams, 1983). Sulphate occurs as water-soluble salts (mainly calcium, magnesium, and sodium sulphates) and as 'adsorbed sulphate' where the sulphate ion is bonded to the soil inorganic components. Adsorbed sulphate is an important fraction in leached tropical soils containing hydrous oxides of aluminium and iron as it prevents the rapid loss of sulphate out of the plant rooting zone. Under anaerobic conditions such as occurs in flooded rice soils, sulphides are the principal stable form of inorganic sulphur. It is generally believed that the water-soluble plus the majority of adsorbed sulphate is the 'available' fraction for plant uptake.

The amounts of water-soluble sulphate vary widely, both within the soil profile itself and among soils developed from different parent materials and in different climatic regions. However, within a given area, it is the factors that relate to man's activities (e.g. crop management, irrigation, fertilization, and industrial processing) that appear to have the greatest effects on sulphate levels.

*Stable Isotopes in the Assessment of Natural and Anthropogenic Sulphur in the Environment*
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### 7.1.1.2 *Organic sulphur*

Current analytical techniques permit only a broad fractionation of organic sulphur compounds in soils. Two major groups have been identified: one in which sulphur is directly bonded to carbon (C-bonded S) and another in which sulphur is linked to carbon through an oxygen or nitrogen atom (organic sulphates). The former group would include free or combined sulphur-containing amino acids and sulphonates, and the latter the sulphate esters, thioglucosides, and sulphamates. Problems with the analytical determination of these fractions have been discussed elsewhere (Freney *et al.*, 1967, 1972). Most workers determine organic sulphate by reduction with hydriodic acid (HI-reducible S) and calculate C-bonded S as the difference between total S and HI-reducible S. Alternately, a substantial proportion of C-bonded S can be determined directly by reduction to $H_2S$ by Raney–nickel–HCl (Lowe, 1965; Freney *et al.*, 1975). It is obvious that these broad fractionation techniques are subject to error and lack 'biological significance'. However, they take on meaning when considered in terms of the soil-forming factors and available sulphur (Bettany and Stewart, 1983).

Generally, the HI-reducible S fraction is considered to be more biologically active or 'labile' (Fitzgerald, 1976), and accounts for 27–78% of the total sulphur in surface soils, with mean values of approximately 50%. The percent HI-reducible S shows considerable variation across environmental gradients and cultivation chronosequences, generally increases with depth in the soil profile, and is concentrated in the clay and fulvic acid fractions of soils (Bettany and Stewart, 1983).

The C-bonded S fraction contains both the labile sulphur amino acids, protein sulphur and the more resistant sulphones, sulphonic acids, and heterocyclic compounds. It is likely that a portion of this fraction is highly labile, since tracer experiments show that recently immobilized sulphate is remineralized from both HI-reducible and C-bonded fractions (Freney *et al.*, 1971; Saggar *et al.*, 1981b; Maynard *et al.*, 1984).

The soil organic fraction comprises a complex heterogeneous mixture of soil organisms and residues of partially decomposed plant, animal, and microbial cells. This is further complicated by the intimate association of the organic fraction with soil minerals. It is therefore not surprising that determination of the two sulphur fractions (C-bonded and organic sulphates) on whole soils gives little information on the dynamics of sulphur turnover in organic matter. Attempts have been made to subdivide soil organic matter into biologically meaningful fractions prior to sulphur analyses. The various approaches that have been taken include:

(a) Isolation, identification, and determination of individual compounds belonging to definite chemical groups

(b) Chemical extraction followed by physical chemical separations of various fractions, such as humic and fulvic acids and humin
(c) Physical separation of soils into various organomineral sized fractions
(d) Biological techniques aided with radio- and stable isotopes, with the object of isolating and identifying fractions that are significant in terms of nutrient cycling

Artefact formation during chemical extraction and purification of organic matter fractions is inevitable but can be minimized. For example, the physical separation of whole soils into organomineral complexes of various particle sizes by densimetric separation and/or centrifugation yields fractions that have minimal chemical alteration. This enables the study of the role of inorganic constituents in the stabilization and transformation of humus (Turchenek and Oades, 1979; Anderson *et al.*, 1981). Distinct differences in the forms and distribution of organic nitrogen and sulphur among particle size fractions have been observed, suggesting that sulphur follows different pathways in humus formation and transformation than carbon and nitrogen.

Consideration of the biologically significant fractions of soil organic matter inevitably involves the role of the soil biomass. Complete understanding of the sulphur cycle requires an understanding of the forms of sulphur in soil microorganisms and the mechanisms involved in microbial transformations. Methodology for the determination of biomass sulphur in soils has just become available and current assays are directed towards the forms of sulphur in microbes and their role in sulphur cycling. Although only 2–3% of the total sulphur in soils is contained in the microbial biomass, it assumes greater significance because of its rapid turnover (mainly bacteria and fungi) (Saggar *et al.*, 1981a). In bacteria, the major portion of sulphur appears to be in the form of amino acids, with about 10% as HI-reducible S. The sparse literature suggests that sulphur compounds other than amino acids and related compounds are rare, although small amounts of organic sulphates (choline sulphate) have been found in bacterial cell walls and a bacterial sulpholipid has also been identified (Fitzgerald and Lushinski, 1977). It has also been shown that some species of chemoautotrophic and photosynthetic purple sulphur bacteria are capable of accumulating elemental sulphur. Like bacteria, the major portion of sulphur in fungi is in the amino acid form. However, fungi have a larger portion of organic sulphates, such as choline sulphate. It appears that fungi are able to store sulphur as choline sulphate when sulphur is in adequate supply. Recent experiments show that the relative percentage of HI-reducible S increases significantly with increase in the concentration of sulphate in the growing medium. There is also evidence that significant amounts of various aryl sulphates may be present in fungi, and elemental sulphur is contained in some species (cf. the review by Bettany and Stewart, 1983).

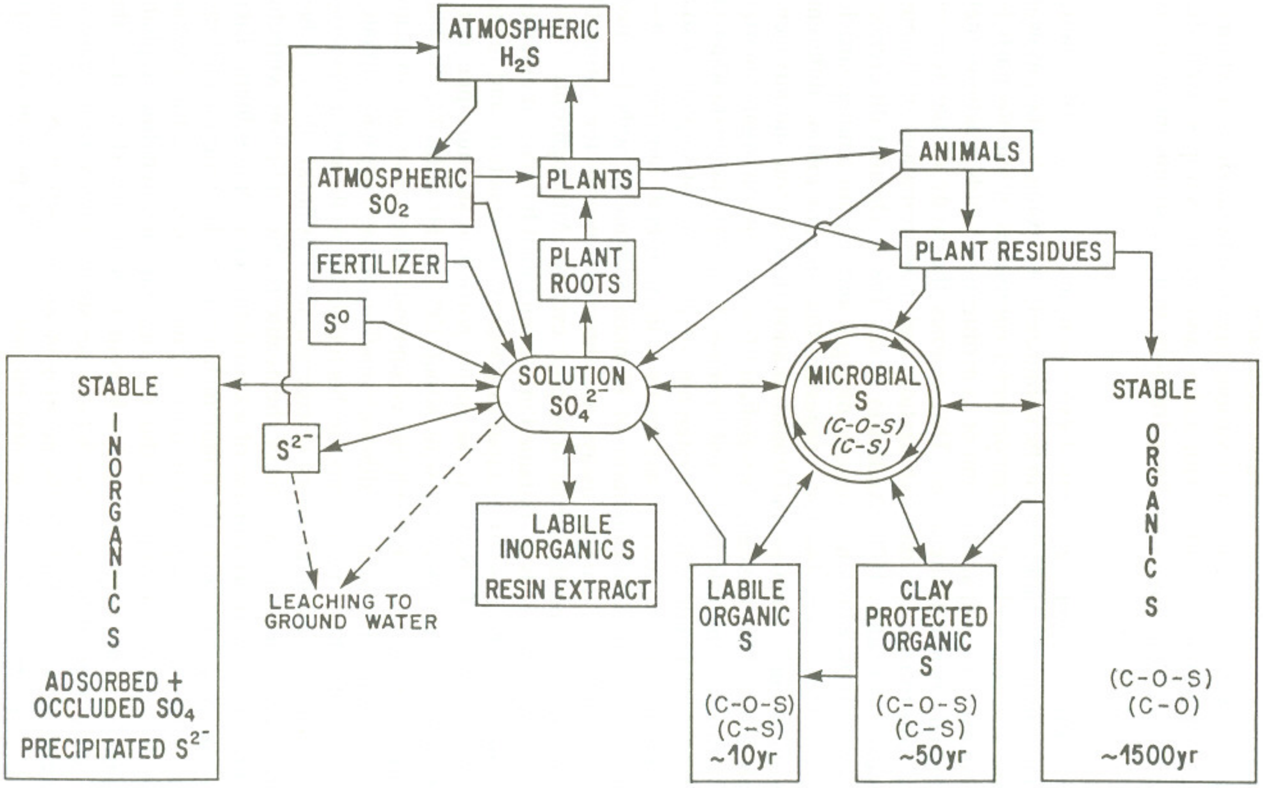

Figure 7.1 Conceptual flow diagram of the main forms and transformations of sulphur in the soil–plant system

The origin of the large organic sulphate pool in soils is still open to question. It has been suggested that in addition to fungal synthesis, a considerable portion of ester sulphate is introduced into soils through animal excretions, decaying animal matter, extracellular synthesis by certain bacteria, and synthesis and subsequent decay of plant tissue, algae, and lichens (Fitzgerald, 1976, 1978).

#### 7.1.1.3 *Transformations of sulphur in soils*

Soil organic sulphur (both C–O–S and C–S) can be subdivided into three compartments representing labile organic S consisting of compounds that are easily mineralized and have a short half-life (~10 years), similar compounds with a longer lifetime (~50 years) due to chemical and physical protection, and relatively stable compounds in the soil matrix with a half-life of hundreds of years (Figure 7.1).

The transformation of sulphur in soils is considered to be mainly microbial (Freney and Williams, 1983), although some strictly chemical processes (e.g. the oxidation of iron sulphide) are also possible (Bloomfield and Coulter, 1973). The microbial processes may be grouped into four distinct processes:

(a) Mineralization: a process in which large organic molecules containing sulphur are broken down to smaller units and eventually to inorganic sulphate.
(b) Immobilization: simple inorganic S molecules (mainly sulphate) are converted to organic compounds.
(c) Oxidation: inorganic sulphur of lower oxidation states (elemental sulphur, thiosulphates, polythionates, sulphides, etc.) are generally converted to sulphate as a stable end-product.
(d) Reduction: sulphate and other partially reduced sulphur-containing anions are converted to sulphide.

Although there are organisms capable of performing all these processes in all soils, mineralization and immobilization are the dominant transformations that occur in well-aerated arable soils of the world.

### 7.1.2 Sources of sulphur compounds in soil

The pedosphere is the site of many complex interactions between the lithosphere, biosphere, atmosphere, and hydrosphere. In terms of the sulphur cycle, the major inputs are dead organic matter, dry and wet deposition of atmospheric sulphur compounds, groundwater leaching of subsurface minerals, and, in cultivated regions, fertilizer applications (Freney and Williams, 1983; Bettany and Stewart, 1983). The main outputs are river runoff and biogenic emissions of gaseous sulphur compounds.

The sources of sulphur compounds in the soil embrace not only inputs from the atmosphere, biosphere, and lithosphere via the hydrosphere, but also transformations within the soil. Solution $SO_4^{2-}$ constitutes the central pool in Figure 7.1. It can 'flow' to the microbial S pool, plants, and various inorganic forms. Most foliar sulphur returns to the soil either directly (e.g. falling leaves) or indirectly (e.g. death of insects, excrement). Volatile sulphide compounds are lost to the atmosphere but they can in turn be oxidized to $SO_2$. The $SO_2$ can return to the soil intact (dry fall), be oxidized to $SO_4^{2-}$ which falls as particulates or precipitation, or be incorporated into plants through the stomata and returned to the soil upon plant decay.

