The Global Biogeochemical Sulphur Cycle
Edited by M. V. Ivanov and J. R. Freney

CHAPTER 3
The Sulphur Cycle in Soil

J. R. FRENEY and C. H. WILLIAMS

3.1 INTRODUCTION

The sulphur in soils was derived mainly from the weathering of plutonic rocks. Sulphides in primary minerals were released and oxidized to sulphate during the weathering process (Whitehead, 1964). Some of the sulphate found its way directly to the oceans in rivers and much of the remainder was incorporated into organic forms by plants or other living organisms or accumulated in the soil as relatively insoluble sulphate salts in semi-arid or arid climates. Some was reduced back to sulphides in anaerobic environments. Soil sulphur now exists in a great variety of forms and oxidation states, takes part in a variety of chemical and biological reactions, and interacts with the lithosphere, hydrosphere, and atmosphere either naturally or as a result of man's interference.

This chapter presents information on the natural cycle of sulphur in the soil, in particular, its reservoirs, the pathways of gains and losses, fluxes into and out of the system, and the influence of man on this cycle.

3.2 THE NATURAL CYCLE OF SULPHUR IN SOIL

3.2.1 Forms of Soil Sulphur

In well-drained, well-aerated soils most of the sulphur in the surface horizons is in organic forms; any inorganic sulphur present is almost entirely in the form of sulphates (e.g. Donald and Williams, 1954; Fedorov, 1954; Walker and Adams, 1958; Williams and Steinbergs, 1958; Williams, 1975b). Organic sulphur generally decreases with depth in the profile except in soils with organic matter accumulation in the B-horizon and in soils which have formed under conditions where erosion–deposition cycles have led to buried profiles. In contrast sulphate–sulphur commonly increases with depth in the profile (e.g. Williams, 1974) and the occurrence of gypsum in subsoil horizons of many soils is a recognized pedological feature.

Sulphides and other sulphur compounds of lower oxidation state than sulphate, including elemental sulphur, can be formed under anaerobic conditions such as occur in tidal swamps and waterlogged soils (Starkey, 1966; Bloomfield, 1969; Begheijn *et al.*, 1978).

A. Organic sulphur

Sulphur is an essential component of soil organic matter in which it is closely associated with carbon and nitrogen. Although appreciable variation occurs in the C : N : S ratio between individual soils, the mean ratios for groups of related soils are often similar (Whitehead, 1964; Williams, 1967). The similarity in C : N : S ratio for surface and subsurface soils seems to be world-wide (see Table 3.1) although, clearly, significant differences occur; these have been attributed to differences in parent material, to differences in soil-forming factors (such as climate, vegetation, leaching intensity, drainage, and temperature), and to differences in cultivation and management practice (Walker and Adams, 1958, 1959; Williams and Steinbergs, 1958; Williams *et al.*, 1960; Lowe, 1965; Bettany *et al.*, 1973; Neptune *et al.*, 1975; Biederbeck, 1978; see Tables 3.2, 3.3, 3.4 and 3.5).

Table 3.1 Relationships between carbon, nitrogen, and sulphur in soils from different regions of the world

Region	C : N : S	Reference
Africa		
Tropical Africa	<100 : 10 : 1.00	Dabin (1972)
North America		
Minnesota	122 : 10 : 1.48	Evans and Rost (1945)
Iowa	109 : 10 : 1.54	Tabatabai and Bremner (1972a,b)
Oregon	145 : 10 : 1.01	Harward *et al.* (1962)
South America		
Brazil	194 : 10 : 1.6	Neptune *et al.* (1975)
Asia		
India	80 : 10 : 0.96	Bhardwaj and Pathak (1969)
Australasia		
Eastern Australia	150 : 10 : 1.26	Williams and Steinbergs (1958)
Western Australia	118 : 10 : 1.20	Barrow (1969a)
New Zealand	120 : 10 : 1.30	Walker and Adams (1958)
Europe		
Scotland	140 : 10 : 1.40	Williams *et al.* (1960)

Table 3.2 Effect of weathering on the C:N:S ratios of soils derived from similar parent materials (graywacke or loess derived from greywacke) in New Zealand (Walker and Adams, 1959)

	C : N : S ratio
Weakly weathered soils	172 : 10 : 1.1
Moderately weathered soils	180 : 10 : 1.2
Strongly weathered soils	206 : 10 : 1.3

Table 3.3 Carbon, nitrogen, and sulphur ratios of Scottish soils derived from different parent materials (Williams *et al.*, 1960)

Parent material	C : N : S ratio
Granite	169 : 10 : 1.45
Slate	148 : 10 : 1.42
Old Red Sandstone	130 : 10 : 1.37
Basic Igneous	140 : 10 : 1.37
Calcareous	113 : 10 : 1.27
Mean	140 : 10 : 1.38

Table 3.4 Change in carbon : nitrogen : sulphur ratios in a chronosequence of New Zealand soils due to superphosphate application and pasture growth (Walker *et al.*, 1959)

Years under pasture	C : N : S ratio
0 (virgin scrub)	300 : 10 : 1.2
1.5	210 : 10 : 1.9
3	210 : 10 : 1.8
5	160 : 10 : 1.6
8	130 : 10 : 1.4
15	140 : 10 : 1.4
25	110 : 10 : 1.2

In general there seems to be less variation in the N : S ratio, both between soil groups and as a result of cultural treatment, than in the C : S ratio. Most agricultural soils have N : S ratios in the range 6.6 to 10 : 1 and C : S ratios in the range 60 to 150 : 1, and it seems reasonable to assume a mean world-wide ratio of C : N : S 130 : 10 : 1.3 for them. Wider ratios, however, seem likely in native grass- and woodland soils which may have ratios of the order of

Table 3.5 Variation in carbon : nitrogen : sulphur ratios with soil type in soils from North Queensland, Canada, and the USSR

Region	Soil type	C : N : S ratio	References
North Queensland	Solodic	133 : 10 : 1.3	Probert (1977)
	Neutral red duplex	148 : 10 : 1.3	
	Red earth	200 : 10 : 1.1	
	Yellow earth	221 : 10 : 1.2	
	Krasnozem	143 : 10 : 1.7	
	Euchrozem	171 : 10 : 1.2	
Canada	Brown chernozem	93 : 10 : 1.64	Bettany *et al.* (1973)
	Dark brown chernozem	94 : 10 : 1.54	
	Black chernozem	113 : 10 : 1.41	
	Grey black transitional	125 : 10 : 1.32	
	Grey wooded	119 : 10 : 1.56	
	Brown chernozem	120 : 10 : 1.41	Lowe (1965, 1969)
	Black chernozem	125 : 10 : 1.30	
	Grey wooded	217 : 10 : 0.80	
	Gleysol	156 : 10 : 2.00	
USSR Bashkir ASSR, Pre-Urals	Chernozems	115 : 10 : 1.15	Balyanin and Evstigneeva (1974)
Central Volga, Tatar ASSR	Greyzems (Orthic and Mollic)	109 : 10 : 1.90	Val'nikov (1970)
		106 : 10 : 2.18	
		108 : 10 : 1.77	
		103 : 10 : 1.88	
		104 : 10 : 1.75	
Central Volga, Chuvash ASSR	Chernozems	112 : 10 : 1.59	Val'nikov *et al.* (1971)
		113 : 10 : 1.44	
		115 : 10 : 1.34	
Uzbekistan	Xerosols, irrigated		Gulimov and Mukhanova (1976)
	(Haplic)	71 : 10 : 2.97	
		81 : 10 : 2.96	
		54 : 10 : 3.10	
	(Takyric)	73 : 10 : 11	
		67 : 10 : 10.5	
		76 : 10 : 10.9	

200 : 10 : 1. Peats and organic soils may have ratios intermediate between these values; approximately 160 : 10 : 1.22 (Williams and Steinbergs, 1958).

Current knowledge of the chemical nature of the organic sulphur is inadequate. Part of the organic sulphur occurs in amino-acid form. Cystine and methionine have been isolated in trace amounts from extracts of soils (Putnam and Schmidt, 1959; Paul and Schmidt, 1961) and their related compounds, cysteic acid, methionine sulphoxide, and methionine sulphone, have been identified in soil hydrolysates (Sowden, 1955, 1956, 1958; Stevenson, 1956). In two podzolic soils, for example, amino-acid sulphur has been found to account for 21–30% of the total organic sulphur (Freney *et al.*, 1972). Approximately 60% of the amino-acid sulphur was cystine sulphur.

Apart from the amino-acid sulphur, present knowledge only permits a grouping of compounds on a very broad basis which is believed to relate to the chemical bonding of the sulphur in them. This grouping is based on the reactivity of the soil organic sulphur with certain reducing agents.

These are as follows:

(1) Organic sulphur which is reduced to H_2S by hydriodic acid. This sulphur is not bonded directly to carbon and is believed to be mainly ester sulphates (Freney, 1961; Houghton and Rose, 1976).

(2) Organic sulphur which is not reduced by hydriodic acid. This sulphur is believed to be bonded directly to carbon (Freney *et al.*, 1970).

(3) Organic sulphur which is reduced to inorganic sulphide by Raney nickel. This makes up a substantial proportion of the carbon-bonded fraction and may consist mainly of sulphur in the form of amino acids (Freney *et al.*, 1975).

In general the hydriodic acid-reducible sulphur accounts for 30–70% of the organic sulphur (Williams and Steinbergs, 1959; Freney, 1961; Lowe and De Long, 1963; Cooper, 1972; Tabatabai and Bremner 1972a; Bettany *et al.*, 1973; Neptune *et al.*, 1975). In some soils the percentage of hydriodic acid reducible sulphur in the total organic sulphur remains constant with depth in the profile (Williams, 1975b), but in others the percentage increases with depth (Tabatabai and Bremner, 1972a; Williams, 1975b). Whether this increase reflects changes in the chemical composition of the organic matter or merely reflects errors in the chemical method of determination is not certain. Much of the hydriodic acid reducible sulphur is associated with the high-molecular-weight (humic acid) fraction of the organic matter (Freney *et al.*, 1969).

The Raney nickel reducible fraction forms part of the carbon-bonded fraction and probably consists mainly of the amino-acid sulphur in the soil organic matter (Freney *et al.*, 1975). This fraction has been found to account for up to 60% of the total organic sulphur (Lowe and De Long, 1963; Lowe, 1965, 1969; Freney *et al.*, 1970; Tabatabai and Bremner, 1972a; Neptune *et al.*, 1975).

The hydriodic acid reducible fraction appears to be readily hydrolysed to inorganic sulphate by acid or alkali, and consequently has been considered by some workers to represent the most labile fraction of the soil organic sulphur (see for example Biederbeck, 1978), while the fraction not reduced by either hydriodic acid or Raney nickel (which may account for up to 40% of the total organic sulphur) because of its resistance to degradation by drastic chemical treatments (Lowe, 1964, 1965) has been considered to be of little value as a source of mineralizable sulphur (Lowe, 1965). However, these chemical fractions all appear to be too broad to allow such generalizations as all three seem to be involved in cycling processes.

B. Inorganic sulphur

The main inorganic forms of sulphur are, sulphate in aerobic soils and sulphide in flooded or anaerobic soils.

Sulphate

Sulphate occurs in soils as water-soluble salts (mainly sodium, magnesium and calcium sulphates), sulphate ions adsorbed on soil colloids, or as insoluble compounds.

Water-soluble sulphate

The amounts of water-soluble sulphate vary greatly both within the soil profile itself and between soil types, depending upon the influence of factors such as leaching intensity, drainage, and the input of soluble sulphate in rain-water, irrigation water and fertilizers. Generally the surface horizons of well-drained soils contain only small amounts of soluble sulphates although under arid or poorly drained conditions high levels may accumulate. The amounts of soluble sulphate in the surface horizons of crop and pasture soils usually fluctuate seasonally (Simon-Sylvestre, 1965; Williams, 1968) as a result of the interactions of plant uptake, removal by leaching, and the impact of environmental factors on the rate of mineralization of organic sulphur. Fluctuation in amounts of soluble sulphate in subsoil horizons may also occur as a result of leaching.

Soluble sulphate often increases with depth in the profile (Williams, 1974; Probert, 1974, 1977) and in some soils, especially soils from semi-arid regions, may reach levels as high as 10%S in the deeper horizons (see Stace *et al.*, 1968). The occurrence of free gypsum in the subsoil horizons of many soils including black earths, red–brown earths, desert loams and grey, brown, and red clays is a well-known pedological feature.

