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Sect 4
25

SULPHUR EMISSIONS IN RELATION TO SULPHUR IN SOILS AND CROPS

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Sulphur inputs from the atmosphere to soils and crops can best be considered in the context of the sulphur cycle in soil, and the sulphur requirement of crops. A general view of the field was given by Whitehead (1964), and in the book edited by McLachlan (1975).

I SULPHUR IN SOIL

i) The soil sulphur cycle

The main features of the sulphur cycle are shown in Figure 1. The small amounts of sulphur in un-fertilized soils have presumably been derived from rock weathering, although natural aerial input must also have made an important contribution (Goldschmidt, 1958). Inputs to the system, whether from precipitation or from fertilizers, are normally in the form of water-soluble sulphates. Plant roots absorb $SO_4^=$ from soil solution. High $SO_4^=$ concentrations are rapidly lowered by adsorption onto clay, hydrous oxide or carbonate surfaces, by the formation of gypsum ($CaSO_4.2H_2O$) and/or leaching. Decomposition of plant and animal residues may release $SO_4^=$ in excess of microbial requirements directly to the solution, but much of the sulphur is incorporated into soil organic matter. Slow mineralization of humus by heterotrophic microbial degradation releases $SO_4^=$ or $S^=$ depending on the oxygen supply. Anaerobic environments encourage reduction to $S^=$ and formation of hydrated iron sulphide with some volatilization of H_2S, while some soil parent materials may contain pyrite, FeS_2. These sulphides are readily oxidised on exposure to air.

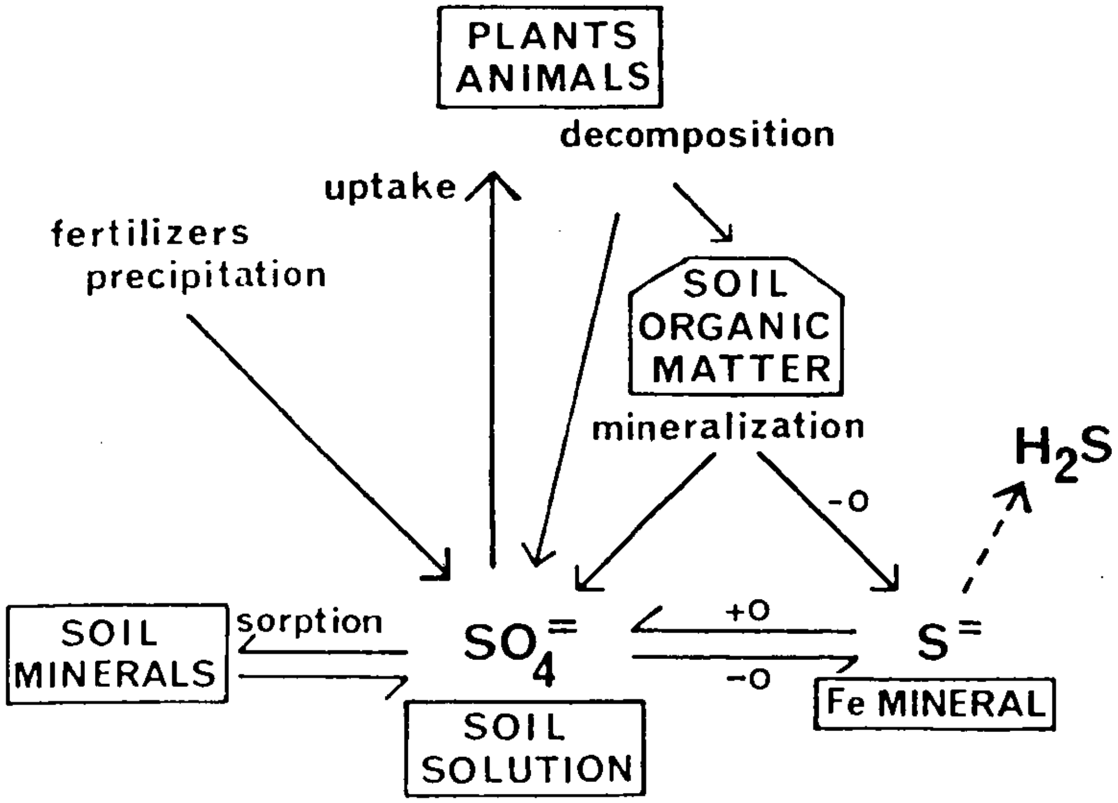

Fig. 1. The soil sulphur cycle (simplified)

ii) Nature and estimation of soil sulphur fractions

Total sulphur in soils may be estimated directly by X-ray fluorescence, or after converting it to inorganic sulphate by ignition, carbonate fusion or wet oxidation. The forms in which it occurs can be estimated approximately by selective extraction and reduction procedures (Beaton et al, 1968).