Anthropogenic sulphur can enter soil by many of the pathways shown in Figure 7.1. When a given flux is augmented by the pollutant S, other fluxes attempt to adjust accordingly. For example, $SO_4^{2-}$ added to soil is rapidly converted to organic sulphur. Consequently, concentration determinations of soil $SO_4^{2-}$ cannot provide an accurate assessment of uptake of pollutant sulphate from the atmosphere. However, if the isotopic composition of the indigenous sulphate differs from that of the added pollutant sulphate, the $\delta^{34}S$ value of the mixture is a direct measurement of the relative amounts of each component, even if the $SO_4^{2-}$ pool is depleted by conversion to organic S. The accuracy of the isotopic approach depends upon whether there is isotopic fractionation during the $SO_4^{2-}$ conversions. During assimilation, the isotopic selectivity is usually small (Sections 7.1.4 and 7.2.3), whereas large kinetic isotope effects accompany dissimilatory (respiratory) sulphate reduction (Section 1.3.1.2). Fortunately most soil situations of interest are aerobic and isotope fractionation during sulphate reduction should not present problems.

### 7.1.3 Sulphur and oxygen isotope variations in soil

Soils range widely in their $\delta^{34}S$ values because of isotopic variations in parent materials and sulphur gains from, and losses to, the atmosphere, hydrosphere, and biosphere.

A world survey of soil $\delta^{34}S$ values has not been conducted. In most cases, data were obtained in areas where concerned environmental agencies wished to evaluate the effects of existing industrial pollution. However, there are sufficient data (Figure 7.2) to draw some conclusions regarding sources of sulphur compounds and their transformations.

The large range of $\delta^{34}S$ values in Figure 7.2 (from below $-30$ to above $+30$‰) can be related to a variety of natural and anthropogenic sources of sulphur. For instance, soils from various locations in New Zealand have $\delta^{34}S$ values approaching those of seawater $SO_4^{2-}$ (Kusakabe *et al.*, 1976). Thus the authors concluded that sea spray as the principal source of soil sulphur even in inland basins with little rainfall. Whereas New Zealand soils

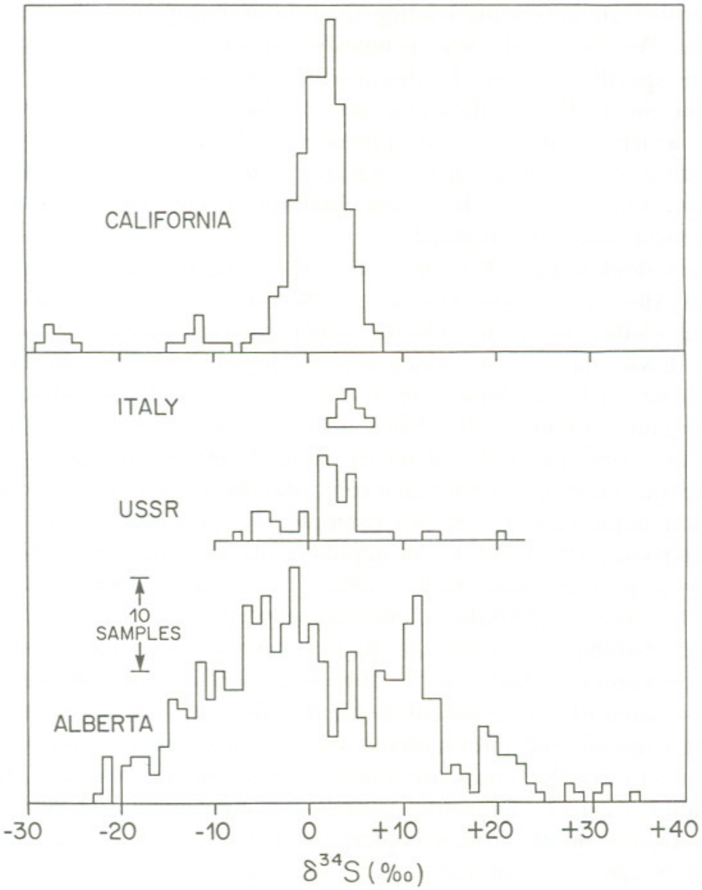

Figure 7.2 Natural sulphur isotope abundance variations in soils (see text for sources of data)

appear to derive marine sulphate from modern sea spray, other soils such as the few studied in Tunisia by Kusakabe *et al.* (1976) derive sulphate from gypsum occurrences related to the ancient ocean.

The data for the Soviet Union in Figure 7.2 are those casually mentioned in the thorough study of plants in various regions by Chukhrov *et al.* (1978). There is a considerable range in sulphur isotope composition with many data near +3‰.

These authors attributed the wide range in $\delta^{34}S$ values to essentially three processes which varied with locality. These are (a) local weathering of rocks containing evaporites and sulphide ores, representing extreme situations, (b) inputs of sulphate from the atmosphere, and (c) bacterial $SO_4^{2-}$ reduction in less aerobic environments leading to differentiation of $\delta^{34}S$ values with soil depth. As this study was primarily concerned with $\delta^{34}S$ values in vegetation, specific data will be discussed in Section 7.2.2.

As in the Soviet Union, data from many other locations in the world fall near 0‰, which is considered to approximate the terrestrial mean (Figure 7.2). In some cases, these signify natural sources but in other situations (e.g. Wawa, Ontario, and Thompson, Manitoba) smelting of sulphide ores of deep crustal origin is involved.

Soils very depleted in $^{34}S$ (−30‰) are often encountered (cf. California, USA, and Alberta, Canada; Figure 7.2). Surface or shallow occurrences of Cretaceous shales, found in Alberta, other parts of western Canada, and Montana, USA, have pyrite which is very depleted in $^{34}S$. Therefore the soil S is believed to be derived from weathering of sulphide minerals and perhaps organic sulphur in the shales. This process may have been ongoing since the last continental glacial retreat some 10 000 years ago.

Organic soils developed under anaerobic and therefore reducing conditions may exhibit depletions in $^{34}S$. An example is a peat deposit in Northern Alberta (Krouse, 1980). At 1.2 m depth, pyrite was the dominant sulphur species with a $\delta^{34}S$ value near −24‰. Upon approaching the surface and more aerobic conditions, elemental sulphur ($\delta^{34}S$ = −28 to −30‰) dominated. Sulphate salts on the surface had a $\delta^{34}S$ value near −33‰ whereas coexistent S° had a $\delta^{34}S$ value near −30‰. This sulphur isotope pattern is diagnostic of sequential kinetic isotope effects whereby $^{32}S$-containing sulphide and intermediates were oxidized preferentially.

Quite positive $\delta^{34}S$ values are found in soils near travertine ($CaCO_3$, minor $CaSO_4 \cdot 2H_2O$) depositing springs reflecting evaporite strata which were dissolved at depth by these waters. In many locations in Alberta, such positive $\delta^{34}S$ values in soil may also be the consequence of emissions from sour gas processing (see below and Section 8.2).

Thus the wide variations in $\delta^{34}S$ values in soil embrace both natural and anthropogenic sources. Sulphur isotope data in combination with concentration measurements can be used effectively to delineate those sources. In the Teepee Creek area of Alberta, more negative $\delta^{34}S$ values of soil specimens were found for higher S contents (Krouse and Case, 1981). The most negative values approached those found for shallow sulphate mineral deposits, believed to have been derived from weathering of Cretaceous shales. Therefore elevated sulphur levels in the soil were attributed to a subsurface source rather than nearby minor industrial emissions.

A subsurface sulphate mineral source is also indicated in Figure 7.3, where the $\delta^{34}S$ value has been plotted against the inverse of concentration. Again, high total S concentrations are identified with quite negative $\delta^{34}S$ values even though the two locations, Teepee Creek and Twin Butte, are over

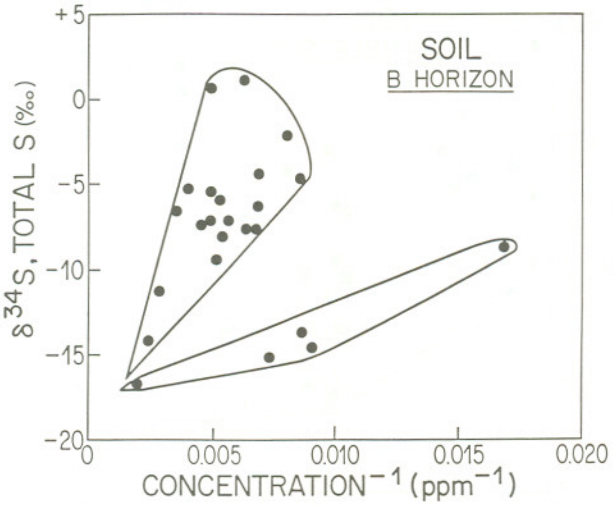

Figure 7.3 Plot of $\delta^{34}S$ values versus the inverse of total sulphur concentration in the B horizon of soils near Twin Butte, Alberta. A dominant sulphur source with $\delta^{34}S$ near −17‰ is indicated along with two minor sources (from Krouse and Tabatabai, 1986)

800 km apart. The two trends in Figure 7.3 suggest that three sources are present with the dominant one corresponding to the point of intersection of the trends and a $\delta^{34}S$ value of −17‰, again indicative of derivation from Cretaceous shales.

The presence of pollutant sulphur in soil enriched in $^{34}S$ has been frequently reported in the vicinity of sour gas processing plants in Alberta (Section 8.2). Data from one of the latter locations are summarized in Figures 7.4 and 7.5. In Figure 7.4, the $\delta^{34}S$ values for soluble S in individual soil horizons are plotted as a function of distance from a gas flare stack which had been operative for 28 years. Within 9 km of the flare, there is evidence that sulphur of industrial origin has penetrated to the C horizon. Beyond 9 km, the $\delta^{34}S$ values of the lower horizons are reasonably constant, suggesting that the preindustrial $\delta^{34}S$ value for soil was about −12‰. The trend of decreasing $\delta^{34}S$ values with distance is maintained beyond 17 km in the upper horizons, attesting to industrial fallout beyond that distance. Using Figure 7.4, statements can be made regarding the relative contributions of industrial and natural sulphur to the $SO_4^{2-}$ pool. For example, in the Ap horizon at 17.5 km, 25% of industrial sulphur with a $\delta^{34}S$ value of +20‰ combined with 75% of natural sulphur with a $\delta^{34}S$ value of −12‰ yields the observed $\delta^{34}S$ value of −4‰.

In Figure 7.5, data for total sulphur in only one soil horizon are plotted for the Valleyview study. The $\delta^{34}S$ values of total S display a similar distance

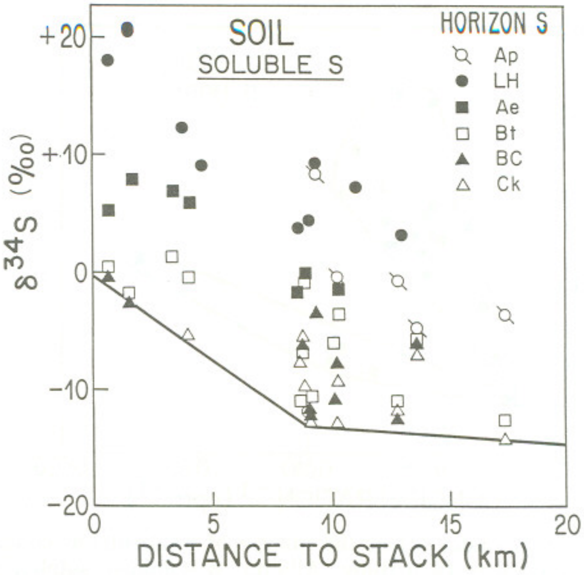

Figure 7.4 Presence of sulphur of industrial origin in soil, documented by sulphur isotope data for soluble sulphur, Valleyview, Alberta (from Krouse and Case, 1982)

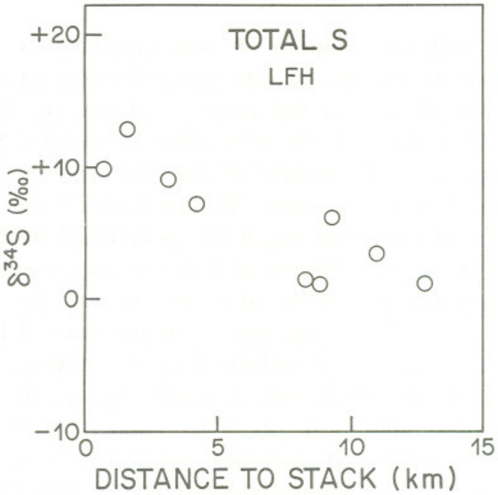

Figure 7.5 Presence of sulphur of industrial origin documented by sulphur isotope data for total sulphur in upper LH horizon, Valleyview, Alberta (from Krouse and Case, 1982)

dependence, although they are 2 to 9‰ depleted in $^{34}S$ compared to the soluble S (see Section 7.1.4).