Subsoil sulphate is readily available to deep-rooted species and is important in reducing the incidence of sulphur deficiency in cereal crops and deep-rooted pasture species (Lichtenwalner *et al.*, 1923; Lipsett and Williams, 1971; Gillman, 1973; Walker and Gregg, 1975).

Adsorbed Sulphate

The capacity of soils to adsorb sulphate varies greatly. In many soils, including those with pH greater than 6 and many light-textured soils, adsorption capacity is negligible or non-existent but in others, especially acid soils with moderate clay content, sulphate adsorption is very important. Adsorption capacity frequently increases with depth in the profile (see for example Table 3.6) and plays an important role in retaining sulphate against leaching and in determining the distribution of sulphate in the profile.

Sulphate adsorption is fully reversible and is concentration dependent (Kamprath *et al.*, 1956; Chao *et al.*, 1962b; Chang and Thomas, 1963). It depends greatly on the amounts and nature of the clay minerals (Ensminger, 1954; Kamprath *et al.*, 1956; Berg and Thomas, 1959; Neller, 1959) and is greatest in soils containing large amounts of aluminium and iron hydroxides, especially the former (Ensminger, 1954; Berg and Thomas, 1959; Chao *et al.*, 1962a,c, 1964; Aylmore *et al.*, 1967; Haque and Walmsley, 1973, 1974a,b). It is generally negligible at soil pH above 6 and increases with decrease in pH below this (Kamprath *et al.*, 1956; Williams and Steinbergs, 1962; Chao *et al.*, 1964) and is also influenced by the nature of the exchangeable cations (Chao *et al.*, 1963).

The amounts of adsorbed sulphate present are determined to a large degree by the sulphate adsorption capacity of the soil (Williams, 1974), especially in the subsoil horizons (see Table 3.6) and are influenced by the annual rainfall, the amounts of sulphate received in rain-water, and the amounts added in fertilizers (Barrow, 1969b; Hasan *et al.*, 1970; Toxopeus, 1970).

Adsorbed sulphate is readily available to plants and in many soils provides a major source of supply of plant available sulphur (Freney and Spencer, 1960; Fox *et al.*, 1964b; Williams and Steinbergs, 1964; Barrow, 1967a; Hasan *et al.*, 1970). The retention of sulphate by adsorption also enhances both the current and residual availability of fertilizer sulphate, especially in the case of deep-rooted species which can exploit subsoil sulphate.

Adsorbed sulphate is readily displaced by phosphate (Ensminger, 1954) so that phosphatic fertilizers tend to displace it from surface soil.

Insoluble sulphates

Of the insoluble sulphates the occurrence of sulphate as an impurity in calcium carbonate is the most important. Naturally occurring calcium carbonate normally contains sulphate as a co-precipitated or co-crystallized impurity which ranges in amount from 25 to 3000 ppmS (Williams and Steinbergs, 1962). Calcareous materials separated from soils have been found to contain between 200 and 2200 ppmS. Calcareous soils thus invariably contain insoluble sulphate in this form which in highly calcareous soils, such as calcareous

Table 3.6 The distribution of sulphur and the sulphate adsorption capacity in a krasnozem from Berry, NSW (Williams, 1974)

Soil	Depth (cm)	pH	Clay (%)	Nitrogen (%N)	Total sulphur	$CaCl_2$-soluble sulphate	Phosphate-soluble sulphate	Organic sulphur	Relative sulphate adsorption capacity
					(μgS g^{-1})				
	0–4	5.3	43	0.53	752	2	25	726	88
Berry Krasnozem Basalt 1900 mm	4–8	5.1	43	0.38	600	<1	25	576	150
	8–15	5.0	45	0.31	502	<1	27	475	231
	15–30	5.0	45	0.26	432	<1	28	404	254
	30–45	5.0	46	0.17	358	<1	66	292	316
	45–60	4.8	47	0.10	431	1	177	254	459
	60–75	4.8	50	0.04	473	4	262	211	530
	75–90	4.7	52	0.03	642	9	440	202	698
	90–105	4.7	58	0.03	786	10	612	174	904
	105–120	4.7		0.01	941	11	804	137	1100

Table 3.7 The distribution of sulphur in soil profiles (Williams, 1974)

Soil	Depth (cm)	pH	Nitrogen (%N)	Total sulphur	Water-soluble sulphate	$CaCO_3$-sulphate	Total organic sulphur	Calcium carbonate (%)
				(μgS g^{-1})				
	0–10	8.7	0.084	136	2	11	123	3.2
Griffith	10–20	8.9	0.052	116	1	31	84	10.0
Brown	20–30	8.9	0.037	116	1	43	72	14.8
Solonized soil	30–45	8.9	0.022	112	4	48	60	15.1
Aeolian deposits	45–60	8.9	0.018	110	5	56	49	17.7
390 mm	60–75	9.0	0.014	118	6	55	57	18.1
Olary, SA	0–2	8.9	0.062	120	12	3	105	<0.1
Solonetz	2–15	9.2	0.016	69	6	0	63	0
180 mm	15–30	9.0	0.027	111	5	3	103	0
	30–45	9.5	0.021	125	8	16	101	0.3
	45–60	9.1	0.021	274	98	103	73	6.9
	60–90	9.0	0.017	616	229	270	117	21.6
	90–120	9.0	0.015	709	291	259	159	23.1
	120–150	9.0	0.015	1353	958	327	68	23.1
	150–180	9.0	0.009	894	448	450	0	19.5

sands, may contribute as much as 1200 ppmS to the total. This often accounts for over 95% of the total sulphur in surface horizons (Williams and Steinbergs, 1962). In subsoil horizons this form frequently accounts for 40–50% of the total sulphur (see for example Table 3.7).

The occurrence of insoluble barium sulphate in some soils, is quite likely, but this has not been generally established. Beattie and Haldane (1958) have identified barytes in small concentrations separated from the deeper subsoil horizons of a red earth in southern New South Wales, but in most soils the total barium content suggests that barium sulphate, if present, would be too small in amount to permit positive identification.

It is also likely that sulphate could occur in soils as basic aluminium and iron sulphates. Basic aluminium sulphates have been prepared in the laboratory by precipitation of aluminium hydroxide in the presence of sulphate ions (Bassett and Goodwin, 1949; Hsu and Bates, 1964; Singh, 1967; Adams and Hajak, 1978). When such precipitations are carried out under appropriate conditions in the presence of clay minerals basaluminite $[Al_4(OH)_{10}SO_4 \cdot 5H_2O]$ or alunite $[KAl_3)OH)_6(SO_4)_2]$ are formed (Singh, 1967; Singh and Brydon, 1967, 1969; Kodama and Singh, 1972) indicating the possibility that such compounds could be formed in soil. On the basis of such studies Adams and Rawajfih (1977) have proposed that retention of sulphate by acid soils could be a consequence of the precipitation and dissolution of aluminium hydroxy sulphates and their iron analogues rather than by adsorption. Wolt and Adams (1979) have shown that basaluminite was readily available to plants when added to a soil of pH 6.5, but that alunite was unavailable. Basaluminite has been isolated from materials occurring in weathered sandstone (Hollingworth and Bannister, 1952). Jarosite $[KFe_3(OH)_6(SO_4)_2]$ and coquinbite $[Fe_2(SO_4)_3 \cdot 5H_2O]$ have been identified in separates from drained tidal marsh ('cat-clay') soils (Clark *et al.*, 1961; Fleming and Alexander, 1961; Schwertmann, 1961; Spek, 1950) although their formation and occurrence in normal well-aerated soils has not been demonstrated. It seems likely that basic aluminium (and possibly iron) sulphates could occur in normal acid soils.

Compounds of Lower Oxidation State

In well-drained, well-aerated soils most of the inorganic sulphur occurs as sulphate and the amounts occurring as compounds of lower oxidation states are negligible (Freney, 1961; Neptune *et al.*, 1975). Under anaerobic conditions—as in poorly drained or waterlogged soils and especially in tidal swamps—considerable amounts of sulphides may be formed (Wiklander and Hallgren, 1949; Harmsen *et al.* 1954; Green, 1957; Fleming and Alexander, 1961; Whitehead, 1964; Brümmer *et al.*, 1971). Sulphite, thiosulphate and even elemental sulphur may also occur (Smittenberg *et al.*, 1951), but usually sulphides make up the greater proportion of the reduced compounds (Brümmer *et al.*, 1971). In poorly drained soils, reduced forms of sulphur are largely confined to the subsoil depths below the water-table.

Sulphides formed under waterlogged conditions in paddy soils can sometimes cause toxicity problems in rice crops (Green, 1957; Vámos, 1964). Tidal marsh conditions favour the accumulation of sulphur, much of it as sulphides and polysulphides of iron (Harmsen *et al.*, 1954), often resulting in total soil sulphur contents in excess of 1%S (Hart, 1959; Fleming and Alexander, 1961; Brümmer *et al.*, 1971). Values as high as 5.5% total sulphur have been reported in some South Carolina soils (Fleming and Alexander, 1961).

Draining such soils and establishing aerobic conditions generally results in rapid oxidation of the sulphides to sulphate with the formation of sulphuric acid and severe acidification of the soil leading to pH values below 2.0 in some cases (Wiklander and Hallgren, 1949; Hart, 1959; Fleming and Alexander, 1961; Moormann, 1963; Walker, 1972; Spek, 1950). Application of lime is thus often necessary in the reclamation of these soils, but in some cases the lime requirements are so high as to make reclamation by drainage uneconomical so that in some cases reclamation attempts must exclude drainage (Moormann, 1963). In some soils some of the sulphide may persist in the soil for many years after the initial drainage and reclamation (Harmsen *et al.*, 1954). Basic iron sulphates, such as jarosites, are often formed in the drained, oxidized subsoils (see above).

Tidal marsh, or acid–sulphate soils, are especially common in tropical regions, but they also occur on a less extensive scale in temperature regions. Particularly large areas of them occur in South-East Asia (Vietnam, Thailand, Pakistan, Indonesian Sumatra and Borneo), tropical Africa and tropical South America (Moormann, 1963).

3.2.2 Geographical Distribution of Sulphur in the Soils of the World

The total sulphur content of soils varies widely and it is difficult to make any simple generalizations. In the surface horizons of mineral soils the sulphur content generally ranges from less than 20 to 2000 ppm; in peats and swamp soils concentrations of up to 5000 ppm or more are found. In saline soils values in excess of 6000 ppmS have been recorded, and in tidal marsh soils values as high as 3000–35 000 ppmS have been reported. Most agricultural soils have sulphur contents ranging from 50 to 1000 ppm in the surface 15 cm (see Table 3.8).

In subsoils wide variation again occurs, depending especially on drainage and rainfall, and values ranging from less than 10 ppm in the subsoils of siliceous sands to as high as 10 000 ppm in the deeper horizons of soils from arid regions, have been reported.