The inorganic fraction, mainly $SO_4^=$ adsorbed by clay materials, can be extracted with phosphate solutions, and will include any water soluble $SO_4^=$. Sulphide can be estimated from the H_2S produced on treating soils with dilute acid but it is normally absent in agricultural soils. The total organic S component is then obtained by difference, although the presence of inorganic sulphates insoluble in the phosphate extractant may cause errors. This organic fraction is thought to contain two main groups of compounds, organic sulphates and carbon-bonded sulphur (Freney et al, 1971: Anderson, 1975).

The organic sulphate fraction is estimated by subtracting phosphate-extractable (inorganic) $SO_4^=$ from the total sulphate, which is determined by reduction to H_2S by hydriodic acid. It consists of sulphate esters which are currently unidentified, but may be compounds such as choline sulphate, phenolic sulphates or sulphated polysaccharides. Organic S which is not reducible by hydriodic acid is assumed to be carbon-bonded sulphur. About half of this can be estimated directly by reduction to H_2S with alkaline Raney-nickel. Failure to account quantitatively for all the apparent carbon-bonded S may be because of interferences in the method or to some of the carbon-bonded S being resistant to this reduction. The carbon-bonded sulphur appears to be a stable and integral part of humus, consisting mainly of the amino acids methionine and cysteine and their derivatives.

iii) Amounts in soils

The total S in soils can be very variable, even within a small geographical area. The figures quoted by Whitehead (1964) vary from 22 to about 8,800 μg/g soil, but marine clays and tidal marsh soils may contain up to 3.5% S. Figures from some more recent papers are given in Table 1, which also indicates the approximate distribution between organic and inorganic forms. As a major part is in organic combination, there is a general increase in total S as organic matter increases (McLaren and Swift, 1977). High proportions of inorganic $SO_4^=$ are found in calcareous soils and in volcanic ash soils. Subsoils usually contain less total S than topsoils, but a higher proportion is inorganic (Probert, 1977).

iv) Microbial transformations

The decomposition of organic matter by the general heterotrophic microflora releases inorganic sulphate into solution. The main source is carbon-bonded S, and although intermediates have been identified the detailed pathways are complex (Freney, 1967). Microbial hydrolysis of sulphate esters is a further component in sulphate production (Fitzgerald, 1976). McLaren and Swift (1977) claim that protein S may pass through an ester form prior to its release as inorganic $SO_4^=$, but the intermediates were not isolated.

Several autotrophic bacteria are involved in soil sulphur transformations (Kelly, 1970). When a soil in a chemically-reducing environment is exposed to air, the oxidation of inorganic sulphides to elemental sulphur may occur by

TABLE 1

AMOUNTS, AND APPROXIMATE FRACTIONATION, OF SULPHUR IN SOME TYPICAL SOILS

Location	Total S μg/g	Percent of total S as:			References
		Inorganic SO_4	Organic		
			ester-SO_4	remainder	
Canada	80 - 700	8 - 15	31 - 72	15 - 61	Lowe (1965)
Minnesota, USA	130 - 940	3 - 5	95 - 98		Rehm and Caldwell (1968)
Iowa, USA	56 - 615	1 - 5	31 - 63	32 - 64	Tabatabai and Bremner (1974)
Australia	64 - 1400	(low)	36 - 59	41 - 64	Freney et al (1970)
Queensland	11 - 725	2 - 18	82 - 98		Probert (1977)
Nigeria	25 - 177	4 - 20	80 - 96		Broomfield (1972) Enwezor (1976)
Costa Rica volcanic ash soils	496 - 1324	48 - 92	8 - 51		Burbano and Blasco (1976)
Scottish acid soils	300 - 800	1 - 8	60 - 67	33 - 40	Scott (1976) Scott and Anderson (1976)
calcareous soils	460 - 1790	19 - 77	11 - 79		Williams, Williams and Scott (1960)
England					
mineral soils	138 - 955	2 - 22	78 - 98		Jones et al (1972)
fen peat	7405	5	95		

spontaneous chemical reactions (Breeman, 1972). The further oxidation of S to H_2SO_4 proceeds via thiosulphate and tetrathionate (Nor and Tabatabia, 1977) and is accomplished by bacteria of the genus *Thiobacillus* at lower pH values, but heterotrophic bacteria may also be involved at pH > 6.5. The reduction of $SO_4^{=}$ to H_2S in waterlogged soils is also mediated by bacteria, the genus *Desulphovibrio* being dominant. The H_2S produced may react with iron compounds to form hydrotroilite, $FeS.nH_2O$.