Although $H_2S$ emission from soil and its subsequent oxidation have not been studied isotopically, sulphur and oxygen isotope data have been obtained for analogous biogenic $H_2S$ emission from thermal springs (van Everdingen *et al.*, 1982; Krouse and van Everdingen, 1984). These emissions after oxidation contributed secondary sulphate to the soil which was depleted in $^{34}S$ and $^{18}O$ by as much as 30 and 20‰ respectively, in comparison to primary $SO_4^{2-}$ in the spring waters. The depletion in $^{34}S$ in the secondary sulphate minerals relates to the kinetic isotope effects during bacterial $H_2S$ generation (Section 1.3.1.2), whereas the $^{18}O$ depletion arises from incorporation of oxygen atoms from the water molecule during oxidation (Section 2.2.1).

Similar isotopic data were reported for $SO_4{}^{2-}$ in groundwater (Shakur, 1982; Hendry *et al.*, 1989) and soil (Chae and Krouse, 1987) at depths near the water table in southern Alberta. Positive $\delta^{34}S$ and $\delta^{18}O$ values were found in the deepest samples, whereas shallower samples were characterized by $\delta^{34}S$ and $\delta^{18}O$ values as low as $-12$ and $-18$‰ respectively. This distribution can arise through changing levels of the water table coupled with $SO_4{}^{2-}$ reduction and mineralization of the product sulphide in the anaerobic zone. If the water level dropped, unreacted $SO_4{}^{2-}$ enriched in $^{34}S$ would remain in solution. The mineralized sulphide depleted in $^{34}S$ would become exposed to a more aerobic environment above the water table. It would tend to be reoxidized, incorporating some oxygen from the $^{18}O$-depleted water of meteoric origin (either vapour or penetrating rainfall). Meanwhile, $SO_4{}^{2-}$ below the water table becomes more enriched in $^{34}S$ and $^{18}O$ as reduction proceeds. Therefore the sulphate tends to be depleted in heavy isotopes in shallower environments with progressive enrichment with depth. This depth trend will be moderated as the soil acquires $SO_4{}^{2-}$ from precipitation and/or dissolution of primary sulphate minerals. The combination of sulphur and oxygen isotope abundances constitutes a unique tool for understanding soil $SO_4{}^{2-}$ transformations and for differentiating primary and secondary sulphate. A precautionary note is appropriate. Dissolved sulphate in standing water in wells or boreholes may not be representative of that in soil. For example, microbial contamination during drilling might alter concentrations and isotope compositions of sulphur compounds over time. If possible, standing water should be pumped out and water entering from the soil horizon sampled immediately.

### 7.1.4 Relationships among $\delta^{34}S$ values of different soil extracts

The $\delta^{34}S$ variations among different S compounds, compound classes, or extracts can be attributed to isotope selectivity in biochemical transformations or different sulphur sources. The extracts usually obtained in soil analyses are mixtures of compounds that cannot be readily related to specific biological processes (Section 7.1.1.2). Although the soluble fraction is mainly $SO_4^{2-}$, some soluble organic S compounds may be included. Since the insoluble S fraction is the remnant of extraction by water or salt solutions, it will contain varying amounts of sulphate inversely related to the soluble S recovery efficiency.

For many locations in Alberta, Canada, the $\delta^{34}S$ values for total soil S are systematically lower than those for soluble S (Figure 7.6). It is unlikely that this resulted from kinetic isotope effects during the conversion of $SO_4^{2-}$ to water-insoluble organic S. An alternate explanation is based on mixing phenomena. At these locations, most of the soluble S, particularly in the upper LFH soil horizon (litter), came from the atmosphere which contained $^{34}S$-enriched sulphur compounds of industrial origin. Deciduous leaves and conifer needles contributed significantly to the litter. Some of this insoluble

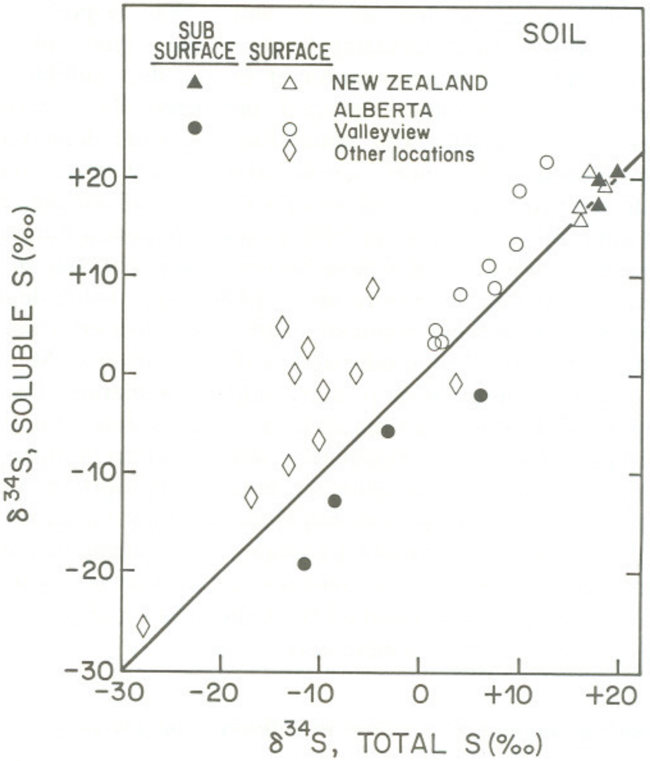

Figure 7.6 The $\delta^{34}S$ values for soluble S versus the same for total S in soil samples of Alberta and New Zealand (New Zealand data from Kusakabe *et al.*, 1976)

organic S was derived from atmospheric $SO_2$, but the bulk was acquired from soil water $SO_4^{2-}$ more depleted in $^{34}S$ (see Section 7.2.5). Hence, the isotopic difference between the two soil components is readily explainable by two sources coupled with the lack of isotopic homogenization. This in turn implies that the different sulphur forms had not interconverted extensively since entering the soil.

In some deeper soil horizons in Alberta the isotopic distribution between soluble and insoluble S is opposite to that described above; i.e. the data fall below the line of unity slope in Figure 7.6. This can be explained by an argument similar to the above except that the dominant source of soluble S is a subsurface mineral depleted in $^{34}S$ (Section 7.1.3). At depth, organic S is much less likely to be oxidized to sulphate under the anaerobic conditions.

In the New Zealand soils studied by Kusakabe *et al.* (1976), the data fall close to the line of slope unity, passing through the origin in Figure 7.6. These authors conclude that there is negligible isotopic selectivity during $SO_4^{2-}$ to organic S transformations and that the soil components which they studied were homogeneous in S isotope composition. The homogenization need not take place in the soil *per se* since sulphate assimilation by plants is accompanied by minimal isotopic selectivity, i.e. the organic S in litter has essentially the same isotopic composition as $SO_4^{2-}$ available to the plant roots if the influence of atmospheric sulphur is minimal.

In summary, if all soil sulphur is derived over a long time from one isotopically uniform source, all S fractions acquire similar isotopic compositions; i.e. kinetic isotope effects involved in the transformations are small. A possible exception is dissimilatory $SO_4^{2-}$ reduction in water-logged soils. If there are a number of isotopically different sources or, alternately, temporal variations in the isotopic composition of one source, there may not be sufficient time for significant interconversions either within the soil or through soil–plant cycling. Then, isotopic variatons will persist between extracts or spatially with the same extract. Whereas the microbial or botanical conversion of $SO_4^{2-}$ to organic S can be rapid, oxidative turnover of the much larger accumulated organic S pool in soil requires more time. Therefore, the latter process would appear to be rate controlling in establishing isotopic uniformity among sulphur pools.

Anthropogenic $S^o$ may enter the soil as applied fertilizer or dustfall from loading operations. The sulphur isotope selectivity was found to be very small during chemical and bacterial oxidation of $S^\circ$ in potted soil (McCready and Krouse, 1982). This implies that the kinetic isotope effect in the rate-controlling step is close to unity. This is consistent with the overall fractionation being determined by reaction on the sulphur surface. Dependent upon the concentration of background $SO_4^{2-}$ and the difference in the $\delta^{34}S$ value of the $S^\circ$ and background $SO_4^{2-}$, S isotopes can be used to determine the oxidation rate. Further, during oxidation, oxygen atoms are incorporated from both $H_2O$ and atmospheric $O_2$. Therefore, both the sulphur and oxygen isotope compositions can be used to delineate natural sulphate from that generated by the oxidation of applied $S^o$.

### 7.1.5 Transfer of sulphur into the soil as revealed by sulphur isotope data

There are a number of pathways by which sulphur may enter the soil (Figure 7.1). Of these, the dominant mechanism is leaching of $SO_4^{2-}$. In acid soils, downward movement will be impeded by sorption of $SO_4^{2-}$ by Al and Fe compounds. Other factors of importance include movement of organic compounds and biological transformations. In forest ecosystems, flow of sulphur compounds from the atmosphere to the subsoil may be blocked by moss and litter (see Figure 7.13).

The trapping mechanism might be physical (low permeability) or $SO_4^{2-}$ assimilation might occur. Groundwater behaviour is relevant. Downward transport of sulphur compounds should be enhanced in recharge areas and suppressed in discharge areas.

Penetration of atmospheric pollutants into the soil does not depend simply upon accumulated fallout. The rates and duration of the emissions are very relevant. Episodes at high $SO_2$ concentrations for short periods can chemically destroy the integrity of the surface and radically upset bacterial balances. In contrast, the same amount of $SO_2$ deposited at a constant rate might be retained in litter and/or botanical cover.

A controversial concept is the possible migration of sulphur compounds to the B or even C soil horizons by downflow within plants to the roots. The evidence, however, suggests that this flux is not substantial (Section 7.2.5).

The downward movement of sulphate in soil is influenced by texture. It has been found that sand has a much higher filtration rate than glaciolacustrine clay (Figure 7.7). At Valleyview, Alberta, industrial flaring over many years generated $SO_2$ with $\delta^{34}S$ values around +20‰. Figure 7.7a shows the concentrations of soluble sulphur (mainly $SO_4^{2-}$) in the Ae horizon as a function of distance from the stack. Site 1 is a thin sand veneer overtill, whereas site 15 is a thin sand veneer over a glaciolacustrine clay veneer overtill. Clay cover exists at all other sites. The soluble sulphur contents at sites 1 and 15 are lower than the trend since the sandy veneer permitted penetration to lower horizons. This interpretation is further supported by the sulphur isotope data (Figure 7.7b and c). In all three plots, movement of points 1 and 15 to higher concentrations align them with the trends found for the clay veneer soils.