Table 3.8 Total sulphur concentrations in the surface layers of soil from different regions of the world

	Country or region	Soil	Range (μgS g^{-1})	References
Africa				
	East Africa	Forest	230–750	Hesse (1957)
	Tropical Africa		20–300	Dabin (1972)
	Ivory Coast	Tropical ferruginous	30–120	Dabin (1972)
	Malawi		35–139	Laurence *et al.* (1976)
	Nigeria		18–180	Watson (1964), Oke (1967), Bromfield (1972)
	Senegal	Saline	6400[a]	Dabin (1972)
	Tanzania		120–439	Singh *et al.* (1979)
	Zambia, Rhodesia		60–100	Grant *et al.* (1964)
America				
(a) *North*	Canada			
	Alberta	Chernozems and podzols	80–700	Lowe (1965)
	British Columbia	Grassland	286–928	Chae and Lowe (1980)
		Forest	162–2328	Chae and Lowe (1980)
		Organic	1122–30430	Chae and Lowe (1980)
		Agricultural	214–438	Chae and Lowe (1980)
	Quebec	Mineral	236–1385	Lowe and DeLong (1963)
		Organic	1620–6450	Lowe and DeLong (1963)
	Saskatchewan	Agricultural	88–760	Bettany *et al.* 1973)
	Eastern Canada	Agricultural	80–2070	Mackenzie *et al.* (1967)
	USA			
	Carolinas	Tidal marsh	3000–35000	Fleming and Alexander (1961)
	Hawaii	Volcanic ash	180–2200	Hasan *et al.* (1970)
	Iowa	Agricultural	56–618	Tabatabai and Bremner (1972a,b), Widdowson and Hanway (1974)
	Kansas	Agricultural	150–910	Swanson and Latshaw (1922)
	Minnesota	Agricultural	32–940	Evans and Rost (1945), Rehm and Caldwell (1968)
	Oklahoma	Agricultural	40–1040	Harper (1959)
	Oregon	Agricultural	82–784	Harward *et al.* (1962)

(b) *Central*				
	Nicaragua	Volcanic	496–1324	Burbano and Blasco (1975)
	West Indies		110–510	Haque and Walmsley (1973, 1974b)
(c) *South*				
	Brazil		27–398	McClung *et al.* (1959), Neptune *et al.* (1975)
	Chile	Volcanic ash	391–1104	Schalscha *et al.* (1972)
Asia	India			
	Bihar		127–2045	Ahmed and Jha (1969)
	Gujarat		42–113	Reddy and Mehta (1970)
	Punjab		130–279	Kanwar and Takkar (1964)
	Rajasthan		91–3250	Ruhal and Paliwal (1978), Shukla and Gheyi (1971)
	Uttar Pradesh		93–189	Bhardwaj and Pathak (1969), Bhan and Tripathi (1973)
	Varanasi		154–207	Tiwari and Ram (1973)
	North-east India		110–272	Virmani and Kanwar (1971)
		Rice	112–275	Venkateswarlu *et al.* (1969)
	Indonesia		200–1490	Ismunadji and Zulkarnaini (1978)
	Iraq	Saline	380–6450	Delver (1962)
	Japan	Grassland	100–3180	Tsuji (1975)
	Malaysia	Acid sulphate	1300–4700	Chow and Ng (1969)
Australasia				
	Australia	Mineral	24–1100	Freney and Williams (1980)
		Basalt[b]	106–1100	
		Acid igneous rocks[b]	24–417	
		Sedimentary or metamorphic rocks[b]	32–340	
		Transported materials[c]	40–430	
		Calcareous sands	560–1030	
		Organic	390–1860	
	New Zealand	Agricultural	240–1360	Walker and Adams (1958), Metson and Blackmore (1978)
Europe				
	Bulgaria	Grey soils, chernozems	149–372	Nikolov (1964)
	England		112–3392	Williams (1975a), Massoumi and Cornfield (1964), Whitehead (1964)

Table 3.8 (continued)

	Country or region	Soil	Range (μgS g^{-1})	References
	Finland	Mineral	130–1140	Korkman (1973)
		Organic	530–1810	Korkman (1973)
	France		56–512	Simon–Sylvestre (1969b)
	Holland	Tidal marsh	100–3600	Harmsen *et al.* (1954)
	Ireland		132–670	Gallagher (1969)
	Italy		70–4210	Olivero (1960), Galoppini (1964), Pallotta *et al.* (1964)
	Poland	Black earths	335[a]	Sklodovski (1969)
		Podzols	152[a]	
		Chernozems	283[a]	
	Romania	Brown, podzols, chernozems	160–440	Davidesco and Palovski (1965)
	Scotland		220–1790	Little (1957), Williams *et al.* (1960)
	Sweden		132–1675	Johansson (1959)
	West Germany		20–800	Buchner (1958)
Europe	USSR			
	Central Volga	Podzoluvisols[d]	145–305	Valnikov and Mishin (1974)
	Tatar ASSR	Greyzems	143–707	
		Chernozems	431–1059	
	Lower Volga	Chernozems	550–657	Ogoleva and Vershinina (1976)
	Volgograd region	Kastanozems	256–362	
		Solonetzes	385[a]	
	Central Chernozemic zone	Chernozems	756–1088	Aderikhin and Tikhova (1969)
		Greyzems	612–648	
	Uzbekistan	Zerosols	220–1030	Gulimov and Mukhanova (1976)
	Ukraine		320–465	Krupskii and Mamontova (1974)
			306–562	Krupskii *et al.* (1971)
	Zei-Burya		200–8000	Shkonde (1957)
	Chuvash	Chernozems	510–620	Valnikov *et al.* (1971)

[a]Mean value. [b]Parent material. [c]Alluvium, parna etc. [d]FAO/UNESCO World Soil Map (Kovda, 1973).

Table 3.9 The total amounts of sulphur present in the surface metre of some Australian soils

Soil group	Total sulphur (tonnes ha^{-1})
Podzolic soils	0.1–1.5
Solodic soils	0.2–1.5
Solonized brown soils	1.4–27
Red–brown earths	1–6
Krasnozems	3–10
Black earths	3–45
Alpine humus	10
Calcareous sand	35
Grey, brown, and red clays	2–25
Calcareous red earths	1.3–550
Desert loams	30–450

As indicated previously, most of the sulphur in the surface layers of well-drained agricultural soils is organic in form while that in the subsoil horizons is predominantly inorganic sulphate.

The total amount of sulphur in the surface metre of Australian soils has been estimated to range between 0.1 and over 500 tonnes S ha^{-1} depending on soil type (Table 3.9; Freney and Williams, 1980) and at least similar ranges could be expected for soils from other regions.

3.2.3 Transformations of Sulphur Compounds in Soil

Since the first weathering of the primary rocks following the cooling of the earth's crust the sulphides of primary minerals have been converted, under well-drained conditions, to sulphate by the processes of soil formation. This sulphate has been converted to many and varied compounds by micro-organisms, plants, and animals. As sulphur exists in various states of oxidation, e.g. sulphate, +6; sulphite, +4; thiosulphate, +6 and −2 or +4 and 0; elemental sulphur, 0; disulphide, −1; and sulphide, −2 (Starkey, 1966), a great diversity of transformations is possible.

These transformations are frequently represented by a cycle which depicts an oversimplified view, because in reality there is not a cycle but an interwoven network of interrelated reactions.

It is generally believed that most of the transformations of sulphur in soil are carried out by micro-organisms, although strictly chemical reactions are also possible. The microbial transformation of sulphur in soil can be grouped into four main categories: (1) immobilization, or assimilation of sulphur into organic compounds by plants or micro-organisms; (2) mineralization, i.e. decomposition of organic sulphur compounds; (3) oxidation of sulphur and inorganic sulphur compounds; (4) reduction of sulphate and incompletely oxidized inorganic compounds of sulphur. The types of transformations are affected by the oxidation state of the sulphur and the environmental conditions, in particular the availability of oxygen (Starkey, 1966).

A. Soil-forming processes

In the lithosphere both sulphide- and sulphate-containing rocks are widespread (Roy and Trudinger, 1970) although in magma and igneous rocks sulphur is believed to be present primarily in the form of sulphides (ZoBell, 1963). The most abundant metallic sulphides in igneous rocks appear to be pyrite (FeS_2), pyrrhotite (Fe_5S_6–$Fe_{16}S_{17}$), chalcopyrite ($CuFeS_2$), pentlandite ($FeNiS_3$), and bornite (Cu_5FeS_4), but sphalerite (ZnS), galena (PbS), molybdenite (MoS_2), argentite (Ag_2S), cinnabar (HgS), chalcocite (Cu_2S), and other metallic sulphides are also found in limited amounts (ZoBell, 1963).

In the absence of water and oxygen most of these metallic sulphides are stable, but in their presence the minerals can be rapidly oxidized to sulphate, producing at the same time hydrogen ions and releasing metal ions to solution (Ivanov, 1968; Ralph, 1980). This has been found to occur when sulphides are exposed naturally or as a result of man's intervention. Some elemental sulphur may also be produced during this weathering process (ZoBell, 1963; Trudinger, 1975). Chemical and electrochemical reactions appear to be involved in these degradative processes, and while some reactions are speeded up by the presence of certain organisms (Ivanov, 1968; Ralph, 1980) there seems to be some doubt about the active role of micro-organisms in the weathering of reduced sulphides (Trudinger, 1975). Although bacteria can attack sulphide minerals, the relative importance of bacterial and chemical reactions is difficult to assess.

The weathering of pyrite is believed to be one of the main natural sources of sulphuric acid. This acid can then react with other mineral sulphides to release hydrogen sulphide which may be dissolved in water, may escape to the atmosphere, or may be oxidized to sulphur and sulphuric acid.

If the dilute sulphuric acid contacts limestones calcium sulphate will be formed. This is one way in which metallic sulphates are formed in the zone of weathering. Other sulphates such as barite ($BaSO_4$), celestite ($SrSO_4$), angelsite ($PbSO_4$), astrakhanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$), kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$), kieserite ($MgSO_4 \cdot H_2O$), glauberite ($Na_2SO_4 \cdot CaSO_4$) and mirabilite ($Na_2SO_4 \cdot 10H_2O$) can be formed through the processes of recombination, base exchange, evaporation, hydration, etc. (ZoBell, 1963).

Little research has been carried out on the effect of the soil-forming factors—climate, organisms, topography, parent material, and age—on the amounts and distribution of sulphur in soil, although they probably would affect sulphur in much the same way as they affect nitrogen (Jenny, 1941).

The nature of the parent material seems to affect the type and amounts of inorganic sulphur in soils (Williams, 1974; Neptune *et al.*, 1975; Scott, 1976; Probert, 1980), but does not appear to be related to the accumulation of organic sulphur (Williams, 1974).

Barrow *et al.* (1969) found relationships between some soil-forming factors and the capacity of soils to adsorb sulphate. Soils formed from basic rocks had a greater capacity to adsorb sulphate than those formed from acidic rocks. This was probably due to the higher contents of iron oxides in the soils formed from the more basic parent materials.

Topography has been shown to have an effect on soil sulphur in certain situations—for example, Barrow and Spencer (1959) found that lateral movement of applied sulphate occurred on soils with a permeable surface layer over a less permeable subsoil on moderate slopes.

Bettany *et al.* (1973), in a study of cultivated soils from grassland and forested areas developed under semi-arid and subhumid conditions, observed the effects of climate and vegetation on the distribution of sulphur. They found that the concentration of total sulphur in the soils along a south-west to north-east transect of the agricultural region of Saskatchewan increased from the arid Chernozemic Brown zone to the Chernozemic Black zone and then decreased to the leached Grey Wooded zone. The C : N : S ratios, however, increased from 58 : 6.4 : 1 to 129 : 10.6 : 1 with the progression from the arid Chernozemic Brown soils to the leached Grey Wooded soils. These differences appear to be the result of different degrees of humification.

Scott and Anderson (1976) found no consistent effects of drainage conditions on the organic sulphur concentration or composition of Scottish soils, although the freely drained soils derived from basic igneous drift contained more organic sulphur than the poorly drained samples.

B. Microbial transformations

The four main microbial transformations that operate in soil (immobilization, mineralization, oxidation, and reduction) are mainly concerned with the internal cycling of sulphur from one pool to another, but they can also affect outputs from the pedosphere by converting immobile forms of sulphur into mobile forms and vice versa. For example, complex organic molecules can be converted to inorganic sulphate (mineralization) and leached to the hydrosphere, or gaseous sulphur compounds can be formed and lost to the atmosphere. Alternatively, inorganic sulphur can be converted into complex organic molecules (immobilization) and thus protected from leaching.

Immobilization and Mineralization

In the process of immobilization, micro-organisms absorb inorganic sulphate and convert it into organic forms for the synthesis of microbial tissue.

The opposing processes of immobilization and mineralization occur together in soil where organic sulphur mineralized is used for the synthesis of new cell material and only that sulphur not needed for synthesis is released as inorganic sulphur. If an abundant supply of carbon is available for energy then all of the inorganic sulphate in soil will be converted to organic forms, but if little carbon is available then inorganic sulphate will be released from the organic matter.

Both plants and micro-organisms are responsible for converting inorganic sulphate to organic sulphur compounds. Plants absorb inorganic sulphate and convert it to organic sulphur compounds which are then returned to the soil in plant residues (Williams and Donald, 1957). Micro-organisms working alone also incorporate significant amounts of sulphate into organic forms. Freney *et al.* (1971) found that when inorganic sulphate was added to soil there was steady incorporation of sulphur into organic matter over a period of 24 weeks and up to 50% of the 10 μgS g^{-1} soil added was converted into organic forms. Addition of glucose increased the incorporation to 82%.

By considering the carbon : sulphur ratio of the added material, attempts have been made to determine whether inorganic sulphate will be immobilized or released when organic residues are added to soil. Stotzky and Norman (1961) concluded from studies using glucose as a carbon source, that a C : S ratio of 900 or lower would provide adequate sulphur for maximum microbial activity. Therefore, sulphur should not be limiting for the decomposition of residues under natural conditions, because most plant residues have a C : S ratio less than 900.