v) Retention of inorganic sulphate by soils

Sulphate is adsorbed by soils much less strongly than is phosphate so that there is little $SO_4^{=}$ accumulation in most soils, in contrast to phosphate where there is much and to nitrate where there is none. In calcareous soils, $SO_4^{=}$ is adsorbed by $CaCO_3$ and presumably micro-crystals of gypsum are formed. In non-calcareous soils, FeOH and AlOH groups associated with the surfaces of minerals in the clay fraction provide the main sites for adsorption. Thus $SO_4^{=}$ sorption tends to increase with clay content, but more specifically with contents of amorphous Al and Fe hydroxides. The role of haematite was shown by Sanders and Tinker (1975), and the formation of basaluminite, $Al_4(OH)_{10}SO_4$, and alunite, $KAl_3(OH)_6(SO_4)_2$, was suggested by Adams and Rawajfih (1977). Sorption maxima occur between pH 3 and 4 where positive charges on Al and Fe surface sites are greatest, and sorption reduces as pH rises until it is zero at pH 7, in the absence of $CaCO_3$ (Chao et al, 1962; Harward and Reisenauer, 1966; Scott, 1976); this corresponds approximately to the effect of pH on sulphur availability to crops (Elkins and Ensminger, 1971).

As with any chemisorption reaction, the amounts sorbed vary with concentration, so that sorption capacities determined with high solution concentrations may not be a reliable indication of field behaviour. Reported soil solution concentrations of sulphate fall within the range 0.2mM to 10mM (Bache, 1979) but 1 to 2mM are probably more typical values. These would correspond to 10 - 30μg/g of adsorbed $SO_4^{=}$ for the sulphate-retentive soils examined by Chao et al (1962) but to almost zero for most of their soils. High adsorption of inorganic sulphate by natural subsoils was reported by Probert (1977), and by subsoils on cultivated land following fertilization by Bromfield (1972).

II CROP SULPHUR REQUIREMENTS

i) Sulphur in plant nutrition : deficiency conditions

Sulphur is a major nutrient element and is needed in plants for the synthesis of the essential amino acids methionine and cysteine and thus for the formation of protein. It is also a component of some enzymes, vitamins and oils.

Sulphur is absorbed by roots from the soil solution $SO_4^{=}$, and in the main is translocated as such to sites of synthesis or organic S compounds. The latter seem to be relatively immobile in plants so that the typical chlorotic signs of S deficiency indicating a shortage of chloroplast protein occur in younger leaves.

It follows from the role of S in proteins that the ratio of N to S in plant tissues is one indicator of the sulphur status of the plant. Threshold N : S ratios between 15 and 20 have been reported for various crops, a higher ratio indicating sulphur deficiency, but the stage of growth and the type of tissue sampled may well affect the apparent threshold N : S ratio (Spencer, 1975). Terman et al (1973) consider that N : S ratios are of limited value for the maize crop.

Sulphur deficiency has been associated with the high levels of amides in plants (Bolton et al, 1976) and this has been suggested as a more reliable diagnostic technique than N : S ratios. Responses of maize to added S were obtained when tissue amide N exceeded 500 ppm (Rendig et al, 1976).

Total S contents of crops generally vary between 0.05% and 0.3% by weight of dry matter, depending on the stage of growth and the portion of the crop sampled. The higher values are typical of seeds where protein is concentrated, and lower values of structural and carbohydrate storage material. Threshold values for many crops, particularly grass and pasture legumes, have been reported (Spencer, 1975; Bolton et al, 1976; Fox, 1976; Eppendorfer, 1977; Scott and Munro, 1978).