Figures 7.4 and 7.7b and c collectively demonstrate how $\delta^{34}S$ data can very effectively assist in interpreting the movement of sulphur in the soil

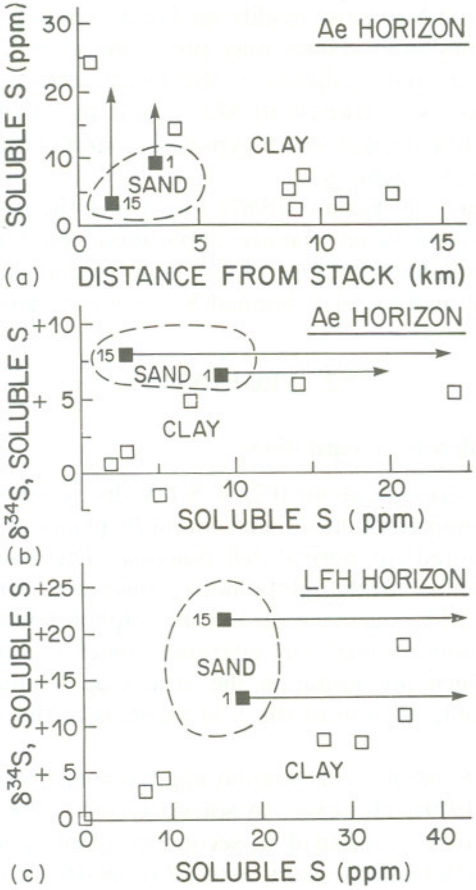

Figure 7.7 Concentration and sulphur isotope data relevant to retention of soluble S in sand and clay, Valleyview, Alberta (from Krouse and Case, 1982). Arrows indicate where data would plot if soluble S had not readily moved downward through upper sandy horizons. (a) Concentration of soluble S in the Ae horizon versus distance from the flare stack. (b) The $\delta^{34}S$ value versus concentration of soluble S in Ae horizon. (c) The $\delta^{34}S$ value versus concentration of soluble S in LFH horizon. The higher $\delta^{34}S$ values in the uppermost LFH horizon attests to a larger proportion of $SO_4^{2-}$ of industrial origin than in the underlying Ae horizon

profile. It must also be stressed that concentrations determined by expedient sampling of soil to a preselected depth, as advocated by some environmental agencies (typically 5–10 cm), may not be reliable indicators of the pollutant S content. Sulphur in each soil horizon in a longer core should be examined and the depth profile fully characterized.

Whereas total soil S is most readily analysed, isotope data from specific compounds or compound classes may prove more informative. For $SO_2$ emissions and $S^o$ dustfall, sulphate is the logical choice for two reasons. The added sulphur is converted to $SO_4^{2-}$ and the natural soil sulphate content is usually low (except where gypsum is found in the parent material) compared to that of organic S.

In contrast, Chae and Krouse (1987) found that the presence of sulphur in lower soil horizons from manure application could not be discerned isotopically with sulphate because of the high natural background. It was demonstrated that analysis of C-bonded S was more appropriate.

## 7.2 VEGETATION

### 7.2.1 Forms of sulphur in vegetation

Plants contain on average about 0.25% S (by dry weight). A wide variety of S-containing compounds have been found in plants, but only a few are known to be required for normal cell function. The essential compounds include the S amino acids, glutathione, thiamine, vitamin B, biotin, ferredoxin, lipoic acid, coenzyme A, and the sulpholipid of the chloroplasts. Compounds of non-essential or unknown functions in plants include glucosinolates, which are found in the cruciferae, choline sulphate, and penicillin. A variable portion of the S in plants is in the form of inorganic $SO_4^{2-}$.

Generally, the S amino acids contain approximately 90% of the S found in plants (Blair, 1979). However, in some species, a considerable portion of the total S may be contained in secondary plant products (Anderson, 1975). The total C/S ratios of plant material ranges from 150:1 in rape seed grain to 450:1 in straw.

The largest portion of S in plants is in protein either as cysteine, cystine, or methionine. Plant proteins generally contain 1 % S and 17% N (Dijkshoorn *et al.*, 1960; Pumphrey and Moore, 1965).

For any plant species, the composition of a given protein, which is controlled by genetics, is constant. Therefore, environmental factors such as the N and S supply, age of plant, etc., should have no influence on the N/S ratio in plant proteins. However, the total N/total S ratio can be greatly affected by environmental factors. When S is adequate, non-protein S (mainly $SO_4^{2-}$) will accumulate in the plant and the total N/total S will be less than the N/S ratio in protein. When S is deficient, protein formation is suppressed and non-protein N accumulates. The resulting bulk plant N/S ratio is greater than the N/S ratio of the proteins.

In most plants, inorganic $SO_4^{2-}$ is the main component of the HI-reducible S fraction. Plants absorb S as $SO_4^{2-}$, which is reduced and incorporated into amino acids as a precursor for protein synthesis. Any excess $SO_4^{2-}$ that is not metabolized accumulates unchanged in the tissue. When S is in short supply, most of this $SO_4^{2-}$ is incorporated into protein and little remains free in the tissue (Janzen and Bettany, 1984).

Studies on the decomposition of plant material indicate that net mineralization of S is mainly related to the content of S in the material added to the soil (Freney, 1967). No net mineralization of S occurred from plant material if it contained less than 0.13% S.

### 7.2.2 Sulphur isotope distribution in vegetation

Variations in $\delta^{34}S$ values for vegetation samples from different parts of the world are summarized in Figure 7.8. The bulk of the data, which include many species and parts of individual plants, displays a range in $\delta^{34}S$ values from −20 to +30‰, comparable to that found for sedimentary rocks (Chapter 4). There are isolated extremes outside this range (Krouse and Tabatabai, 1986). For example, plants growing near a biogenic $H_2S$ emitter had $\delta^{34}S$ values as low as −33‰ (Krouse and van Everdingen, 1984). Whereas parts of some trees were found to vary by less than 1‰, in other cases variations of over 15‰ were encountered (Section 7.2.5). In some studies, vegetation had uniform $\delta^{34}S$ values over a large area whereas in the vicinity of natural or industrial emitters variations could be significant over distances of a few metres.

The average and most frequently encountered $\delta^{34}S$ value for vegetation over extensive areas of the Soviet Union was found to be near +3‰ (Chukhrov *et al.*, 1975, 1978; Figure 7.8). These authors discussed a number of factors that influence the sulphur isotope composition of vegetation. These include lithospheric sources, groundwater leaching and transport, bacterial redox reactions in soil solutions, and the relative contribution of $SO_4^{2-}$ in precipitation.

In the Lena River in the Republic of Central Yakutia, $SO_4^{2-}$ with $\delta^{34}S$ values as high as +26‰ was identified with evaporite dissolution. The $\delta^{34}S$ values for plants in the vicinity were as high as +17‰, even at considerable distances from the river. Plants in the flood plain of the Lena River and nearby marshy lowlands possessed higher $\delta^{34}S$ values. Whereas ground water played a role in transporting $^{34}S$-enriched sulphur to the vegetation, the authors considered local precipitation to be a major factor. They believed that the $\delta^{34}S$ values ranging from +5 to +22‰ in rain and snow reflected atmospheric uptake from this vast water body.

At some locations, metal sulphide deposits influenced the isotopic composition of plants whereas in other cases there were no correlations. For example, at Zhosaly Sopka, pyrite deposits apparently contributed negative $\delta^{34}S$ values to vegetation whereas, at Alaygyur, there was no

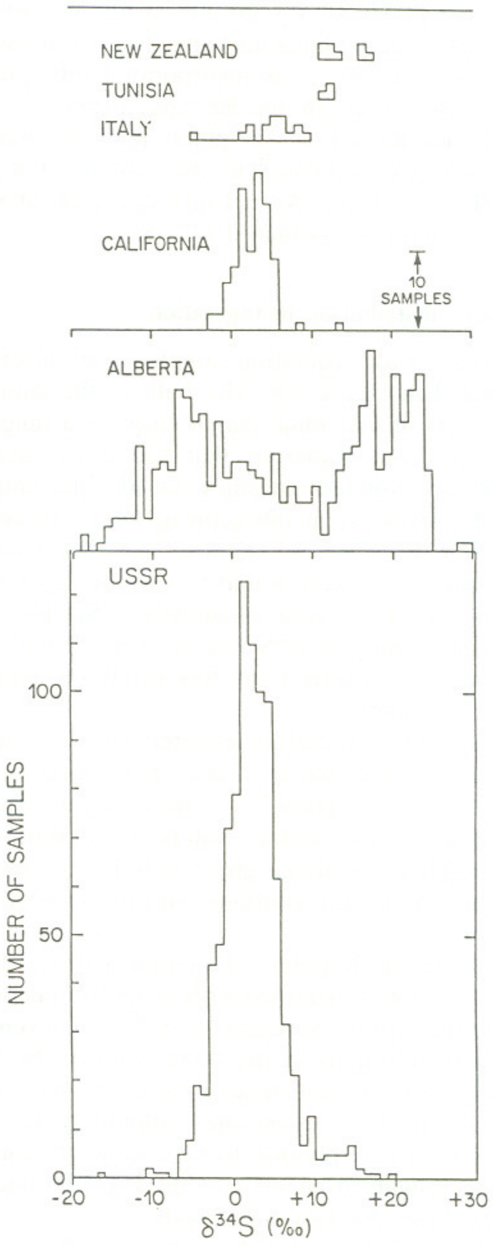

Figure 7.8 The $\delta^{34}S$ values for vegetation from various locations in the world. (see text for sources of data)

evidence of such a contribution. This inconsistency was attributed to groundwater circulation and the effects of elevation. Sites below ore deposits could be influenced by leachate carried by ground water whereas sites above the ore occurrences would not be affected. Negative $\delta^{34}S$ values in vegetation near copper sulphide occurrences at Kounrad peaks were in part attributed to ore dust which entered the atmosphere during pit-blasting operations.

In some locations, trees growing in igneous rock fissures had foliar $\delta^{34}S$ values close to the atmospheric average and the seasonal variations were quite small (+1 to +4‰) as compared to the average value of +2.1‰ found in snow. Precipitation $SO_4^{2-}$ should be rapidly lost through crevices where extensive humic matter had not built up to provide a soil sulphur reservoir. In contrast, large temporal $\delta^{34}S$ variations were found in locations where plants derived most of their sulphur from soil solutions, particularly under anaerobic conditions. As the consequence of bacterial $SO_4{}^{2-}$ reduction, the $\delta^{34}S$ values of residual $SO_4{}^{2-}$ in stagnant water in a marsh location was found to increase from 0 to 5‰ in the spring to as high as +29.6‰ in late summer. Birch and willow trees in the same area some distance from the marsh had $\delta^{34}S$ values near 0‰ whereas grass growing near the stagnant water acquired $\delta^{34}S$ values as high as +15.4‰.

The data from Alberta contrast with those of the Soviet Union in that the former display two peaks. The highly negative values are found near Cretaceous shale exposures, particularly in the Peace River area (Krouse and Case, 1981). It is believed that these plants assimilated $^{34}S$-depleted $SO_4{}^{2-}$ generated by weathering of reduced S species in the shales. Occasionally, a highly positive $\delta^{34}S$ value relates to groundwater dissolution of evaporites. However, in most cases, the vegetation is enriched in $^{34}S$ because foliar S has been derived from atmospheric $SO_2$ emitted during sour gas processing (Section 8.2).

In contrast to the above, limited data from other locations emphasize single sources of soil sulphur (Figure 7.9). Plants in New Zealand are enriched in $^{34}S$ in coastal areas because of marine $SO_4{}^{2-}$ in precipitation (Kusakabe *et al.*, 1976). The positive $\delta^{34}S$ values for the few specimens from Tunisia relate to gypsum occurrences in the soils (Kusakabe *et al.*, 1976).

### 7.2.3 Assimilation of sulphate by plants and algae

It is important to know the isotopic fractionation during $SO_4{}^{2-}$ assimilation to assess uptake of pollutant sulphur by plants. This can be best measured in the laboratory to avoid problems with multiple sources of sulphur in the field. In the case of algae, the isotopic composition of total sulphur as well as insoluble organic sulphur is typically depleted in $^{34}S$ by 1–2‰ with respect to $SO_4{}^{2-}$ in the medium (Section 6.2.2; Section 1.3.1.1).