However, other workers have found that immobilization of sulphur will occur during the decomposition of plant residues with C : S ratios well below 900 : 1 (Barrow, 1960; Massoumi and Cornfield, 1965; Stewart and Whitfield, 1965; Stewart *et al.*, 1966a). For example, Barrow (1960) found that if the C : S ratio was below 200, sulphate usually accumulated in the soil; when the ratio was above 400, sulphate was incorporated into organic matter; and when the ratio was between 200 and 400, sulphate could either be incorporated into or released from the organic matter.

This suggested that the organic sulphur was not readily available for the requirements of the micro-organisms, or that the organisms involved had a higher sulphur requirement for the decomposition of plant residues than for glucose. Stewart *et al.* (1966b), working with pure compounds, showed that micro-organisms required more sulphur for the maximum decomposition of cellulose (1 part S : 300 parts C) than for glucose (1 part S : 900 parts C) and thus the latter explanation is more likely.

It is believed that micro-organisms are mainly responsible for the conversion of organic sulphur compounds to inorganic sulphate in soil (Alexander, 1961). Any variable which affects the growth of micro-organisms should therefore affect the mineralization of sulphur. In agreement with this supposition it has been shown that temperature, moisture, pH (Chaudhry and Cornfield, 1967a,b; Williams, 1967), and availability of food supply (Barrow, 1960) all affect the mineralization reaction (Blair, 1971; Biederbeck, 1978).

Mineralization of sulphur was markedly suppressed at 10 °C, but increased with increasing temperature from 20 °C to 40 °C and then decreased again with further temperature increase (Williams, 1967).

Sulphur mineralization was considerably retarded at moisture contents appreciably below or above field capacity (Williams, 1967), and the optimum for mineralization seemed to be at 60% of the maximum water-holding capacity (Chaudhry and Cornfield, 1967a).

The amount of sulphur mineralized from untreated soils does not appear to be directly related to soil type, to carbon, nitrogen, or sulphur contents, to C : S, N : S or C : N ratios, to soil pH, or to mineralizable N (Williams, 1967; Simon-Sylvestre, 1969b; Haque and Walmsley, 1972, 1974b; Jones *et al.*, 1972; Tabatabai and Bremner, 1972b). The pattern of release of sulphur from soil organic matter also does not appear to be related to any particular soil property, but is probably due to the chemical nature of the decomposing fraction of the soil organic matter.

The mineralization of sulphur in the presence of plants is often greater than in their absence (Freney and Spencer, 1960; Barrow, 1967a; Cowling and Jones, 1970; Nicolson, 1970; Jones *et al.*, 1972) and this may be due to the greater proliferation of organisms under plants.

Cycles of wetting and drying are known to accelerate the breakdown of soil organic matter (Birch, 1960a,b) and Barrow (1961) suggests that this is a major factor involved in the increased availability of sulphur under field conditions. A cumulative effect of wetting and drying on sulphur mineralization was found by Williams (1967) in laboratory studies, but cycles of wetting and drying of planted soils in the greenhouse did not stimulate mineralization of sulphur (Freney *et al.*, 1975).

Seasonal changes in sulphate sulphur in bare soils, cultivated fields, and soils under pasture have been studied in a number of locations (Barrow, 1966, 1969a; Simon-Sylvestre, 1965, 1967a,b, 1969a, 1972; Williams, 1968). In soil under subterranean clover pasture, sulphate accumulated in the surface soil during summer immediately after senescence of the pasture. High concentrations were maintained throughout the summer–autumn period and these decreased to low values in the winter and spring. The higher values in summer probably resulted from mineralization of soil organic sulphur under favourable moisture and temperature conditions and lack of plant uptake. The low values in winter and spring were probably due to leaching, plant uptake, and low rates of mineralization at low soil temperatures (Williams, 1968). Barrow (1966), however, suggests that the high levels of mineral sulphur in summer are due to the release of sulphur from organic matter by desiccation (as had been shown by Freney, 1958; Barrow, 1961; Williams, 1967; Tabatabai and Bremner, 1972b). Williams (1968), however, believed that only small amounts of sulphate were released from under the subterranean clover pasture by this mechanism. The sulphate that accumulates in summer, whatever the mechanism responsible for its accumulation, is vulnerable to leaching or erosion by sudden summer storms.

Little information is available on the total amount of sulphur mineralized from organic matter each year and which may therefore be lost from the soil reservoir by leaching, or absorbed by plants and removed in plant or animal products. However, it is generally believed that 1–3% of the organic sulphur is converted to inorganic sulphate annually.

Oxidation of Sulphur and Inorganic Sulphur Compounds

Sulphur-oxidizing organisms

The best-known, and usually considered to be the most important group of sulphur-oxidizing microorganisms are the autotrophic bacteria belonging to the genus *Thiobacillus*. This group can use elemental sulphur and incompletely oxidized inorganic sulphur compounds as specific electron donors for the assimilation of carbon dioxide. Carbon dioxide can supply all of their carbon requirements.

There are a number of species of *Thiobacillus*. Most, including some of the better-known species, *T. thiooxidans, T. thioparus, T. denitrificans*, and *T. ferrooxidans* are obligate autotrophs, but a few are facultative autotrophs, being able to use either oxidizable sulphur or organic substances as their energy source. Although the latter group are less well known, Vitolins and Swaby (1969) found that in 288 Australian soils one species of facultative autotroph (*T. intermedius*) was more numerous than all other species of *Thiobacilli* together. Most thiobacilli are strictly aerobic, but *T. denitrificans* is a facultative aerobe, being able to use nitrate under anaerobic conditions as an electron acceptor in place of oxygen in the oxidation process (Starkey, 1966; Weir, 1975).

The *Thiobacillus* group of bacteria has been more closely studied than the heterotrophic bacteria, fungi, and actinomycetes, whose importance in the oxidation of sulphur in soil has often been overlooked. Vitolins and Swaby (1969) found that heterotrophic yeasts and several genera of heterotrophic and facultative autotrophic bacteria were far more numerous than the strict autotrophs, and could play an important role in many soils. Strict autotrophs were generally low in numbers, absent from over one-third of the soils and poor competitors when oxidizable sulphur was added to soils. They were, however, more efficient than the heterotrophs when conditions suited them (Starkey, 1966).

A host of organisms can take part in sulphur oxidation, some of which carry the process only a step or two, but the overall reaction results in the production of sulphuric acid (Tisdale and Nelson, 1966).

The mechanism of oxidation of sulphur by autotrophic bacteria is obscure despite much investigation. Several pathways have been suggested and the one given below was proposed by Vishniac and Santer (1957).

$$S^0 \rightarrow S_2O_3^{2-} \rightarrow S_4O_6^{2-} \rightarrow S_3O_6^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-} \qquad (1)$$

Factors affecting the oxidation of elemental sulphur in soil

The oxidation of elemental sulphur in soil is affected by (a) the population of micro-organisms, (b) soil moisture and aeration, (c) soil temperature, (d) soil pH, and (e) particle size.

Microbial population Soils differ markedly in their ability to oxidize sulphur and this is commonly ascribed to differences in microbial populations. The rate of oxidation of elemental sulphur in soil can often be increased markedly by addition of a suitable inoculum. Inoculation either with *Thiobacillus thiooxidans* (Li and Caldwell, 1966) or heterotrophic organisms (Vitolins and Swaby, 1969) produced a marked improvement in the initial rate of oxidation in pot and incubation studies.

Soil moisture and aeration The most rapid oxidation of elemental sulphur takes place at a moisture level near to field capacity, i.e. in the soil moisture range that is optimum for the growth of agricultural plants. The rate of oxidation is markedly depressed at very low or very high soil moisture levels (Moser and Olson, 1952).

Soil aeration is intimately associated with soil moisture and thus at high moisture levels oxygen will be limiting for sulphur oxidation (Tisdale and Nelson, 1966).

Soil temperature Microbial oxidation of sulphur will occur at temperatures as low as 4 °C, but the process is slow below 10 °C. Increasing the temperature up to 40 °C increases the rate of sulphur oxidation, but between 55 °C and 60 °C the organisms responsible for this oxidation are inactivated (Tisdale and Nelson, 1966). Optimum temperatures are not the same for all of the micro-organisms involved in the oxidation of sulphur, but temperatures between 25 °C and 40 °C are close to the optimum for most of the organisms (Weir, 1975).

pH *Thiobacillus thioparus* and *T. denitrificans* grow best at reactions close to neutrality, whereas *T. thiooxidans* and *T. ferrooxidans* develop best in the pH ranges 2.0–3.0 and 2.2–4.7, respectively (Starkey, 1966). Addition of lime to soil can increase sulphur oxidation (Fox *et al.*, 1964a), have no effect (Shedd, 1928), or inhibit oxidation (Hart, 1959). These conflicting results may be due to an effect on pH or to an indirect effect through a reduction in solubility of other elements (Weir, 1975).

Particle size Because elemental sulphur is insoluble in water it appears that its rate of oxidation would be a function of the surface area exposed to micro-organisms. Thus the smaller the particle size, the greater the surface area and the greater the rate of oxidation. This has been frequently demonstrated in incubation studies, pot and field trials (for references see Weir, 1975).

Oxidation of sulphide

The oxidation of iron sulphides in soil is more complex than the oxidation of elemental sulphur. The oxidation appears to consist of chemical as well as biological processes. The oxidations of both ferrous sulphide (FeS) and pyrite (FeS_2) appear to be basically similar.

The following sequence has been proposed for the oxidation of pyrite (Temple and Delchamps, 1953). The first step in the oxidation is non-biological and ferrous sulphate is formed (equation 2)

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4 \qquad (2)$$

This reaction is then followed by the bacterial oxidation of ferrous sulphate, a reaction which is normally carried out by *T. ferrooxidans* (equation 3)

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad (3)$$

Subsequently, ferric sulphate is reduced and pyrite is oxidized by what appears to be a strictly chemical reaction (equation 4)

$$Fe_2(SO_4)_3 + FeS_2 \rightarrow 3FeSO_4 + 2S \qquad (4)$$

Elemental sulphur so produced may then be oxidized by *T. thiooxidans* (equation 5) and the acidity generated favours the continuation of the process

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad (5)$$

The main difference between the oxidation of iron sulphide and pyrite is the very much greater resistance of the latter to attack by atmospheric oxygen (Weir, 1975).

Reduction of Sulfate

Sulphate is unstable in anaerobic environments where conditions are favourable for bacterial development. It serves as a hydrogen acceptor for sulphate-reducing bacteria and is reduced to sulphide. This dissimilatory sulphate reduction is the distinctive property of a small number of bacteria that are strict anaerobes. Two principal genera are recognized: *Desulfovibrio* and *Desulfotomaculum* (Roy and Trudinger, 1970).*

These bacteria use a variety of fermentation products and molecular hydrogen to reduce sulphate, they tolerate high concentrations of salt and hydrogen sulphide, and function best in the pH range 5.5–9.0. Nitrate or low temperature retards the reaction (Starkey, 1966; Ponnamperuma, 1972).

Whereas oxidation of sulphur results in an increase in H-ion concentration, reduction of sulphate leads to an increase in pH (equation 6)

$$Na_2SO_4 + Fe(OH)_3 + 9H \text{ (organic matter)} \rightarrow FeS + 2NaOH + 5H_2O \quad (6)$$

The sodium hydroxide produced reacts with carbon dioxide from the decomposition of organic matter to produce carbonate and bicarbonate.

Most of the sulphide that accumulates as iron sulphide in waterlogged soils, bogs, ditches, and marine sediments is produced by sulphate-reducing bacteria. Hydrogen sulphide formed in the soil reacts with iron compounds to form FeS; under certain conditions the disulphide, usually pyrite, is formed more slowly (Bloomfield, 1969).

Partly reduced sulphur, such as that in sulphite, polythionate, thiosulphate, and elemental sulphur, is reduced more readily than sulphate. Many bacteria and other micro-organisms, in addition to the sulphate-reducing bacteria, produce sulphide from these substances (Starkey, 1966).

The pathway of reduction of sulphate to sulphide by *Desulfovibrio* has been discussed recently by Kelly (1972) and Roy and Trudinger (1970) and is described by scheme 7

$$SO_4^{2-} \xrightarrow{\text{ATP}} \text{APS} \xrightarrow{2e} SO_3^{2-} \xrightarrow{6e} S^{2-} \qquad (7)$$

where APS = adenylylsulphate.