The rather poor mobility of S in plants indicates that the time of sampling and the part of the plant sampled is likely to be even more critical for S than for other nutrients. The sulphate content of the younger leaves may therefore provide the most sensitive indication of internal S supply (Bouma, 1975). Eppendorfer (1977) found that sulphur additions increased yields of ryegrass when total $SO_4^=$ concentrations were less than 0.03% S. For maize growing in Rhodesia, $SO_4^=$ concentrations in the leaves gave the most consistent differences between normal and deficient plants (Grant and Powell, 1978).

ii) Amounts of sulphur needed by crops

As with other nutrients, the amounts of S taken up by crops depend mainly on the type of crop and its yield, while smaller variations occur between cultivars and with environmental conditions. Table 2 therefore lists only approximate S removal by a variety of crops giving the yields indicated. These yields were typical of intensive agriculture in developed countries in the early 1970s. The annual uptake of S of about 20 - 40 kg/ha is roughly double what it was 20 years ago with lower crop yields (Jordan and Ensminger, 1958) and is much greater than for subsistence agriculture in developing countries which remove 1 - 5 kg/ha. 20 kg/ha is equivalent to about 8 μg/g in the cultivated topsoil.

iii) Available sulphur in soils

The immediate source of S for crop nutrition is $SO_4^=$ in the soil solution. Depletion of the solution concentration by crop uptake initiates desorption or dissolution of surface-adsorbed $SO_4^=$. Therefore the inorganic $SO_4^=$ fraction extracted by phosphate or $NaHCO_3$ solutions is the most appropriate indicator of the ability of soils to supply S to crops (Reisenauer, 1975). In a comparison of a number of extractants for predicting the response of alfalfa in field plots to applied S on 49 soils, Hoeft et al (1973) found that 2N HOAc containing 500 mg/l P as $Ca(H_2PO_4)_2.2H_2O$ was most effective. This extractant may remove a small portion of organic S as well as adsorbed $SO_4^=$. Probert (1975) showed that phosphate-extractable $SO_4^=$ came from the same labile pool, measured with ^{35}S, that plants use, but that $NaHCO_3$ removed some S that was not available to plants.

TABLE 2

APPROXIMATE AMOUNTS OF SULPHUR REMOVED BY SOME TYPICAL CROPS, PER ANNUM

Crop	Yield	Approx. Sulphur Content	
	tonne/ha	kg/ha	kg/tonne
Timber	5	1	0.2
Sugar cane	100	50	0.5
Potatoes	40	20	0.5
Turnips	55	40	0.7
Cabbage	50	50	1.0
Grass forage	9	20	2.2
Maize	11	30	2.7
Legume forage	14	40	2.9
Cereal grains	5	20	4.0
Groundnuts	4	30	7.5
Rapeseed	2	40	20

Source: Beaton and Fox (1971); Terman (1978)

The depletion in the phosphate-extractable fraction of soils has corresponded closely with the amounts of S taken up by plants in glasshouse experiments, although a small amount of the crop uptake appears to be derived from mineralization of S from the organic fraction (Barrow, 1967; Jones et al, 1972). Soil levels of inorganic $SO_4^=$ that are adequate for crop production vary considerably. Jones et al (1972) found that 25 µgS/g was needed for maximum production of ryegrass in pots at low N levels and 45 µg/g at high N levels. These workers took care to exclude atmospheric S supplies, but one would still expect much less than this to be needed in the field. Thus McLaren (1975) suggests 12 µg S/g for herbage in S.E. Scotland, and Reisenauer (1975) suggests 4 - 8 µg/g for pasture grasses and 10 - 13 for alfalfa. Hoeft et al (1973) found 6 - 10 µg/g was an adequate soil level for alfalfa. Fox (1976) found that sugar cane in pots, supplied with adequate N, required 9 µg S/g initially, but 5 µg/g at later stages in growth; again field requirements can be expected to be lower. For maize in the field, 5 µg/g was suggested by Rehm (1976) and 8 µg/g by Kang and Osinawe (1976).

Inorganic $SO_4^=$ adsorbed by subsoils can be an important component for crop nutrition, and the amounts may not necessarily be correlated with those in surface soils. Thus Probert and Jones (1977) studying the establishment of pasture legumes in Australia found that some sites containing less than 10 µgS/g in the surface soils gave responses to applied S while others did not, but a weighted profile mean of 4 µg/g based on three layers of the profile to a depth of 60 cm distinguished responsive soils much more effectively.