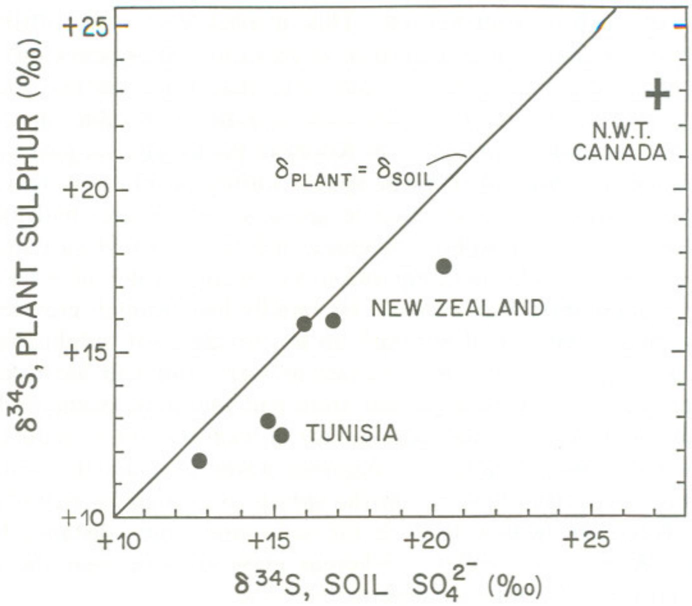

Figure 7.9 The $\delta^{34}S$ values for plant sulphur versus those for soil sulphate in situations where uptake from the atmosphere is minor compared to derivation of foliar S from the soil (data sources: New Zealand and Tunisia, Kusakabe *et al.*, 1976; Northwest Territories, Canada, Krouse *et al.*, 1984)

With higher plants, either negligible fractionation or an average depletion of $^{34}S$ by 1 to 2‰ in the organic sulphur has been realized (Section 1.3.1.1; Section 6.2.2). In studies with very high $SO_4^{2-}$ or $HSO_3^-$ concentrations, the foliar S may become enriched in $^{34}S$ due to release of reduced S compounds which are depleted in $^{34}S$ (Section 7.2.7).

For land plants, the isotopic selectivity during assimilation of $SO_4^{2-}$ in soil water is difficult to evaluate since the foliage may also acquire gaseous atmospheric S (Section 7.2.5). Therefore, one should examine data from areas where the ambient sulphur oxide concentrations are low compared to the soil $SO_4^{2-}$ content. Further, data for soil water sulphate should be obtained in the vicinity of the roots.

Isotopic similarity of total or organic sulphur in plants and $SO_4^{2-}$ in the soil has been frequently reported. For example, Mekhtiyeva *et al.* (1976) found the foliar total sulphur to be slightly depleted in $^{34}S$ with respect to soil sulphate for six perennial plants growing near Moscow. There were temporal trends with the conifers becoming more depleted and the deciduous trees (linden, poplar, birch, and elm-leaved spirea) becoming more enriched in $^{34}S$ during the period May–September. This isotopic similarity is usually found where soils are high in S content and ambient $SO_2$ is low. Examples are locations shown in Figure 7.9 where soil sulphur is derived from dissolution of evaporites or sea spray fallout. An alternative scenario is where the sulphur available to the plants is derived almost entirely from precipitation. This was found to be the case for plants growing in granitic rock fissures (Chukhrov *et al.*, 1975). In highly polluted areas, the $\delta^{34}S$ value of atmospheric sulphur may be the same as the soil and in turn the foliar sulphur in the absence of sulphur stress (Section 7.2.7).

An alternate approach for determining the isotopic selectivity during $SO_4^{2-}$ assimilation is to compare the $\delta^{34}S$ value of foliar $SO_4^{2-}$ to the total or insoluble S. Data from one such study are shown in Figure 7.10. The bulk of the samples had sulphate levels (extracted by sonication in 0.1 N LiCl) lower than 0.02% whereas the total sulphur content by oxidation with a Parr combustion bomb was as high as 0.2%. With a few exceptions, the sulphur isotope composition of the sulphate was similar to that of total sulphur and averaged −7‰. The soil had similar $\delta^{34}S$ values. Since atmospheric sulphur compounds had an average $\delta^{34}S$ value of +10‰, the higher $\delta^{34}S$ values for some sulphate extracts in Figure 7.10 probably relate to uptake from the atmosphere. This illustrates how sulphur from different sources make it difficult to determine kinetic isotope effects in natural settings.

In Figure 7.11, data for water-soluble S in plants are plotted against total plant S for specimens from various parts of Japan. It is noted that many

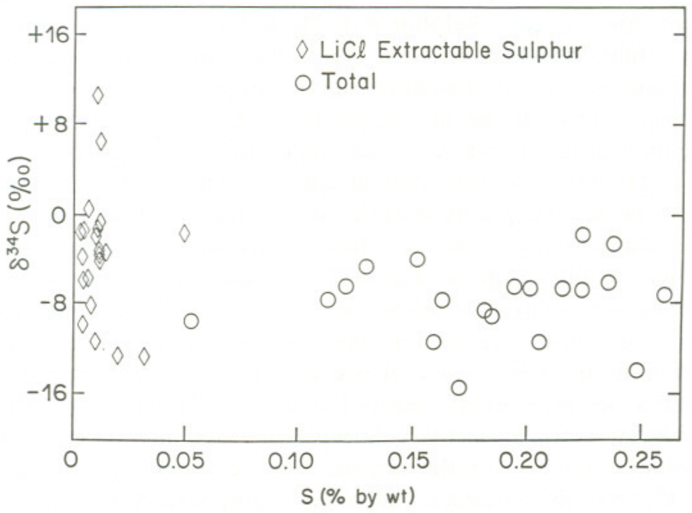

Figure 7.10 The $\delta^{34}S$ values versus S content for LiCl extractable and total S in *Populus tremuloides* leaves, Teepee Creek, Alberta (from Krouse and Case, 1981)

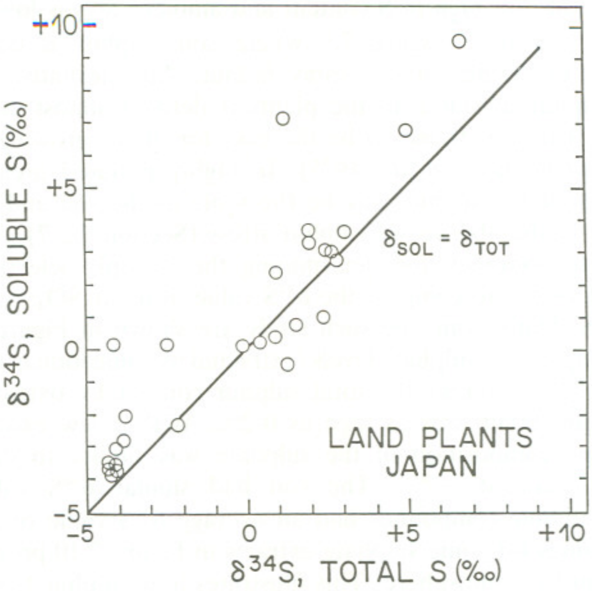

Figure 7.11 The $\delta^{34}S$ values for water-soluble S versus those for total sulphur in plants from Japan (data provided by N. Nakai)

points fall close to the line of unity slope going through the origin. There is a slight preference for points to plot above the line, suggesting that, on the average, foliar organic sulphur is 1–2‰ lighter than the soluble S.

Thus, in situations where ambient $SO_2$ is low and uptake of soil sulphate dominates, the soluble and insoluble sulphur in plants have similar sulphur isotope compositions. If the uptake of atmospheric sulphur compounds is extensive, then different extracts, and indeed different locations in a plant (Section 7.2.5), may differ markedly in isotopic composition. It is interesting to note that the soluble S component is more mobile and on average should have been acquired more recently than the organic S. Hence, deviations from the line of unity slope in Figure 7.11 could reflect temporal changes in the isotopic composition of the source $SO_4^{2-}$. Therefore, comparisons of foliar $SO_4^{2-}$ and insoluble S over time can potentially serve to monitor changes in pollutant S levels and/or sources in the soil or atmosphere.

In summary, as with aquatic plants (Section 6.2.2) and bacteria (Section 1.3.1.1), sulphur isotope selectivity during $SO_4^{2-}$ assimilation by land plants is small with a tendency for the organic S to be relatively depleted in $^{34}S$ by 1–2‰. There is also evidence that when atmospheric $SO_2$ is incorporated by lichens, the transformation to organic sulphur involves very little isotopic selectivity (Krouse, 1977).

### 7.2.4. Uptake of sulphide by plants and algae

Fry *et al*. (1982) found submerged and emerged rooted plants in anoxic sediments to have $\delta^{34}S$ values near that of the sulphide species (−24‰) rather than the $SO_4^{2-}$ in the interstitial pore water (+15 to +17‰). They could not ascertain whether sulphide was incorporated directly or whether it was oxidized at the root–sediment interface. Carlson and Forrest (1982) found the salt marsh cordgrass, *Spartina alterniflora*, to be isotopically similar to sulphide in the marsh pore water. They concluded that sulphide had been oxidized within the plant.

Sulphur in marine algae is generally slightly depleted in $^{34}S$ with respect to seawater sulphate (Section 6.2.2). Lacking roots, algae do not have access to sulphide in the sediments. These observations contrast to studies with algae in thermal springs (Krouse *et al*., 1970; H.R. Krouse and A. Sasaki, unpublished data). Rather, algae tend to acquire the $\delta^{34}S$ value of dissolved sulphide even though the concentration of $SO_4^{2-}$ may be two or three orders of magnitude higher (Figure 7.12). Sulphate crusts were found on some specimens and their $\delta^{34}S$ values were similar to the dissolved sulphide species. The sulphur-oxidizing bacteria *Beggiatoa* sp. were also found associated with some algae (F.D. Cook, personal communication). The above data are consistent with the ability of cyanobacteria to carry out anoxygenic photosynthesis using sulphide (Castenholz, 1973; Cohen *et al*., 1975). This topic will be thoroughly reviewed in another SCOPE publication.

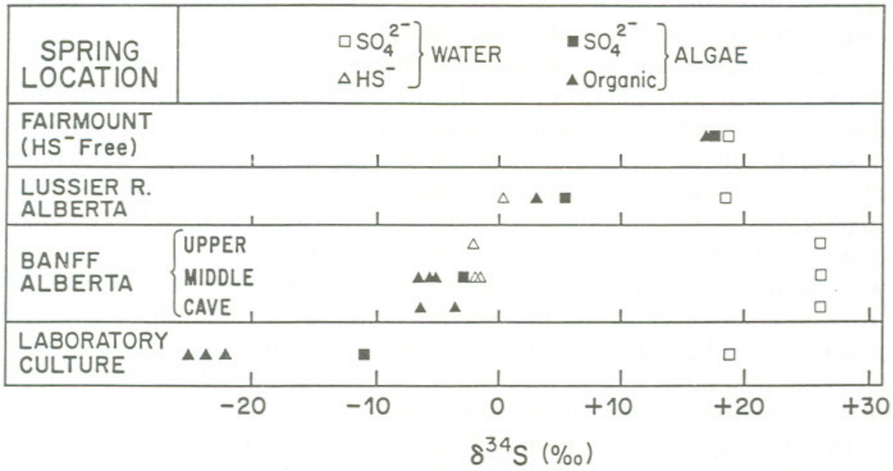

Figure 7.12 The $\delta^{34}S$ values of algal growths, $HS^-$, and $SO_4^{2-}$ in thermal springs of western Canada. The laboratory culture comprises algae which developed in a clear stoppered glass bottle of spring water during storage on an open shelf for several months (data provided by A. Sasaki and H.R. Krouse)

For the purposes of the current volume, it is significant that this process represents a mechanism by which the biosphere may respond to pollutant S in the form of sulphide.