C. Nature of the gaseous sulphur compounds produced in soil and emitted to the atmosphere

Little information is available on the nature of the volatile sulphur compounds produced in soil or on the rates of emission of these volatiles to the atmosphere under natural conditions. Much of the information available comes from laboratory studies with pure organic sulphur compounds and isolated strains of micro-organisms.

---

*See footnote Chapter 1, page 23.

Hydrogen Sulphide

As hydrogen sulphide is often produced under laboratory conditions (e.g. Kondo, 1923; Almy and James, 1926; Tarr, 1933a,b; Tamiya, 1951a,b; Kadota and Ishida, 1972), and is formed in waterlogged soils as a result of protein decomposition or sulphate reduction (Vámos, 1964), many workers have assumed that hydrogen sulphide will be emitted to the atmosphere when organic matter is decomposed, or when sulphate is reduced under waterlogged conditions. Because no data on the rate of hydrogen sulphide emission to the atmosphere from land or sea surfaces were available, this emission was used to balance the flows of sulphur in models of the global sulphur cycle (Eriksson, 1963; Junge, 1963; Robinson and Robbins, 1968; Kellogg *et al.*, 1972; Friend, 1973; Cadle, 1975).

However, apart from a recent paper by Jørgensen *et al.* (1978) on hydrogen sulphide emission from coastal environments there does not appear to be any evidence for significant emission of hydrogen sulphide from soil in a natural environment (Bremner and Steele, 1978). No trace of this gas could be detected in the atmosphere above soil when inorganic and organic sulphur compounds, plant materials, animal manures, and sewage sludges were incubated in aerobic or waterlogged soils (Lewis and Papavizas, 1970; Banwart and Bremner, 1975a,b, 1976a,b). Even when sulphate and sulphide were added to a sandy soil, with a low capacity for sorption of hydrogen sulphide, under waterlogged conditions, no emission of hydrogen sulphide was detected during subsequent incubation (Bremner, 1977). Harter and McLean (1965) were also unable to detect hydrogen sulphide emission from a waterlogged soil which produced large quantities of sulphide ($>2000\ \mu g\ g^{-1}$ soil).

On the other hand, some publications indicate that hydrogen sulphide has been emitted during incubation studies with soil under aerobic or anaerobic conditions (Bloomfield, 1969; Swaby and Fedel, 1973; Sachdev and Chhabra, 1974; Siman and Jansson 1976a). However, these publications show either that the emission of hydrogen sulphide was extremely small, or that the results are of doubtful validity because of the analytical technique used to detect hydrogen sulphide or because the incubation conditions were atypical of natural environments (Bremner and Steele, 1978).

In general it appears that soils have a high capacity to sorb hydrogen sulphide (Smith *et al.*, 1973) and to hold hydrogen sulphide formed *in situ* from reduction of sulphate or decomposition of organic residues; this may be due to reaction of hydrogen sulphide with cations to form metallic sulphides. However, there may be certain situations where soils are high in sulphate and available organic matter but deficient in the cations required for the precipitation of metallic sulphides when the soils become waterlogged. Hydrogen sulphide may be emitted under those conditions or when organic residues are allowed to decompose on the surfaces of soils (Bremner and Steele, 1978).

Under certain conditions it appears that even living plants can emit hydrogen sulphide directly to the atmosphere. Wilson *et al.* (1978) found that hydrogen sulphide was emitted from squash, pumpkin, cantaloupe, corn, soybean, and cotton. The emission occurred after the roots were treated with sulphate, was higher if the roots were mechanically injured, was completely light-dependent and increased with light intensity. The maximum rates of emission observed were ~8 nmol $\text{min}^{-1}\,\text{g}^{-1}$ fresh weight. Spálený (1977) found that Norway spruce (*Picea abres* (L) Karsten) seedlings treated with 5 g potassium sulphate per day for 7 days exhaled 2.22 μg of hydrogen sulphide per hour per kg dry weight of needles when illuminated. No hydrogen sulphide was emitted when the seedlings were kept in darkness. Other plants such as tomato, beans, and grapevines have been reported to exhale hydrogen sulphide after treatment with sulphur dioxide (de Cormis, 1968a,b).

In summary then, there seems to be very little evidence in the literature to support the allocation by Eriksson (1963), Junge (1963), Robinson and Robbins (1968), Kellogg *et al.* (1972) and Friend (1973) of high flux rates for the emission of hydrogen sulphide and land surfaces.

Volatile Organic Compounds of Sulphur

Micro-organisms isolated from a variety of habitats and cultured under artificial conditions produce a variety of volatile organic sulphur compounds, including carbon disulphide, carbonyl sulphide, and a number of homologous sulphides and disulphides (Kadota and Ishida, 1972; Bremner and Steele, 1978).

A much smaller number of compounds has so far been isolated from soils or during the decomposition of organic compounds, plant materials, animal manures, and sewage sludges. The volatiles isolated and identified in significant quantities are carbon disulphide, carbonyl sulphide, methyl mercaptan, dimethyl sulphide, and dimethyl disulphide; however, the total amounts released from soils or decomposing organic materials under aerobic or waterlogged conditions appear to be very small (Barjac, 1952; Greenwood and Lees, 1956; Frederick *et al.*, 1957; Takai and Asami, 1962; Lewis and Papavizas, 1970; Banwart and Bremner, 1975a,b; 1976a,b; Bremner and Steele, 1978).

Carbon disulphide was produced from the decomposition of the sulphur-containing amino acids, cysteine and cystine; these two compounds may be the source of this gas in soils and manures (Banwart and Bremner, 1975b). When lanthionine and djenkolic acid were decomposed in soil carbonyl sulphide was produced (Banwart and Bremner, 1975b); this gas was also found when thiocyanates and isothiocyanates were metabolized (Bremner, 1977). Methyl mercaptan, dimethyl sulphide, and dimethyl disulphide seem to be produced principally from the decomposition of methionine and related compounds or from sulphonium compounds (Frederick *et al.*, 1957; Kadota and Ishida, 1972; Banwart and Bremner, 1975b; Salsbury and Merricks, 1975; Bremner, 1977).

Lovelock *et al.* (1972) found that living leaves of cotton, oak, spruce, and pine trees emitted from 2 to 43 × 10^{-12} g of dimethyl sulphide per g of oven-dried tissue per hour, while decaying leaves from the same plants emitted 10 to 100 times as much. Soils also exhaled dimethyl sulphide when incubated in air and the emission rates varied from 21 to 84 × 10^{-12} g^{-1} $soil^{-1}$ (Lovelock *et al.*, 1972). Hitchcock (1977) used these figures, together with estimates of the global mass of plant materials and soils, to calculate the global production of dimethyl sulphide from these sources. She calculated that fresh leaves, senescent leaves, and soils could emit 0.01, 0.53 and 1.5 to 4.9 TgS $year^{-1}$, respectively. Hitchcock (1977) concluded that soil was a major source of dimethyl sulphide and that the global production of this gas was unlikely to exceed 5 TgS $year^{-1}$.

Aneja *et al.* (1979) estimated the emission rates of carbon disulphide and carbonyl sulphide emanating from salt marshes in North Carolina. Emission rates for carbon disulphide over the mud flat zone were less than 0.05 gS m^{-2} $year^{-1}$, and over a clipped marsh grass (*Spartina alterniflora*) area averaged 0.13 gS m^{-2} $year^{-1}$ for all measurements, suggesting that carbon disulphide emanated from *S. alterniflora*. They calculated the global emission from marshes to be 0.07 TgS $year^{-1}$, assuming that all marshes emit uniformly and that the only species present was *S. alterniflora*. This they calculated to be <0.07% of the total biogenic emission of sulphur. In the same study it was found that carbonyl sulphide emission was not associated with the presence of marsh grass; the mean emissions of this gas from mud-flats and from the clipped marsh grass were 0.05 and 0.03 gS m^{-2} $year^{-1}$, respectively (Aneja *et al.*, 1979). They calculated that carbonyl sulphide emission from marshlands was responsible for only a small portion of the total biogenic sulphur emission.

D. Adsorption of sulphur compounds from the atmosphere by soil and their subsequent metabolism

Sulphur can be removed from the atmosphere by various mechanisms of which dry deposition on the soil surface and absorption by vegetation, soil, and stone are important. Sorption of certain atmospheric compounds by soil and their subsequent metabolism is believed to be an important mechanism for the removal of gaseous pollutants (Rasmussen *et al.*, 1975).

Sulphur Dioxide

Numerous workers have shown that soils can absorb sulphur dioxide (e.g. Vandecaveye *et al.*, 1936; Alway *et al.*, 1937; Fuhr *et al.*, 1948; Terraglio and

Manganelli, 1966; Seim, 1970; Abeles *et al.*, 1971; Payrissat and Beilke, 1975; Yee *et al.*, 1975) and it is now known that soils have the capacity rapidly to remove significant amounts of sulphur dioxide from the overlying gas (e.g. Smith *et al.*, 1973; Bremner and Banwart, 1976; Ghiorse and Alexander, 1976).

Sulphur dioxide was more rapidly absorbed by moist soils than by dry soils (Terraglio and Manganelli, 1966; Smith *et al.*, 1973) and there are reports that soil properties such as pH, texture, specific surface, organic matter content, ion-exchange capacity, and porosity affect the degree of absorption (Nakayama and Scott, 1962; Terraglio and Manganelli, 1966; Faller, 1968; Seim, 1970; Smith *et al.*, 1973; Yee *et al.*, 1975; Lockyer *et al.*, 1978).

There are conflicting reports on the role of micro-organisms in the sorption of sulphur dioxide by soil; Abeles *et al.* (1971) found that autoclaved soils sorbed less sulphur dioxide than untreated soils, but Ghiorse and Alexander (1976) and Smith *et al.* (1973) observed that steam sterilization had no effect on the rate of sorption, and Smith *et al.* (1973) found no effect on the amount sorbed. Microflora may, however, be involved in the removal of the sorption products.

Few estimates have been made on the amounts of sulphur dioxide that are absorbed by soils; generally deposition velocities for soils, defined as

$$v_g(\text{cm sec}^{-1}) = \frac{\text{SO}_2 \text{ deposited } (\mu\text{g cm}^{-2}\,\text{sec}^{-1})}{\text{SO}_2 \text{ concentration } (\mu\text{g cm}^{-3})}$$

have been found to be in the range 0.2–0.7 cm sec^{-1} (e.g. Spedding, 1969b; Owers and Powell, 1974; Garland, 1977; Lockyer *et al.*, 1978), and Smith *et al.* (1973) found that air-dry soils could absorb 1.1–15.3 and wet soils 9.3–66.8 $\text{mgSO}_2\,\text{g}^{-1}$ soil. Eriksson (1963) estimated that 25 TgS year^{-1} was absorbed by soil globally, while Junge (1963), Robinson and Robbins (1968), Kellogg *et al.* (1972), and Friend (1973) estimated dry deposition on land surfaces to be 10–20 TgS year^{-1}.

It has been known for many years that plants can sorb sulphur dioxide directly from the atmosphere and use it for their metabolism (e.g. Thomas and Hill, 1937; Thomas *et al.*, 1944; Fried, 1948; Olsen, 1957). Sulphur dioxide uptake by plants has been assessed by a number of different methods including micrometeorological techniques (e.g. Garland, 1977; Fowler, 1978; Galbally *et al.*, 1979), the use of $^{35}\text{SO}_2$ (Owers and Powell, 1974; Garland and Branson, 1977) and sulphur isotope abundances (Belot *et al.*, 1974; Krouse, 1977).

Surface wetness has a major influence on dry deposition rates (Fowler and Unsworth, 1974) and there appear to be diurnal and seasonal variations in uptake by grasses (Shepherd, 1974; Fowler, 1976, 1978). Uptake of sulphur dioxide occurs through the stomata, although there is evidence for some uptake on or through the cuticle (Belot *et al*., 1974; Fowler, 1976, 1978; Garland and Branson, 1977; Garland, 1978).

Deposition velocities for grasses have been found to be in the range 0.3–1.2 cm sec^{-1}, soybeans 1.25 and forests 0.1–2 cm sec^{-1} (Fowler and Unsworth, 1974; Garland, 1977; Garland and Branson, 1977; Garland, 1978; Galbally *et al.*, 1979).