III INPUTS AND LOSSES TO THE SOIL-CROP SYSTEM

i) Release from soil organic matter

Organic matter is the main S reserve in soils. It contains 1.0 to 1.5 parts by weight of S for every 10 of N, so that decomposition might be expected to release mineral S and N in approximately this ratio, but in practice less S is released than expected (Stewart, 1967). This slow decomposition is a sufficient source of S when crops also rely on natural reserves for their N supply. The annual decomposition of 1% of the organic matter in a topsoil containing 5% organic matter would release about 10 kg/ha of S, and proportional amounts for different rates of decomposition and soil organic matter contents. Many arable soils in continuous cultivation contain less than 5% organic matter. While the factors affecting S release are known (Williams, 1967), accurate estimates of release do not appear to have been made in the field, partly because of the difficulty of separating the atmospheric component.

ii) Fertilizers and manure

The main source of sulphur for crops in developed agriculture has been that added incidentally in NPK fertilizers. In the immediate post-war era most of the nitrogen was added as ammonium sulphate, most of the phosphorus as single superphosphate (a mixture of monocalcium phosphate and gypsum), and a little of the potassium as potassium sulphate. Fertilizer usage in the United Kingdom in the mid-1950s would have added an average of 80 kg S per annum to every hectare of arable and grassland (about 35 µg/g of topsoil), little more than a tenth of which would have been removed in crops. By the mid-1970s, S in high-N fertilizers was reduced to practically zero because sources of N and P containing only trace impurities of S were used. However, low-N fertilizers of the large manufacturers, and all mixtures of the small companies, still contain ammonium sulphate. Some single superphosphate and a little potassium sulphate is still used. Over this period, the estimated total sulphur content in fertilizers has dropped from 380 to 100 thousand tonnes S (personal communication, British Sulphur Corporation Ltd.). We therefore estimate that about 20 kg/ha S per annum is still being added to agricultural land in the United Kingdom, although its distribution will be uneven.

An amount of S is applied to farmland in animal manure, either mixed with straw in the traditional farmyard manure (FYM) or, more recently, applied directly as slurry. From the use of these materials in England and Wales (Cooke, 1967) and in Scotland, we estimate a mean input to the arable and grassland of the United Kingdom of about 2 kg/ha S per annum from this source. Most of this would be mineralized within a few years.

iii) Leaching losses

The massive S inputs from fertilizers and manure between 1945 and 1960 could be expected to supply crop needs for many years to come, but this assumes that the added S remains within the root zone. In fact, this is unlikely to be so and much of the added $SO_4^=$ has probably already been leached out. Thus drainage waters from the well-established Craibstone lysimeters (Hendrick and Welsh, 1938) for the 10 year period 1927 - 1936 showed an average loss of 14 kg/ha of S from plots that had been unmanured since 1914, but a loss of 54 kg/ha from plots receiving a mean of 70 kg/ha S in fertilizers and FYM. More recent results of the composition of drainage waters from Saxmundham and Woburn experimental farms (Williams, 1975) over a 5 year period are very variable because of contrasting patterns of rainfall and uncertainty over the area of land drained, but they indicate a similar continuing loss of sulphate by leaching. Sulphate applied to grassland in the spring on a sandy soil had leached out of the topsoil by the end of the growing season (McLaren, 1976). Leaching losses of 110 kg/ha were reported from lysimeters in Germany (Kuhn and Weller, 1977), and between 4 and 84 kg/ha from fresh lysimeters in Australia (Till and McCabe, 1976).

Where leaching losses occur, sulphur inputs have little permanent effect on the available sulphur status because this is determined mainly by the $SO_4^=$ retention ability of the soil (Jones et al, 1972); Rowell and Grant, 1977).

iv) Losses to the atmosphere

Simàn and Jansson (1976) quote a global estimate by Eriksson for S lost from land areas by direct exchange to the atmosphere, which is equivalent to about 7.5 kg/ha per annum. Losses occur as hydrogen sulphide, methyl mercaptan and dimethyl sulphide, and the latter has been shown to form even under aerobic conditions (Lovelock et al, 1972). Losses of 2 - 3 kg/ha were reported from soil growing crops that had received S fertilizer, but very little from unfertilized soil (Simàn and Jansson, 1976). Gaseous losses on reduction are much greater if an energy source is added to encourage microbial growth (Bloomfield, 1969). The sulphur lost in this way depends very much on local conditions, and will eventually be returned to the land surface in precipitation.

*S
H_2S
$(CH_3)_2$
mercaptan
*

v) Inputs from the atmosphere

Many estimates have recently been made of S in the atmosphere and in deposition. These values and the factors affecting them are reviewed elsewhere in this symposium. Figures collected by Whitehead (1964) showed that the annual inputs of S from precipitation varied from 1 kg/ha in rural inland areas of Australia to about 100 kg/ha in industrialized areas of the west. Recent estimates of 14 - 16 kg/ha S in bulk deposition from six forested sites (Miller and Miller, 1979) and 8 - 14 kg/ha from four agricultural sites (Scott, 1979), have been made for Scotland.