### 7.2.5 Relative incorporation of soil and atmospheric sulphur by vegetation

Vegetation incorporates sulphur rather directly from the atmosphere, e.g. gases entering stomata, or by assimilating $SO_4^{2-}$ and other S-bearing ions in soil or water bodies. Relative uptakes of atmosphere S gases and soil $SO_4^{2-}$ can be readily ascertained if the sulphur isotopic compositions of these two sources differ significantly (Krouse, 1977).

In some situations, one uptake mechanism dominates. Epiphytic lichens have $\delta^{34}S$ values close to that of ambient $SO_2$ (Figure 7.13) unless under severe stress (see Section 7.2.7; Figure 7.20). Further, there may be topographical effects. Lichens on the leeward side of hills were found to contain less S and lower $\delta^{34}S$ values than those facing a source of industrial emissions enriched in $^{34}S$ (Case and Krouse, 1980). In the former case, the $[SO_2]$ was lower and a greater proportion of it came from natural sources.

Another example of one dominant uptake mechanism is shown in Figure 7.14. In this case, bark acquired sulphur dust introduced to the atmosphere during loading operations. Some of the dust was oxidized, and the sulphate in turn converted to insoluble organic S. However, large quantities of elemental S were also entrapped. The decrease in $\delta^{34}S$ values with lower concentrations of $S_o$ and derived compounds was coincident with greater distances from the source of $S_o$ dust. (The rationale for plotting $\delta^{34}S$ versus concentration $^{-1}$ is discussed in Section 5.5.1.)

Conifer needles and deciduous leaves have $\delta^{34}S$ values between those of soil $SO_4^{2-}$ and atmospheric S gases (Figure 7.13). The proportion of sulphur derived from each source depends upon many factors, including availability of suitable sulphur forms and plant response. Although high concentrations of $SO_2$ may damage higher plants, there is also evidence that atmospheric sulphur compounds can provide nutritional needs (Faller *et al.*, 1970; Cowling *et al.*, 1973). The concentration at which $SO_2$ exposure is injurious is not well defined. It depends upon factors such as duration and intensity of exposure, susceptibility of the species, stage of growth, humidity, soil moisture, and light intensity. On the basis of experiments of Zahn (1961), 0.15 ppm (420 $\mu g\ SO_2\ m^{-3}$) is gaining acceptance as a threshold below which prolonged exposure will not be detrimental.

The two S uptake mechanisms are also expressed in the isotopic variability among different parts of an individual plant. In the studies of Chukhrov *et al.* (1975, 1978), plant parts were found to be uniform in isotopic composition. In other studies, considerable variability has been found (Figure 7.15). The roots and tops for bull rushes were compared in a number of shallow-water

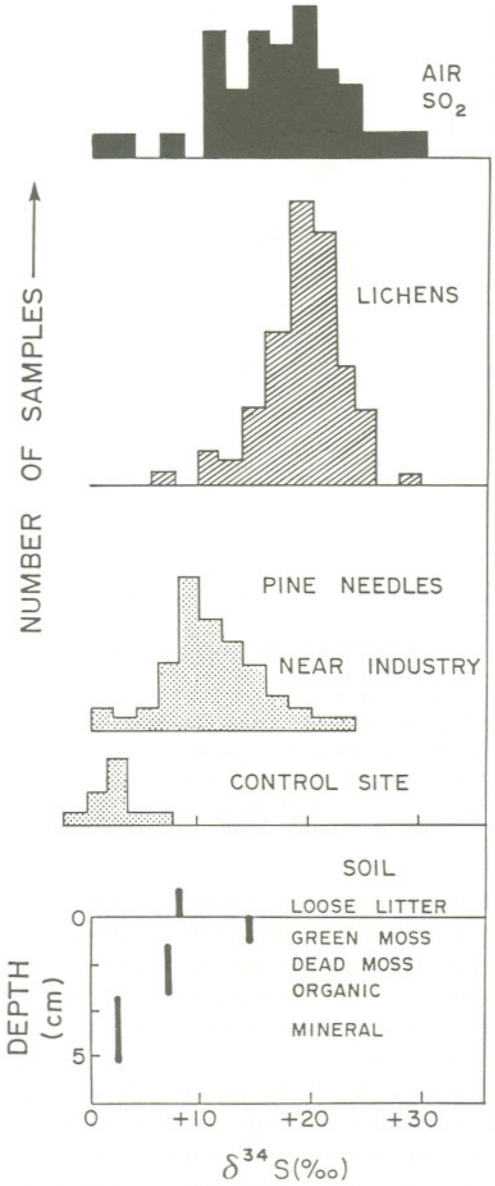

Figure 7.13 The $\delta^{34}S$ values for atmospheric $SO_2$, vegetation, and soil, Ram River Area, Alberta, 1971–2. Note how vegetation reflects S uptake from the atmosphere and soil. Note also that moss cover impeded the transport of atmospheric S to the soil subsurface

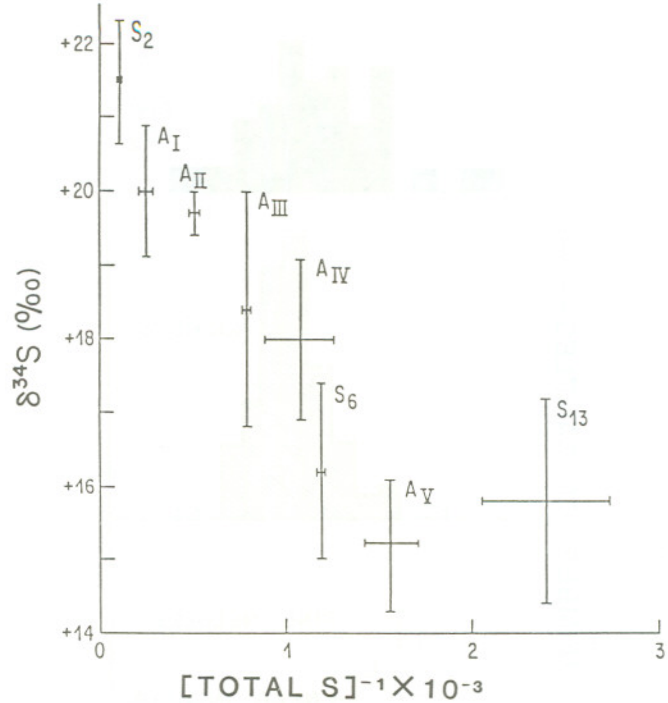

Figure 7.14 The $\delta^{34}S$ values versus the inverse of concentration for sulphur in bark specimens, West Whitecourt, Alberta. The bars signify the ranges in concentration and $\delta^{34}S$ values for several specimens at a given site. The $\delta^{34}S$ values decreased with increasing distance from the industrial operation (data provided by A. Legge and H. R. Krouse)

bodies around a sour gas processing plant near Twin Butte, Alberta. The isotopic composition of $SO_4^{2-}$ in the water and associated flooded soil (or sediment) varied, with higher $\delta^{34}S$ values corresponding to greater S inputs from the industry. Roots tended to have the same isotopic composition as surrounding soil. For some specimens, the tops of the plant had nearly the same $\delta^{34}S$ value as the roots. These corresponded to situations which had been influenced very little by the industrial emissions or those containing high $[SO_4^{2-}]$ with a considerable anthropogenic component. The ambient $[SO_2]$ was small in comparison so the upper parts of the plant derived sulphur dominantly from $SO_4^{2-}$. With ponds containing low $[SO_4^{2-}]$ the plant tops acquired considerable atmospheric S. These locations correspond to points significantly above the line, $\delta^{34}S_{tops} = \delta^{34}S_{roots}$.

The concept of uptake of both soil and atmospheric S was pursued with potted plant experiments (Winner *et al.*, 1978). Soil and plants grown therein

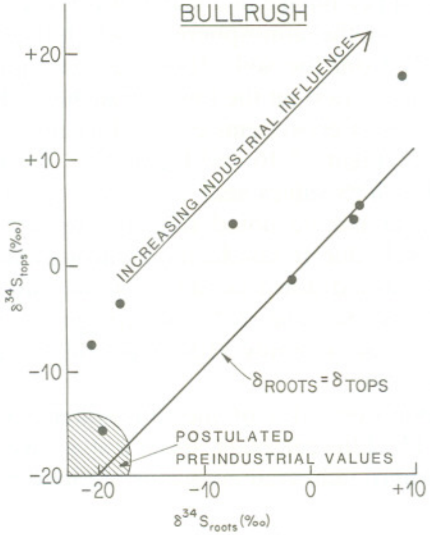

Figure 7.15 Comparison of $\delta^{34}S$ values in the tops and roots of bullrushes (*Typha latifolia*) near a sour gas processing plant (from Krouse and Tabatabai, 1986). Points above the line of slope unity correspond to proportionally greater uptake of atmospheric S compounds by the exposed upper parts of the plant

had initial $\delta^{34}S$ values near −8‰. In early June, they were exposed to ambient $SO_2$ with $\delta^{34}S$ values near +20‰, near an industrial operation. The $\delta^{34}S$ values of both the plants and soil increased uniformly throughout the growing season if the soil surface was exposed. If charcoal, peat, or moss were placed on the surface, the soil tended to retain the $\delta^{34}S$ value established in the laboratory. The foliage of plants grown in covered soils did not increase in $\delta^{34}S$ values as quickly as those in uncovered soils. In the bare soil surface case, pollutant S was acquired ultimately from the atmosphere since atmospheric S entered the soil. In the covered soil case, sulphur of industrial origin was acquired by the plants from atmospheric gaseous S but little atmospheric S had entered the soil. Moss cover has also been shown to be effective in blocking the movement of sulphur compounds from the atmosphere to the subsoil in natural situations (Figure 7.13).

The potted plant experiments imply that in the environments examined by Chukhrov *et al.* (1975, 1978), either the uptake of atmospheric S compounds by foliage was minimal or the soil and air had similar isotopic compositions.

The relative rates of uptake of sulphur from the soil and atmosphere may result in a height dependence for the isotopic composition of foliage in a single plant. Whereas upper foliage in a stand of trees tends to interact with sulphurous compounds in the atmosphere, lower foliage may take up its sulphur almost entirely from the soil. This is a consequence of the upper foliage exerting a canopy action on the lower branches. This has been noted on many occasions in forest ecosystems exposed to emissions from the sour gas industry in Alberta (Figure 7.16 and Figure 7.21 in Section 7.2.7). The atmospheric sulphur had $\delta^{34}S$ values near +20‰ whereas that of soil sulphur was closer to 0‰. It should be noted that uptake of $SO_2$ by the upper growth may not be solely due to conductance through stomata. Some $SO_2$ may be oxidized and washed down as $SO_4^{2-}$. Other species such as fungi may utilize atmospheric S. The $\delta^{34}S$ height gradient becomes more pronounced if the vegetation emits $H_2S$ under high sulphur stress (see Section 7.2.7; Figure 7.21).