Fowler (1978) has estimated the dry deposition of sulphur dioxide on the agricultural area of Britain to be ~0.5 TgS $year^{-1}$, of which 0.14 TgS is deposited in soil in winter and the remainder is deposited on the vegetation. Galbally (1980) calculated the dry deposition of sulphur dioxide over Australia by dividing the continent into two areas; a desert and semi-arid region and a temperate and wet tropical region with deposition velocities of ~0.1 and 0.85 cm sec^{-1}, respectively. Assuming that the background concentration of sulphur dioxide was in the range 0.5–2 $\mu gSO_2\ m^{-3}$ he estimated the dry deposition to be between 0.3 and 1 TgS $year^{-1}$. Estimates of the global uptake of sulphur dioxide by vegetation vary from 15 to 75 TgS $year^{-1}$ (Eriksson, 1963; Junge, 1963; Robinson and Robbins, 1968; Kellogg *et al.*, 1972; Friend, 1973).

Sulphur dioxide can also be removed from the atmosphere by reaction with stone and an estimate of the global removal by this process is 4.5 TgS $year^{-1}$ (Rasmussen *et al.*, 1975).

Reduced Sulphur Compounds

Soils also have the capacity to sorb hydrogen sulphide and volatile organic sulphur compounds such as methyl mercaptan, dimethyl sulphide, dimethyl disulphide, carbonyl sulphide and carbon disulphide (Fuhr *et al.*, 1948; Carlson and Gumerman, 1966; Carlson and Leiser, 1966; Kanivets, 1970; Smith *et al.*, 1973; Bremner and Banwart, 1976).

Both air-dry and moist soils will sorb dimethyl sulphide, dimethyl disulphide, carbonyl sulphide and carbon disulphide, but moist soils sorb larger amounts of these compounds. The capacity of soils for sorption of these gases is much smaller than their capacity for the sorption of sulphur dioxide, hydrogen sulphide, or methyl mercaptan (Bremner and Banwart, 1976; Bremner and Steele, 1978).

Bremner and Banwart (1976) working with sealed systems found that four soils from Iowa absorbed 23–442 μg dimethyl sulphide, 101–306 μg dimethyl disulphide, 14–104 μg carbon disulphide, and 72–2340 μg carbonyl sulphide per gram of soil from the gas phase initially containing 500 ppm of the gas. Smith *et al.* (1973) using the same system and 100 ppm of gas found that the same four soils absorbed 40.6–65.2 mg hydrogen sulphide and 18–321 mg of methyl mercaptan per gram of soil.

Micro-organisms are partly responsible for the sorption of dimethyl sulphide, dimethyl disulphide, carbonyl sulphide, and carbon disulphide from moist soils (Bremner and Banwart, 1976), but do not appear to be involved in the sorption of hydrogen sulphide or methyl mercaptan by soils (Smith *et al.*, 1973). When carbonyl sulphide is absorbed by moist soils, carbon disulphide is released in small amounts, and this appears to be due to the metabolism of carbonyl sulphide by micro-organisms (Bremner and Banwart, 1976).

Little information seems to be available for the uptake of reduced sulphur compounds by vegetation; however, Granat *et al.* (1976) suggests that uptake of hydrogen sulphide and dimethyl sulphide may be much slower than the uptake of sulphur dioxide because of the lower solubility of these gases in water.

3.2.4 Leaching, Runoff, and Erosion of Sulphur Compounds from Unamended Soil

Sulphur can be lost from soils by leaching with rain or irrigation water; the amount lost varies widely depending on the chemical and physical form of the sulphur, soil type, and properties, fertilization practices, cropping system, amount and distribution of rainfall, and temperature (see Harward and Reisenauer, 1966; Tisdale and Nelson, 1966; Jones and Woodmansee, 1979).

In most agricultural soils the bulk of the sulphur is present in complex organic molecules and there is no evidence for appreciable leaching of this organic sulphur. Sulphate appears to be the usual form leached and thus any factor which affects the transformation and movement of sulphate will affect the rate and amount of sulphur leached. Thus, reactions such as mineralization of organic sulphur, immobilization of sulphate, oxidation of sulphide, reduction of sulphate (section 3.2.3A), and adsorption of sulphate are important in promoting or preventing leaching.

Sulphate sorption capacity varies from soil to soil and also from layer to layer within the soil profile. It is affected by pH (retention increases as pH decreases), type of clay mineral (kaolinite type minerals retain more sulphate than the montmorillonite group; aluminium and iron hydrous oxides absorb strongly), and associated cations, and is concentration dependent (Harward and Reisenauer, 1966; Barrow, 1967b, 1975; Walker and Gregg, 1975).

More sulphur can be lost by leaching from bare soil than from soil under grass (Dutil and Ballip, 1979). Losses are reduced by cropping and are less with deep-rooted and perennial crops than with annual crops (Gachon, 1972).

Leaching losses have been determined by lysimeter studies and have been shown to vary from very small amounts to more than 310 kgS ha^{-1} year^{-1} (see Harward and Reisenauer, 1966; Baker *et al.*, 1975). For example, a study in New Zealand showed that, after the initial losses due to cultivation when the lysimeters were filled, the sulphur content of the soil actually increased rather than decreased (Muller, 1975). On the other hand, Kuhn and Weller (1977), working with two unfertilized mineral soils in Germany, found leaching losses of the order of 110 kgS ha^{-1} $year^{-1}$. Leaching there occurred mainly in the winter and to a lesser extent in the spring. A lysimeter study on unfertilized soil in Norway showed that the annual loss of sulphur in drainage water (30–40 kg ha^{-1}) was up to seven times higher than that supplied in rainwater; it was suggested that the balance came from sulphur absorbed from the air, weathering of inorganic sulphur, and mineralization of organic sulphur in soil (Ødelien, 1965).

Apart from the lysimeter studies, very few field studies on sulphate movement as a result of mineralization of soil organic matter have been made. Bromfield (1972) showed that mineralized sulphur moved down the soil profile but accumulated at depth.

Because leaching of sulphur varies so greatly with amount and distribution of rain, vegetation, soil type, etc., it is very difficult to estimate leaching losses from unamended soils on a global basis.

The extent of water erosion, or runoff, depends on the climate, topography, vegetation, and soil type (Baver, 1956) and it is well established that man's activities accelerate erosion. The average loss of soil due to erosion has been estimated at 22.4 tonnes ha^{-1} $year^{-1}$ (Rhoades and Bernstein, 1971). Organic matter losses have been estimated to range from 378 to 1290 kg ha^{-1} (Barrows and Kilmer, 1963), while soluble sulphur and total sulphur have been found to vary from 12.9 to 29.7 and 47 to 113 kgS ha^{-1} $year^{-1}$, respectively (Stallings, 1957; Barrows and Kilmer, 1963).

Loss of sulphur due to wind erosion is discussed in Chapter 4.

3.3 THE EFFECT OF MAN ON THE SULPHUR CYCLE IN SOIL

3.3.1 Agricultural Practices and the Cycling of Soil Sulphur

Bringing native forest, bush or grassland under cultivation leads to appreciable loss of soil organic matter through mineralization processes (Allison, 1973). Such losses are invariably accompanied by corresponding losses of soil organic sulphur (Harper, 1959; Williams and Lipsett, 1961; Bettany *et al.*, 1973; McLaren and Swift, 1977).

These losses sometimes occur without appreciable change in the C : N : S ratio of the soil organic matter (Harper, 1959; Williams and Lipsett, 1961), but in some soils substantial changes in the ratio occur (McLaren and Swift, 1977; Bettany *et al.*, 1980). Following the clearing of native scrub—or grassland—and establishing clover pasture, large changes can occur in the C : S ratio of soils (Walker *et al.*, 1959; Jackman, 1964; Bettany *et al.*, 1979, 1980). In most cases, however, some changes in the chemical nature of the organic sulphur clearly occur since most of the mineralized sulphur appears to be derived from the carbon-bonded sulphur (Freney *et al.*, 1975; McLachlan and De Marco, 1975; McLaren and Swift, 1977).

A. Effect of fertilizer additions, and pasture production or cropping practices on soil sulphur

The losses in sulphur from surface horizons during cultivation generally take place whether or not fertilizer sulphur is applied. Table 3.10 summarizes a number of reports showing changes in soil sulphur as a result of cropping. In all cases a decrease in total soil sulphur had occurred even although, in some cases, fertilizer sulphur considerably in excess of that removed in crop produce had been applied. Sears *et al.* (1965) found that losses of sulphur from soil kept continuously under fallow exceeded the losses occurring under cropping and pasture. It is thus apparent that the losses of sulphur from the soil under cropping are largely due to the mineralization of organic sulphur to sulphate. Part of this may be recovered by the crop, but the remainder is leached to deeper horizons of the soil profile. In many cases this sulphate may be retained in the subsoil horizons by adsorption and can be recovered, at least in part, by deep-rooted species (Broomfield, 1972).

Effects of Liming

Addition of liming materials to soils may increase the availability of sulphur to plants and its potential for leaching in three ways.

1. It stimulates the rate of mineralization of soil organic matter, and consequently the rate of mineralization of organic sulphur (Freney *et al.*, 1962; Williams and Steinbergs, 1964; Williams, 1967; Probert, 1976).
2. By raising the soil pH it releases adsorbed sulphate from exchange sites, thereby favouring leaching and plant uptake.
3. Liming materials frequently contain insoluble sulphates which can be released to soluble forms after reaction of the liming materials with the soil (Williams and Steinbergs, 1964).

Liming then enhances the uptake of sulphur by plants (Williams and Steinbergs, 1964), but it may also enhance the leaching of sulphate and could be expected to increase the rate of depletion of sulphur in the surface soil under cultivated systems.

Effect of Pasture

Organic matter frequently accumulates in the soil under permanent pasture until eventually an equilibrium level is reached (e.g. Richardson, 1938). There is thus a concurrent accumulation of organic sulphur. Accumulation of

Table 3.10 Loss of sulphur from the cultivated layer of soils under continuous cropping

Country	Virgin soil (μgS g^{-1})	Cropped soil (μgS g^{-1})	Average period of cropping (years)	Estimated soil sulphur loss (kgS ha^{-1})	Probable addition in fertilizers (kgS ha^{-1})	Estimated soil and fertilizer loss (kgS ha^{-1})	Estimated removal in crops (kgS ha^{-1})	References
Australia	128	92	50–60	50	90	140	35	Williams and Lipsett (1961)
Canada	497	308	65	345	Nil	345	230	Bettany *et al.* (1973)
USA								
Oklahoma Kansas	197	139	*a*	110	*a*	*a*	*a*	Harper (1959)
Humid regions	350	260	39	180	*a*	*a*	140	Swanson and Latshaw (1922)
Subhumid regions	440	420	32	40	*a*	*a*	110	Swanson and Latshaw (1922)
Semi-arid regions	280	250	25	60	*a*	*a*	85	Swanson and Latshaw (1922)
England	410	330	100	150	600	750	*a*	Cowling and Jones (1970)
Scotland	597	351	*a*	460	*a*	*a*	*a*	McLaren and Swift (1977)
New Zealand	340	307	3	60	Nil	60	90	Sears *et al.* (1965)
	340	318	3	30	250	280	190	Sears *et al.* (1965)

[a] Not known.

organic sulphur is to be expected, especially in soils from which organic matter has been depleted by extensive cropping, and in soils naturally low in organic matter when improved pastures are established under regimes of regular fertilizer application. Substantial increases in the total sulphur content of the surface layers of soils treated in this way have been recorded (Donald and Williams, 1954; Hingston, 1959; Barrow, 1969a; Walker and Adams, 1959; Watson, 1969). An example of the accumulation of sulphur in soils under permanent subterranean clover pasture is given in Fig. 3.1.