IV SULPHUR AND AGRICULTURE - THE PRESENT POSITION

i) Current soil-crop sulphur levels

Recent reports from England and Wales (Jones et al 1972) and from Scotland (McLaren, 1976; Scott and Munro, 1978) show that while soils have very variable available $SO_4^=$ contents, in general they are reasonably well supplied with this nutrient. Fertilizer experiments with oilseed rape (an S-demanding crop) on a number of sites in the United Kingdom gave no indication of S deficiency, although unspecified but significant increases in yield were obtained on two sites (Holmes and Ainsley, 1977,1978). Nevertheless it seems that sensitive crops on British soils with low humus contents and low sulphate retention ability may be at risk from sulphur deficiency (McLaren, 1975; Bolton, 1975). Recent work at the Macaulay Institute (Scott, 1979) on such soils in Scotland has shown considerable response of oats to added S at high N levels under the relatively intensive conditions of pot experiments, particularly if protected from S additions in rainfall. The results in Table 3 illustrate these effects. Forage crops growing on low-S soils in the field are probably heavily dependent on the atmosphere to meet their S needs if fertilizers containing only traces of S are used.

TABLE 3

OVEN-DRY YIELDS (g/pot) OF OATS GROWN (a) EXPOSED TO NATURAL RAINFALL AND (b) PROTECTED FROM NATURAL RAIN BUT OPEN TO THE ATMOSPHERE (From Scott, 1979)

Soil	Extractable S µg/g	Extractable S mg/pot	S addition mg/pot	(a) Rain exposed Grain	(a) Rain exposed Straw	(b) Rain protected Grain	(b) Rain protected Straw
Loamy sand			0	32.9	32.6	12.6	24.2
Fluvic-glacial gravel	4.4	29.1	10	41.3	40.3	21.3	31.4
Boyndie series			50	60.9	54.6	46.2	47.9
Loam			0	47.4	48.4	28.6	36.6
Till from lower ORS marl	7.9	43.2	10	46.4	51.2	37.5	42.2
Laurencekirk series			50	53.9	62.8	48.7	49.8
Loam			0	49.9	46.7	38.6	44.0
Till from lower ORS marl	12.5	61.8	10	53.1	48.0	45.2	45.9
Laurencekirk series			50	50.7	54.8	48.5	52.1

Basal nutrients added per pot: 1.2 g N as NO$_3$
0.5 g P and 0.7 g K as KH$_2$PO$_4$
0.2 g Mg and 0.2 g Na as chloride

Estimated S in bulk deposition over growing season: 26 mg S/pot

Sulphur deficiencies in the field have been reported from most other countries, particularly in areas where atmospheric S supplies are low, such as Australia, Western Canada, many parts of the USA, and in tropical countries (Beaton and Fox, 1971; McLachlan, 1975; Terman, 1978). In many of these areas S-containing fertilizers are in regular use.

ii) Balancing the soil-crop sulphur budget

If the trend towards low-S fertilizers continues, a reduction in S emissions to the atmosphere must eventually put stress on crop sulphur supplies in Western Europe, similar to that experienced in other parts of the world where improved agriculture is practised under low atmospheric S inputs.

The large number of ways of incorporating S into fertilizer mixtures are discussed by Bixby and Beaton (1970) and Beaton and Fox (1971). The following materials seem to be most widely used in different parts of the world:

Elemental sulphur
Ammonium sulphate (24%S)
Ammonium sulphate-nitrate (6 - 12%S)
Single superphosphate (13%S)

The extra cost of adding S to high analysis fertilizers may not be very high. For instance, in Britain the nitrogen in ammonium sulphate costs about 35% more than it does in urea, but this material has an S/N ratio of 1.15. Relatively little of it is required in a mixture to provide the S/N ratio of 0.2 - 0.3 needed by crops, so that the extra sulphur should cost below 10% of the cost of the nitrogen. Sulphur-coated urea (12 - 20%) is a slow-release source of nitrogen as well as a source of S, and thus combines two features lacking in many fertilizer mixtures. Beaton and Fox (1971) estimate that the N it contains is only 20 - 25% more expensive than in urea or ammonium nitrate, and again the small amount required would not cost much extra.

iii) Conclusions

The great variability in sulphur contents, sorption properties and organic matter turnover in soils, combined with differences in crop uptake and the vagaries of the atmospheric supply, mean that it is impossible to generalize about soil-crop sulphur requirements in relation to atmospheric emissions. It is clear that only broad trends can be predicted, and that each soil-crop-environment situation must be assessed on its own merits.

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