The relative incorporation rates of the atmospheric and soil sulphur is also found to vary with different plant species at a given location. In the data of Figure 7.17, where industrial emissions are minimal, the $\delta^{34}S$ values

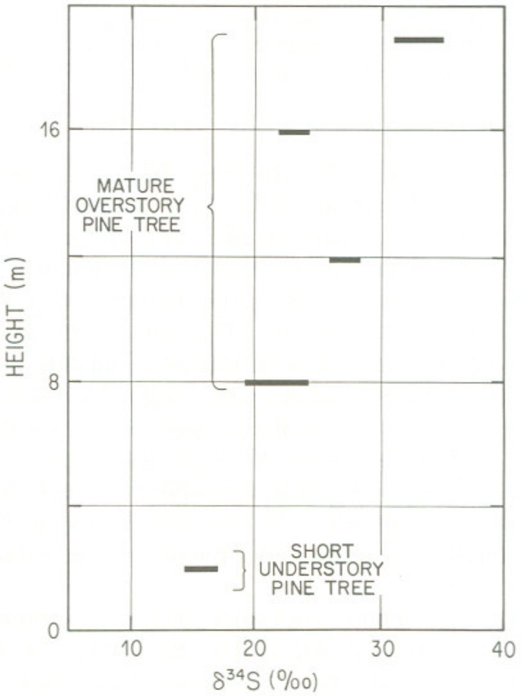

Figure 7.16 Variation of $\delta^{34}S$ values in conifer needles with height at one location in a forest stand near a sour gas plant operation, West Whitecourt, Alberta (from Krouse *et al.*, 1984)

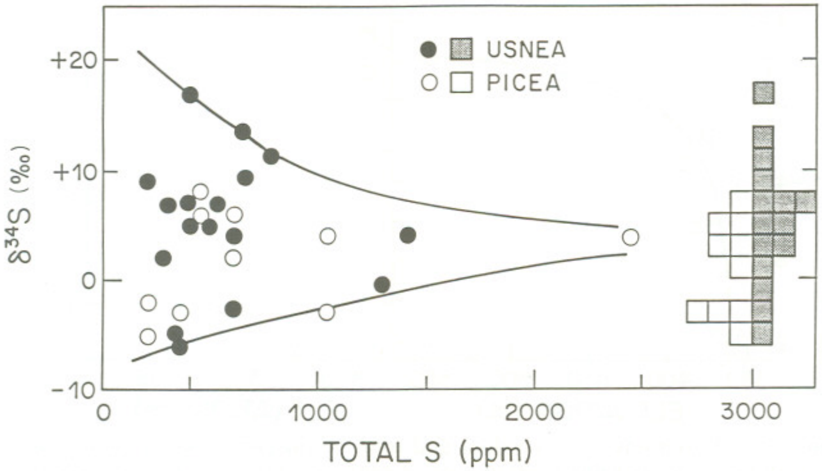

Figure 7.17 Comparison of $\delta^{34}S$ values for total S in lichens and spruce as a function of concentration in an area of Alberta where industrial emissions are minimal. Note that the mean values are similar (in contrast to Figure 7.13)

for both lichens and pine needles tend towards a similar $\delta^{34}S$ value at high concentrations. This is not the case in Figure 7.13 where the difference of 20‰ in the $\delta^{34}S$ values of the air and soil is reflected in the different $\delta^{34}S$ distributions for lichens and needles.

There are topographical factors that indirectly influence the relative amounts of sulphur acquired by the plants from soil and air. This concept is illustrated by $\delta^{34}S$ data for needles from conifers growing in rolling terrain around a sour gas plant operation near Zama, Alberta, Canada (Figure 7.18). High foliar sulphur concentrations are not consistent with the positive $\delta^{34}S$ values of the industrial emissions. Further, conifer needles at higher elevations contain less sulphur but have $\delta^{34}S$ values closer to that of the emissions. This apparent inconsistency can be resolved by considering the soil water behaviour. Subsurface $SO_4^{2-}$ (negative $\delta^{34}S$ values) leached from knolls has migrated and accumulated in depressions. Trees growing in the depressions with high $[SO_4^{2-}]$ near the roots have high foliar S contents. Some of these trees are under sulphur stress and vulnerable to small additions of industrial S. However, their needles with a high S content would retain a $\delta^{34}S$ value close to that of the soil sulphate and not reflect the minor industrial addition. In contrast, trees growing on exposed knolls with sulphur-deficient soil may be effectively fertilized by pollutant $SO_2$. Their foliage would acquire $\delta^{34}S$ values approaching near to those of the industrial emissions.

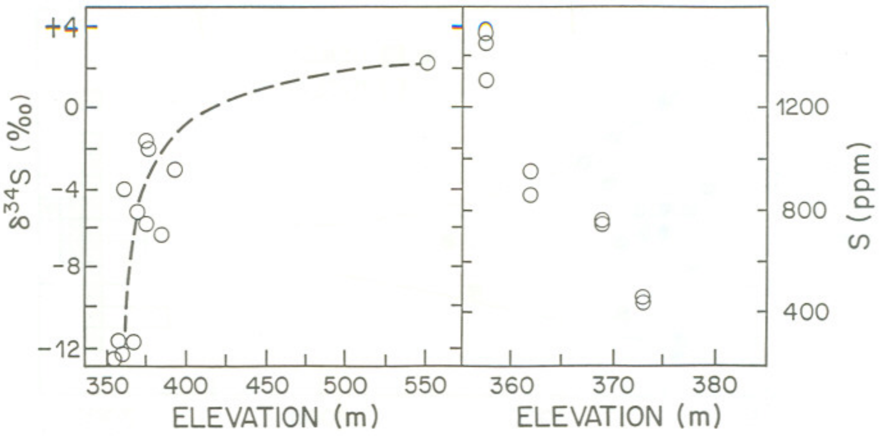

Figure 7.18 Variations in $\delta^{34}S$ values and total S concentrations in conifer needles with elevation in rolling terrain near a sour gas plant operation in Alberta

### 7.2.6 The influence of biological parameters on the sulphur isotope composition of plants

Sulphur isotope abundances can be used very effectively for determining sources of sulphur in the environment. Assessing the environmental consequences of pollutant sulphur is not straightforward. One approach is to search for correlations between biological parameters and the isotope data.

One biological indicator of possible environmental damage is areal extent (coverage) of species. Data from mosses growing in the Fox Creek area of Alberta are shown in Figure 7.19. Traverse A was downwind from the industrial source which emits $SO_2$ enriched in $^{34}S$. The second, angular traverse B is designated as the direction in degrees from downwind. The coverage increases with distance from the stack and greater angle from the dominantly downwind direction. For both traverses, the isotope data attest that reduction in coverage of mosses corresponds to an increase in the proportion of sulphur of industrial origin in the vegetation.

Biological damage indicators can often be related to sulphur isotope compositions and, in turn, excessive pollutant sulphur. However, this coincidence is not proof that any damage was due to the anthropogenic sulphur. Other pollutants may be the cause, or their presence promoted damage by the sulphur stress. There may also be secondary effects of the sulphur increment, such as lowering of the Se/S ratio or undesirable chemical reactions, e.g. dissolution of metals.

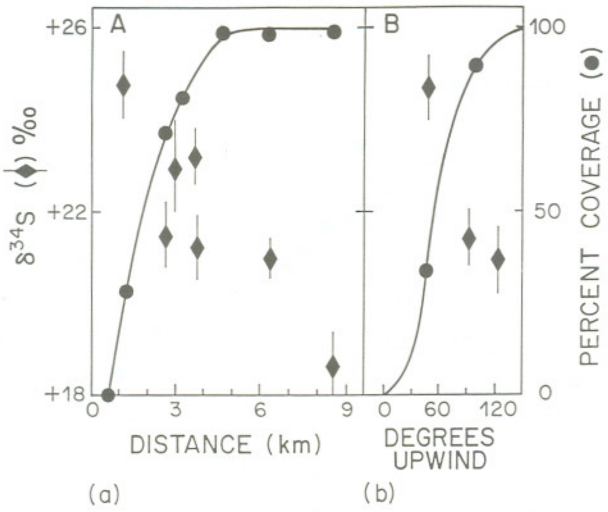

Figure 7.19 Variation in $\delta^{34}S$ values of total S in mosses with coverage: (a) traverse with distance downwind, (b) traverse with direction in degrees from downwind of a sour gas refining operation (data from Winner *et al.*, 1978)

### 7.2.7 Emission of reduced sulphur compounds by vegetation

Plants have been shown to emit $H_2S$ (DeCormis, 1968; Spaleny, 1977; Wilson *et al.*, 1978). Sulphur stress, light, and other factors such as root damage have been shown to enhance these emissions. The process was found to be isotopically selective in laboratory experiments with cucumber plants, *Cucumis sativus* (Winner *et al.*, 1981). Whereas the $\delta^{34}S$ values of the leaves were similar to that of $SO_4^{2-}$ and $HSO_3^-$ available to the roots, the emitted $H_2S$ was comparatively depleted in $^{34}S$ by about 15‰.

Indirect evidence that such gaseous emissions occur in nature is provided by stable sulphur isotope data. In areas of high S stress, foliar S has $\delta^{34}S$ values that are considerably higher than any available S sources. For example, data for the epiphytic lichen, *Usnea scabrata*, sampled downwind from a sour gas processing operation near Fox Creek, Alberta, fit a plot of $\delta^{34}S$ versus concentration$^{-1}$ (see Section 5.5.1) with the exception of two specimens designated by asterisks in Figure 7.20. These two samples with $\delta^{34}S$ values of +31.9 and +27.2‰ contain 2394 and 1430 ppm S respectively, and were collected within 2.2 km of the emission stack of a sour gas processing plant. Thus the high $^{34}S$ enrichments, which equal or exceed the maximum for ambient atmospheric S compounds, are identified with elevated sulphur contents and high exposure to $SO_2$. There is a 'reservoir effect'

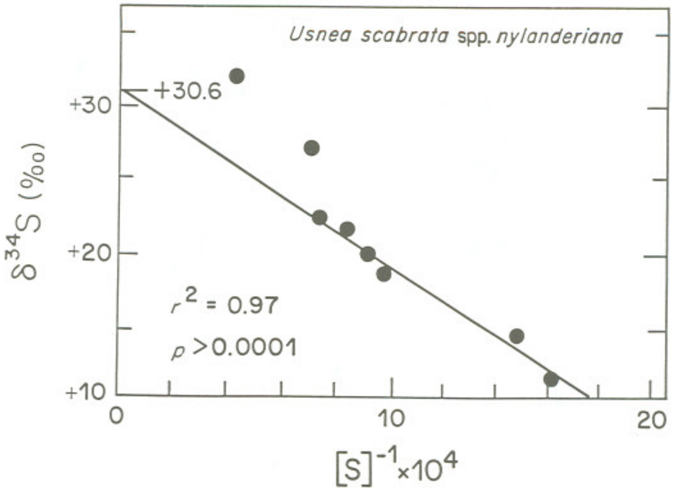

Figure 7.20 The $\delta^{34}S$ values versus the inverse of total S concentration for *Usnea scabrata* sampled near Fox Creek, Alberta, Canada (data from Case and Krouse, 1980)

(Section 1.2.3) in the foliage whereby the loss of $^{34}S$-depleted (or $^{32}S$-enriched) sulphur as emissions progressively increases the relative concentration of foliar $^{34}S$.

The $\delta^{34}S$ values for total S in conifer needles may increase with height in the vicinity of sour gas processing operations (Section 7.2.4). This effect is usually less pronounced than that found for a Lodgepole X jack pine tree in the West Whitcourt region (Figure 7.21). For this specimen, the $\delta^{34}S$ value for the uppermost crown exceeded the maximum $\delta^{34}S$ value of atmospheric S by 10‰, consistent with the reservoir effect described above.

Further evidence is suggested by the isotopic composition of salt crystals which occur occasionally on plant leaves. Two situations were examined by Shakur (1982). Evaporite crystals on vegetation near Kelly Lake Springs (65°24′ N, 126°06′ W) were found to have $\delta^{18}O$ and $\delta^{34}S$ values very similar to those for $SO_4^{2-}$ in the spring waters. In these springs, the $[SO_4^{2-}]$ ranged from 250 to 800 ppm. This contrasts markedly with an unusual natrojarosite, $NaFe_3(OH)_6(SO_4)_2$, depositing spring (65°12′ N, 124°38′ W) near Norman Wells, NWT, Canada. The $[SO_4^{2-}]$ is much higher, 5300 ppm, in these waters. The $\delta^{34}S$ values of the mineral deposits are very close to that of $SO_4^{2-}$ in the spring. Crystals of various sulphates occur on vegetation around this spring. In contrast to the brilliant yellowish-orange colour of the jarosite deposit, the crystals on plants are white and do not contain iron. They are also enriched in $^{34}S$ by over 3‰ as compared to the spring $SO_4^{2-}$ and mineral deposit (Figure 7.22).