In most well-drained soils nearly all of the sulphur in the surface horizons is accumulated in organic forms (Donald and Williams, 1954) and indeed, in many cases, that portion of the total sulphur input converted to organic forms is permanently retained, the rest being lost by leaching as sulphate. The accumulation of sulphur in the surface layers of soil under permanent pasture is thus influenced by several factors which include the rate of sulphur input, the intensity of leaching, level of pasture production, and the soil and environmental factors governing the rate of accumulation of soil organic mat-

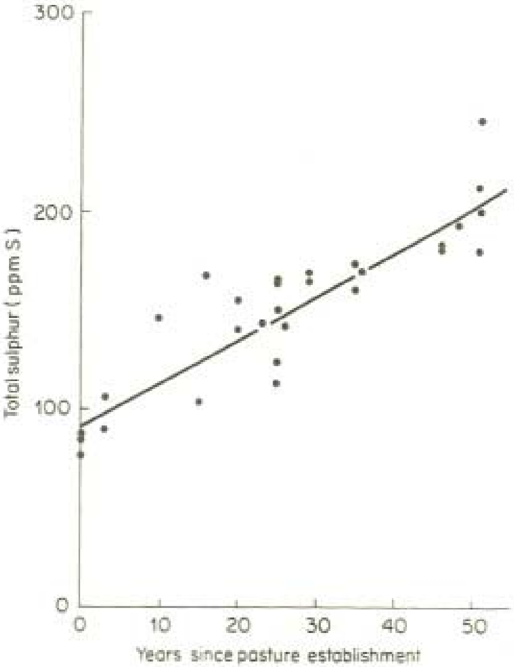

Fig. 3.1 The accumulation of sulphur in the surface 10 cm of soil under permanent subterranean clover pasture top-dressed regularly with single superphosphate ($S = 92.3 + 2.20t$; S = total sulphur in $\mu gS\ g^{-1}$ soil, and t = time in years)

ter. Fertilizer and environmental sulphate leached from the surface layers is frequently not lost from the profile but is retained by adsorption in the subsoil horizons and can sometimes be utilized by deep-rooted species (Walker and Gregg, 1975).

In Australian pasture soils the total carbon-bonded sulphur fraction was found to account for 84% of the organic sulphur accumulated under subterranean clover pastures (Freney *et al.*, 1975). Of this only 42% was reducible by Raney nickel. Similarly, when organic sulphur was lost from red–brown earths under a cereal cropping system, 80% of the loss was from the carbon-bonded fraction (McLachlan and De Marco, 1975). Similar changes have been found by McLaren and Swift (1977). In incubation and pot culture studies (Freney *et al.*, 1975) it was found that all three fractions contributed available sulphur for plant uptake. Approximately 60% of the sulphur taken up by sorghum plants was derived from the carbon-bonded fraction and involved both Raney nickel and non-reducible fractions.

Leaching of Fertilizer Sulphur

As pointed out earlier, the amount of sulphur lost by leaching will vary depending on the climate, soil type, agricultural practice, fertilizer rate and form, sulphate sorption capacity of the soil, immobilization potential, etc. (e.g. Jones *et al.*, 1968; Rhue and Kamprath, 1973; Gregg and Goh, 1978). In some soils, especially under pasture, it is apparent that little leaching of sulphur occurs as most of the fertilizer sulphur can be accounted for in the surface organic matter (Donald and Williams, 1954). Studies using radioactive sulphur also showed that there was little leaching of the applied sulphate (<0.1 kg ha^{-1} year^{-1}) from grazed pastures in spite of apparent total sulphur losses of 25 kg ha^{-1} year^{-1} (Till and McCabe, 1976). At low rates of fertilization very little sulphur seems to be leached beyond the plant root zone (May *et al.*, 1968; Till and May, 1971).

However, other work using lysimeters with different soil types and pastures and much larger amounts of applied sulphur demonstrated that considerable sulphur could be leached (Jones *et al.*, 1968; McKell and Williams, 1960).

The same principles concerning leaching apply to cropped soils as well as pasture soils, with large losses of fertilizer sulphur occurring in some soils sown to wheat and oats (Jones *et al.*, 1971; Rhue and Kamprath, 1973), and small losses occurring in other situations (Bromfield, 1972).

Irrigated Agriculture

Irrigation and use of fertilizer on semi-arid and arid soils for the production of pastures or crops can have a marked effect on the quality of the drainage water percolating through or draining off the land. For example, Sylvester and Seabloom (1962) compared the sulphate content of the applied irrigation water with that of the surface and subsurface drainage water and found that the sulphate concentration had increased markedly, from 5.4 to 37 and 39 mg litre^{-1}, respectively. They estimated that 280 kg of sulphate per hectare per year were lost from the irrigated Yakima River valley in Washington (Sylvester and Seabloom, 1962; 1963). Similarly in the San Joaquin valley in California the subsurface drainage water had a concentration of 3600 mg of sulphate per litre compared with 170 for the surface drainage water (Walton, 1966).

Some of the sulphur in the drainage waters comes from sulphur applied in the fertilizer or absorbed from the atmosphere and some is dissolved from gypsum previously precipitated in the soil profile (Doneen, 1966).

B. Effect of grazing animals on the sulphur cycle

The increasing world population and rising standards of living in many parts of the world has brought about an increase in the consumption of animals products. Consequently, there have been large increases in animal numbers, animal excreta, and sulphur removal in animal products. The production of greater numbers of animals has required an increase in land sown to forage crops and because of their greater requirement for sulphur a greater use of sulphur fertilizers (Saalbach, 1965/66; Spencer, 1975). These various interactions have increased the amounts and rates of sulphur cycling within the soil–plant–animal system and the potential for increased losses from that system by gaseous loss to the atmosphere or by runoff and leaching to the hydrosphere. The problems, such as degradation of vegetation, soil erosion, and the depletion or silting up of water resources, which arise when native pastures are over-grazed have been well documented (Till, 1980).

Sulphur fertilization improves not only the quantity of pasture available to the grazing animal but also the quality of that feed; for example improvement in the protein quality and vitamin A content of alfalfa, and increases in the protein content of legumes and grasses have been recorded (Tisdale *et al.*, 1950; Fox *et al.*, 1964a; Saalbach, 1966; Blenkhorn, 1974) as a result of sulphur addition. Increases in the dietary intake of sulphur by animals has led to increases in wool growth and quality, meat production (e.g. Rendig and Weir, 1957; Wagnon *et al.*, 1958; Pund, 1969; Kennedy and Siebert, 1972; Morozov, 1972; Odynets *et al.*, 1972; Stepanov and Yakimchuk, 1973; Doyle and Moir, 1979), and milk production by lactating dairy cows (Bouchard and Conrad, 1973a,b).

When plant material or feed supplements are ingested by stock a small amount of sulphur is retained by the animal, but the bulk of the sulphur is returned to the soil in urine or faeces (Walker, 1957; Barrow, 1967c). Sulphur losses through the skin of sweating animals such as man and cattle may be important, while additional losses of organic sulphur must occur during the shedding of epithelial cells of the skin of all animals (Doyle and Moir, 1979). Possible losses during respiration or through the skin of sheep are not considered to be important, but considerable sulphur as hydrogen sulphide may be lost by belching during supplemental feeding (Doyle and Moir, 1979).

The proportion of sulphur excreted in the faeces or urine varies and seems to be related to the metabolic fate of the dietary or supplemental sulphur (Doyle and Moir, 1979). The proportion of the total sulphur excreted in the urine varies from 6 to ~90% (Warth and Krishnan, 1935; Walker, 1957; Barrow and Lambourne, 1962; Till, 1975; Doyle and Moir, 1979) with the proportion for a non-deficient pasture being about 50–60%. Work with ruminants has shown that the excretion of sulphur increases as the intake of sulphur increases (Bird, 1971; Bird and Hume, 1971; Bird and Moir, 1972; Langlands *et al.*, 1973; Kennedy *et al.*, 1975; Doyle and Moir, 1979).

Most of the sulphur in faeces is in organic combination although some inorganic sulphate is present (Walker, 1957; Bird, 1971; Bird and Hume, 1971; Doyle and Moir, 1979). The amount and form of sulphur excreted in urine appears to vary with sulphur intake, but inorganic sulphate seems to be the major form excreted. Considerable ester sulphate is also present (Walker, 1957; Bird, 1971; Bird and Hume, 1971; Kennedy *et al.*, 1975; Doyle and Moir, 1979) and this would probably be rapidly converted to inorganic sulphate in soil.

Thus the sulphur in urine is in a form which is immediately available to plants or in a form which is readily converted into an available form (Barrow, 1967c). Depending on the climate, soil type, etc., this available sulphur can also be readily leached. On the other hand, little of the sulphur in faeces is sulphate and the organic sulphur in faeces has to be mineralized before it is available for plant uptake or leaching. The rate of mineralization of sulphur depends on the concentration of sulphur in the faeces and it needs to be higher than that in plant material for mineralization to occur (Barrow, 1961). Even though faeces are mineralized more slowly than plant material, the passage of plant material through the animal, and the partitioning of the sulphur between urine and faeces in favour of urine, means that sulphur is mineralized more rapidly than if the plant material was returned directly to the soil (Barrow, 1961, 1967c; Till, 1975). The stocking rate will thus have a large effect on the proportion of the plant sulphur that is mineralized by the comparatively slow process of microbial breakdown of plant residues and that mineralized by the faster process in the grazing animal (Till, 1975).

However, faeces and urine are not uniformly distributed over a pasture (Petersen *et al.*, 1956; Lotero *et al.*, 1966) and there can be a transfer of sulphur from one part of the paddock to another. Sulphur ingested over a large area is voided on to a small area, thus concentrating the sulphur at that site. Losses by leaching can therefore be accentuated (Petersen *et al.*, 1956). Doak (1949) reported that a large part of the sulphur returned in a urine patch by sheep (at a concentration of ~42.5 kgS ha^{-1} per urination) may be lost by leaching.

In addition to this random return of sulphur in excreta, sulphur can also be concentrated in one particular area of the field by the tendency of animals regularly to congregate in a specific area (camp-site), by the use of feedlots to fatten cattle, or by dairy farmers bringing their animals to a chosen area twice daily for milking. For example, Hilder (1964) in a study on the return of sulphur in faeces by grazing sheep found that the concentration of faeces increased towards the centre of the camp-site and that 34% and 22% of the total faeces were voided on areas which comprised only 10% and 3%, respectively of the total area. The distribution of urine is not known. Wrenford (1968) measured soil sulfate levels of ~31 ppm in sheep camps compared to 7 ppm in grazed areas removed from the camps.

Till (1980) has estimated the amount of sulphur present in plant (~6×10^2 Tg) and animal pools on a global scale to be about 3×10^{-5}% of the total sulphur in the biogeochemical cycle.

Till (1980) also estimated the overall quantities of sulphur present and the major flows for the Australian pastoral industry. These are reproduced in Table 3.11. He estimated the total soil sulphur pool in the top 30 cm of soil to be 1.2×10^2 TgS assuming the mean concentration to be 75 μgS g^{-1}. The Australian pastoral industry supports about 150×10^6 sheep and 30×10^6 cattle on an area of approximately 400×10^6 ha of which only ~30×10^6 ha are improved pasture. The stocking rate varies from 1 to 30 sheep ha^{-1} with an overall stocking rate of 1 sheep ha^{-1} assuming that one cattle beast is equivalent to eight sheep (Till, 1980). He calculated that for Australia as a whole, animals would contain ~0.022 TgS and the sulphur removed in animal products would be 0.019 TgS $year^{-1}$, assuming that the average sheep weighed 40 kg and had a sulphur content of 0.14% S. As only 5–10% of the sulphur ingested is retained by animals, the amount excreted and available for uptake by pasture plants or leaching would be ~0.016 TgS.

Volatiles

Recent work has shown that volatile sulphur compounds can be released to the atmosphere during the aerobic and anaerobic decomposition of manures (Burnett, 1969; Elliott and Travis, 1973; Banwart and Bremner, 1975a; Smith *et al.*, 1977). Cattle, sheep, swine, and poultry manures have been studied.

Banwart and Bremner (1975a) found that trace amounts of dimethyl sul-

Table 3.11 Sulphur budgets for grazed pastures (after Till, 1980)

			Typical values for sheep grazing systems			
	Australian totals		Native pasture		Improved pasture	
Component	Mass (tonnes)	Flux (tonnes year^{-1})	Mass (kg ha^{-1})	Flux (kg ha^{-1} year^{-1})	Mass (kg ha^{-1})	Flux (kg ha^{-1} year^{-1})
Inputs						
Atmosphere		$2–4 \times 10^5$		<1		1–4
Fertilizer		$1–2 \times 10^5$				25
Soil						
Total (0–30 cm)	1.2×10^8		300		1000	
Available (0–10 cm)	1.6×10^6				20	
Plants						
Total	0.8×10^6		2		12	
Production		1.5×10^6		3		50
Domestic animals						
Total	2.2×10^6		0.06		1.2	
Products		1.9×10^4		0.05		1.0
Intake		1.6×10^5		0.5		20
Microfauna and flora						
Total	—		—		0.6	
Production		—		—		35

phide were emitted from fresh poultry and sheep manure, but no emission could be detected from air-dried manures. They also found that all of their manure samples released hydrogen sulphide, methyl mercaptan, and dimethyl sulphide when incubated under anaerobic conditions, and that some samples also released dimethyl disulphide, carbonyl sulphide, and carbon disulphide. Most of the sulphur emitted was in the form of hydrogen sulphide and methyl mercaptan.