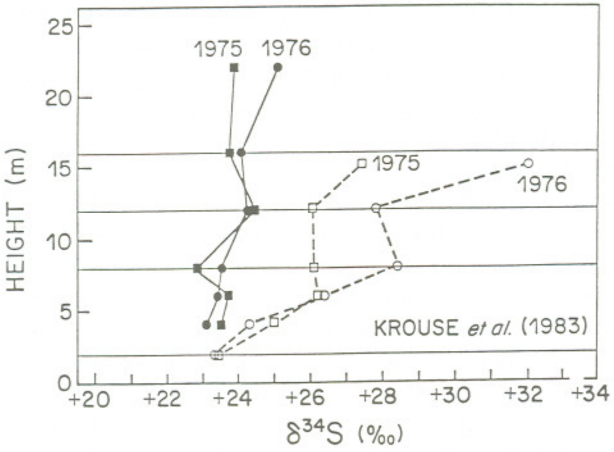

Figure 7.21 The $\delta^{34}S$ variations in needles of two Lodgepole × Jack Pine trees (indicated by closed and open symbols) as a function of height, West Whitecourt area, Alberta (from Krouse *et al.*, 1984)

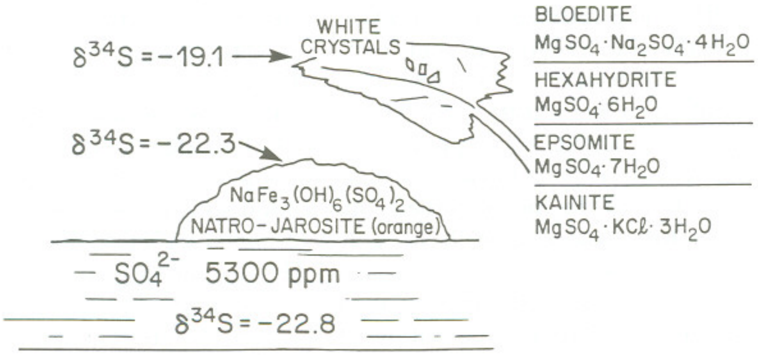

Figure 7.22 The $\delta^{34}S$ values for crystals on vegetation and minerals at a natrojarosite depositing spring, Norman Wells, NWT, Canada (data from Shakur, 1982)

Thus, in areas of high S stress, $\delta^{34}S$ values have been found for lichens, needles, and salt crystals on vegetation that are higher than those of sulphur sources in the vicinity. This phenomenon is consistent with a reductive process in which the $^{32}S$ species react at a faster rate.

## 7.3 FOOD WEBS AND HIGHER ANIMALS

Higher animals cannot assimilate $SO_4^{2-}$, i.e. to convert it to amino acids such as cysteine and methionine. They must ingest these essential organosulphur compounds and interconvert them as required. Isotopic selectivity during assimilation by aqueous plants and animals tends to be small (Section 6.2.2). Similarly, assimilation of sulphate by terrestrial plants appears to be accompanied by minimal isotopic fractionation (Section 7.2.3). Sulphur isotope fractionation or 'shifts' in a food web must be evaluated where one source of sulphur dominates.

In marine food webs, $SO_4^{2-}$ with a $\delta^{34}S$ value near +21‰ is the primary S source. Shifts to lower $\delta^{34}S$ values by as much as 3‰ are found for marine algae and plants. Salmon off the coast of western Canada have $\delta^{34}S$ values of +17 to +18‰ for inner flesh and +19‰ for the skin (Krouse and Herbert, 1988). These same authors reported that the fur of polar bears in the Canadian Arctic had $\delta^{34}S$ values near +17‰ as compared to the range of +16 to +18‰ for the fur of seals, their main food source. Thus sulphur of marine origin has progressively moved up this food chain. With higher animals, it is difficult to differentiate small kinetic isotope effects during metabolism from preferential metabolism of different food constituents (carbohydrates, fats, proteins, etc.) which had slightly differently $\delta^{34}S$ values.

Heron Island on the Great Barrier Reef of Australia has a large bird population because of the absence of predators. The combination of sea spray sulphate and fertilization by birds that are primarily fish feeders has resulted in the soil, vegetation, and feathers of birds having a remarkably uniform $\delta^{34}S$ value near +19‰ (Krouse and Herbert, 1988).

The fur of koala bears at the Lone Pine Sanctuary, Queensland, Australia, was found to be about 2‰ depleted in $^{34}S$ as compared to their diet of eucalyptus leaves. Hair clipped from kangaroos at the same location had $\delta^{34}S$ values close to the mean of their known food sources (Krouse, 1989).

Sulphur isotopic compositions have been determined for hair, nails, blood, urine, and cystine kidney stones in humans. The overall variation in $^{34}S$ of these components in a given human is about 2‰ and appears to approximate the mean sulphur isotope composition of the diet. Data for residents at Calgary, Alberta, Canada, were reported by Krouse *et al.* (1987). The $\delta^{34}S$ values for available foods range from −7 to +20‰. Locally produced meat, dairy products, and grain constitute a large part of the diet and have $\delta^{34}S$ values close to 0‰. It was found that hair, nails, blood, urine, and cystine kidney stones in Calgary residents also have $\delta^{34}S$ values close to 0‰. Incidentally, there was no discernable difference in the sulphur isotope composition of kidney stone formers and non-formers.

In contrast to the narrow range of isotopic composition within one individual, large variations have been found in the isotopic composition of hair, nails, and kidney stones with geographical location (Krouse and Levinson, 1984; Krouse and Herbert, 1988; A. Sasaki, unpublished data). For example, the $\delta^{34}S$ values for nails of attendees at the 1983 SCOPE/UNEP Sulphur Workshop in Pushchino ranged from +3 to +14‰.

From the above, it follows that if a human increases the marine food content of his diet, the $\delta^{34}S$ value of his tissues and fluids should increase. Whiskers of a Calgarian with $\delta^{34}S$ values ranging between +1.5 and +2.0‰ increased to +3.1‰ after he resided for one month in Japan. Upon returning to Calgary, they returned to the pre-visit values after about six weeks (Table 7.1).

The oxygen isotope data for $SO_4^{2-}$ in urine from the above study are also interesting (Table 7.1). They reflect the greater $^{18}O$ depletion in drinking water of Calgarians in comparison to Japanese and imply that some oxygen from body water molecules is incorporated into $SO_4^{2-}$ during biochemical oxidation.

Whereas the above study relates to changes in diet with location, the food sources at a given location may be seasonally dependent and might be reflected in the sulphur isotope composition of animal tissues. This may be the case for the data from consecutive fingernail clippings shown in Figure 7.23.

The ability to incorporate reduced inorganic sulphur compounds appears not to be limited to certain plants and algae (Section 7.2.4). Dense animal assemblages near deep sea hydrothermal vents, including vestimentiferan worms, brachyuran crabs, and giant clams, were found to have $\delta^{34}S$ values near 0‰, close to the range for nearby sulphide minerals (Fry *et al.*, 1983). It seems unlikely that the vent fauna utilized sulphide directly. Primary productivity was probably due to chemoautotrophic bacteria utilizing sulphide as an energy source. In some instances, sulphur oxidizing bacteria may have functioned symbiotically within tissues of host animals.

Preliminary isotopic data attest to sulphur originating from industrial processing, moving up to higher members of food webs. The feathers of

Table 7.1 Changes in isotope composition of a Calgarian who visited Japan for one month

| Sample time | $\delta^{34}S$ (‰) | | $\delta^{18}O$ (‰) |
|---|---|---|---|
| | Whiskers | Urine $SO_4^{2-}$ | Urine $SO_4^{2-}$ |
| Pre-visit | +1.5 to +2.0 | −0.1 | −5.8 |
| End of visit | +3.1 | +2.1 | −2.3 |
| Back in Calgary | | | |
| 3 days | | +1.5 | −3.0 |
| 7 days | +2.4 | +0.6 | −3.7 |
| 14 days | | +0.4 | −4.2 |
| 28 days | +2.0 | +0.2 | −5.8 |
| 35 days | +2.0 | | |

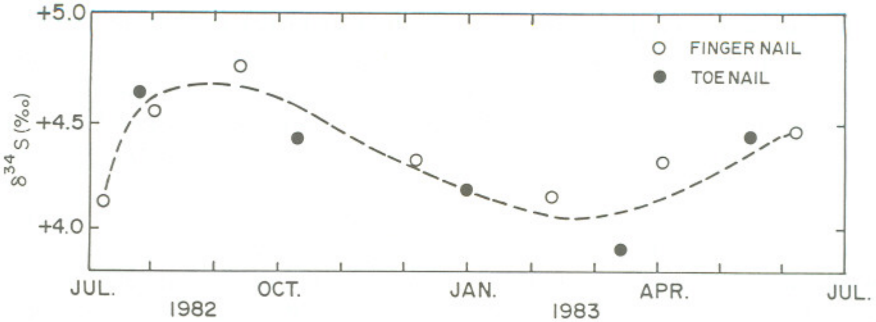

Figure 7.23 Variation in sulphur isotope composition of fingernail clippings over a one-year period (unpublished data of A. Sasaki, 1983)

grouse living downwind of a sour gas plant ($\delta^{34}S$ value of emissions near +22‰) in Alberta, Canada, were found to have $\delta^{34}S$ values near +10‰ whereas specimens not exposed to the emissions had $\delta^{34}S$ values near 0‰ (W. Winner and H.R. Krouse, unpublished data). This suggests that about one-half of the sulphur in the former can be attributed to industrial sulphur emisisons which were directly or indirectly incorporated into vegetation of the bird's diet.

Environmental studies of higher members of the food chain have logistic advantages in the sense of integration and therefore the possibility of fewer measurements. For example, the isotopic composition of one bee should represent the average for thousands of plants in an area. Ideally, the animal should not roam over a large region. It must be emphasized that such data are only relevant to long-term phenomena. Although a short-term exposure to low levels of $H_2S$ may be lethal, it would not be measurably reflected as a change in isotopic composition because of the large mass of biological sulphur in the animal. Further, unlike plants and soil, one should not expect to observe radical variations in sulphur concentration. For example, the sulphur content of hair is about 4% as dictated by its molecular composition.

Sulphur isotope data may prove useful for studying related environmental problems. The extent to which the Se/S ratio is depressed in the environment by industrial sulphur additions should be discernable by plotting this ratio against the $\delta^{34}S$ value. Since Se deficiency incurs such problems as white muscle disease in sheep, this plot should be constructed with data from soils, grass, and animals.

The isotopic composition of metals, with the exception of lead, are difficult to determine. However, if excess metals arise in the environment from a process where sulphur emissions are involved, e.g. ore roasting, then plots of metal concentrations versus $\delta^{34}S$ values should prove informative.

The use of stable isotopes of several elements can prove very useful for complex food web analyses. A combination of stable isotopes of sulphur, carbon, and nitrogen were found to eliminate many ambiguities in tracing organic matter flow in salt marshes and estuaries (Peterson *et al.*, 1985). Although birds on Heron Island, Great Barrier Reef, had a narrow range of $\delta^{34}S$ values (+17.9 ± 0.4‰), there was a wide range in the carbon isotope composition of their feathers (Krouse and Herbert, 1988). More restricted ranges in carbon isotope composition accrued when the data were assigned to the categories: tree top dwellers, ground nesters, fish eaters, and waders.

In the case of human hair, populations can be differentiated in a plot of $\delta^{34}S$ values versus carbon isotope composition more effectively than with data from either element alone. Residents of Canberra and Brisbane, Australia, have similar $\delta^{34}S$ values (+12 to +13‰) which are markedly different from those of residents of Calgary, Canada (near 0‰). However, the residents of Canberra can be distinguished from those of Brisbane because diets of the latter are more enriched in the heavier carbon isotope $^{13}C$. On the other hand, the mean carbon isotope composition of Calgarians is not too significantly different from that of residents of Canberra (Krouse and Herbert, 1988). Clearly, extension to include stable isotope data for other elements, such as N, H, and O, would further remove ambiguities.

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