When homogenized manures were incubated in sealed bottles for 30 days the total amount of sulphur volatilized was between 0.02 and 0.53% of the total sulphur in the manure. Hydrogen sulphide and methyl mercaptan were the main gases evolved and together they accounted for 70–97% of the sulphur volatilized (Banwart and Bremner, 1975a). However, when the manures were incubated with a sandy soil under aerobic or waterlogged conditions no hydrogen sulphide was evolved (Bremner, 1977). Dimethyl disulphide and carbon disulphide were emitted from these mixtures under aerobic conditions but, with an anaerobic atmosphere, methyl mercaptan, dimethyl sulphide, and carbonyl sulphide were emitted in addition to the two disulphides (Bremner, 1977). The total emission amounted to 0.1–0.4% of the sulphur added. Other work by Banwart and Bremner (1976b) on the amounts of sulphur emitted from soils amended with animal manures, sewage sludges, and plant materials incubated under aerobic or waterlogged conditions showed that, on the average, less than 0.5% of the sulphur added was volatilized from manures or sewage sludges, whereas up to 3.3% was volatilized from plant materials. The range of values was quite large, 0–15.6%.

Volatile sulphur compounds are emitted from soil during the decomposition of certain pesticides. Moje *et al.* (1964) detected the emission of carbonyl sulphide from soil during the decomposition of nabam (disodium-ethylene-bis-dithiocarbamate) while Munnecke *et al.* (1962) reported the formation of carbon disulphide in soils treated with nabam, thiram, and zineb and methylisothiocyanate from soils receiving vapam and mylone.

Acidification of Soils

The importance of leguminous pastures and the sulphur fertilizer, superphosphate, in improving soil fertility by increasing soil organic matter and plant-available nitrogen is well known (Russell, 1973). Unfortunately, growth of clover pastures also leads to a gradual increase in soil acidity. Decreases in soil pH under subterranean clover pastures have been reported on a wide range of soil types in southern Australia (Cook, 1939; Donald and Williams, 1954; Russell, 1960; Barrow, 1969a; Watson, 1969; Flemons and Siman, 1970; Kohn *et al.*, 1977), and Williams (1980) has calculated a relationship between pH and years of pasture growth over a 50-year period (equation 8)

$$\mathrm{pH} = 5.95 - 0.905\,(1 - e^{-0.045t}) \qquad (8)$$

where t = time in years During this period an average of ~55 kg superphosphate was applied per hectare each year to the pastures. The increase in exchangeable hydrogen in the surface 10 cm of these soils due to pasture growth and fertilization is shown in Fig. 3.2 (C. H. Williams, unpublished).

In some pasture soils acidity has reached levels high enough to depress plant growth and, in some cases, to cause serious losses in crop or pasture production (Flemons and Siman, 1970; Williams and David, 1976; Osborne *et al.*, 1978; Cregan *et al.*, 1979). In most cases the problems are due to the development of manganese or aluminium toxicities (Williams, 1980), but can also be due to a decrease in molybdenum, calcium, potassium, phosphorus, and magnesium availability to plants, reduced nodulation, and increased fungal disease of the pasture plants.

The increase in acidity appears to be due, in part, to increases in the cation-exchange capacity of the soil as a result of the accumulation of soil organic matter (Williams and Donald, 1957; Russell, 1960) and cation depletion by increased leaching with rainwater (Williams, 1980).

Figure 3.1 shows the build-up in total sulphur, in the surface 10 cm of soils derived from granodiorite, due to pasture improvement at Binda, NSW. This build-up in sulphur, due to an average application of ~55 kg superphosphate ha^{-1} $year^{-1}$, reflects changes in total soil organic matter as the changes in sulphur were closely correlated with the increases in total soil nitrogen

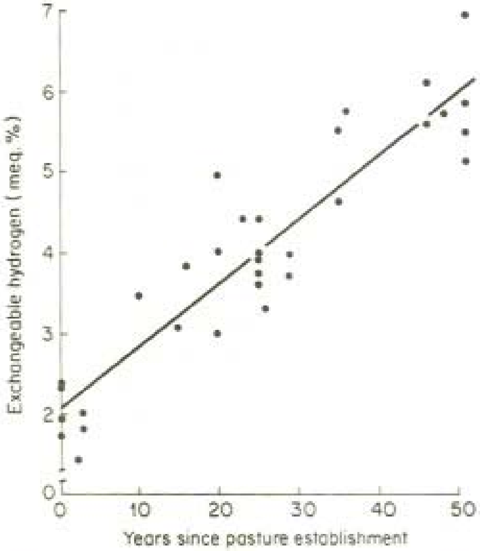

Fig. 3.2 The relationships between the period under subterranean clover pasture and the exchangeable hydrogen at pH 7.0 of the surface 10 cm of yellow podzolic soils

(r = 0.95) and organic phosphorus (r = 0.95) (Williams, 1980); there were also corresponding changes in cation-exchange capacity (r = 0.85).

The accumulation of organic matter is mainly confined to the surface 10 cm of soil (Williams and Steinbergs, 1958), but the decrease in pH extends well below this depth. This indicates the importance of other factors such as cation depletion associated with increased leaching of nitrate following the input of legume fixed nitrogen (Helyar, 1976; Williams, 1980).

It seems unlikely that the acidity of the superphosphate itself was directly responsible for the increase in soil acidity. Long-term field experiments involving the application of large amounts of superphosphate to crops have generally shown little measurable effect on soil pH (Leeper, 1952; Williams and Lipsett, 1961; Piper and de Vries, 1964; Russell, 1973). However, addition of sulphur fortified superphosphates and other acid-forming sulphur fertilizers such as elemental sulphur and ammonium sulphate would be expected to increase soil acidity.

The rate at which pH decreases in soil under improved pasture depends upon several interacting factors such as the buffering capacity of the soil, the rate of build-up of organic matter and nitrogen, stocking rate, leaching intensity, soil type, and climate, and thus is likely to vary from soil to soil.

About half of the coastal areas and tablelands of New South Wales now have soils sufficiently acid for non-tolerant plants to be affected, and in the wheat belt on the western plains about one-sixth of the soils have become too acid for optimal growth. Soils in other areas of Australia that have a Mediterranean climate are also likely to be affected.

Approximately 75% of the improved pastures in southern Australia are less than 30 years old and it is, therefore, likely that the areas affected by acidity problems will increase in the future. Where legume-based pastures are grown in other parts of the world similar effect could be expected.

C. Removal of sulphur in crops and animal products

The amounts of sulphur removed in crops depends on the yield of the crop, the portion of the crop removed, and the treatment of the crop residues. Obviously, any factor which affects the yield of the crop, such as level of an essential nutrient, will affect removal. Some crops have a far greater requirement for sulphur and thus will remove more sulphur from soil during growth. Thus Spencer (1975) has grouped plants into three categories—high, moderate, and low—according to the magnitude of their needs in kgS ha^{-1} for sulphur. Group I (high) contains the cruciferous forages (40–80), lucerne (30–70), and rapeseed (20–60); Group II includes (moderate) sugar-cane and coffee (20–40) clovers and grasses (10–40), and cotton (10–30); while Group III includes sugar-beet (15–25), cereal forages (10–20) cereal grains (5–20), and peanuts (5–10). An adequate supply of readily available sulphur is required for vegetable crops which have a short growing season.

Table 3.12 Sulphur in farm produce

		Sulphur in product (kg ha^{-1})			
Product		Tisdale and Nelson (1966)	Beaton and Fox (1971)	Biederbeck (1978)	C. H. Williams (unpublished)
Grains	Corn	16[a] 11[c]	49[b]	16–18[b]	16[a] 17[c]
	Wheat	6[a] 10[c]	25[b]	14–17[b]	2–4[a] 3–6[c]
	Barley		28[b]		4[a] 5[c]
	Oats	7[a] 10[c]	22[b]		3[a] 5[c]
	Sorghum		43[b]		7[a]
	Rice	3[a]	20[b]		8–17[b]
Forage crops	Lucerne	34	34[b]	23–28	6[b]
	Clover	11	20[b]	17–22	6[b]
	Grass		18–56[b]	9–13	
Oil crops	Soybeans	11 (beans)	11 (beans)		
	Peanut	18 (nuts)	28[b]		
	Rapeseed		39[b]		
Vegetables	Potatoes	11 (tubers)	30 (tops and tubers)	8–11	2 (tubers)
	Cabbage		41 (heads)	22–43	4
	Turnip		43 (tops and roots)	28–29	
	Onions		28 (tops and bulbs)	22–23	
	Tomatoes	24 (fruit)			2
Miscellaneous	Sugar-cane		90[b]		20
	Sugar-beet		55 (tops and roots)	21–31	
	Cotton	2 (seed)	26[b]		3 (seed and lint)
	Tobacco	22 (leaves)	24[b]		
	Apples				2
Animal products	Milk				2
	Cattle beast				2
	Fat lambs				3
	Wool				1

[a] Grain.
[b] All above-ground parts.
[c] Stubble.

The figures for crop removal given in Table 3.12 are an indication of the rate at which the reserve supply in soil is being depleted.

Not all of the sulphur in a crop would necessarily be removed because in many cases only part of the crop plant is harvested, for example in many areas cereal straw is incorporated into the soil and in others it is burned *in situ*.

The amounts of sulphur removed in animal products, e.g. in wool production and beef or fat lamb production are very small compared with the amounts removed in plant products (Table 3.12), and play virtually no part in determining the requirements for available nutrients (Till, 1980).

D. Flooded rice production and the sulphur cycle

Sulphur is required for the nutrition of paddy rice as well as for upland rice, and sulphur deficiency has been found to reduce markedly rice yields and quality (Aiyar, 1945; Sen, 1938; Saran, 1949; Wang *et al.*, 1976a,b; Mamaril *et al.*, 1976; Ismunadji and Zulkarnaini, 1978; Wang, 1978; Blair *et al.*, 1979a,b).

Dramatic responses to sulphur fertilization by flooded rice have been recorded in the tropics (e.g. Wang *et al.*, 1976a,b) although excessive rates of application can decrease grain yield (e.g. Wang, 1978). Application of high rates of sulphur ($>$400 kgS ha^{-1}) caused burning of the tips and margins of the old leaves.

Not all of the sulphur added in fertilizer, irrigation water, or from the atmosphere is absorbed by the rice crop; some is leached and some may be reduced to sulphide in the anaerobic zone. Under anaerobic conditions sulphate can be reduced to sulphide by anaerobic bacteria (*Desulfovibrio* and *Desulfotomaculum*) which use sulphate as the terminal electron acceptor in respiration (Roy and Trudinger, 1970; Ponnamperuma, 1972). Under these flooded conditions sulphide can also be formed during the metabolism of the sulphur-containing amino acids, cysteine, cystine, and methionine (Barker, 1961).

Under flooded conditions the reduction of soil components is more or less sequential; after the disappearance of oxygen the sequence of reduction is nitrate, nitrite, manganic compounds, ferric compounds, and sulphate. Reduction of one component does not have to be completed before reduction of the next one can commence, although there are exceptions. Oxygen and nitrate must be depleted before ferric iron is reduced and sulphate is not reduced to sulphide whenever oxygen or nitrate are present. Sulphate can be found in waterlogged soils in the presence of reduced iron and reduced manganese. Redox potentials low enough for sulphate to be reduced do not generally occur until most of the reactable iron is in ferrous form. Therefore, whenever reactable iron and sulphur are present in a soil there will always be ferrous iron to react with and precipitate any sulphide formed when reduction processes are sufficiently intense to produce hydrogen sulphide (Patrick and Mikkelsen, 1971). More sulphide is produced when organic matter is added to a flooded soil (Yamane and Sato, 1961).

Although large amounts of hydrogen sulphide can be produced in waterlogged soils, the concentration of water-soluble hydrogen sulphide may be extremely low (Misra, 1938; Mortimer, 1941; Hutchinson, 1957) due to its reaction with ferrous iron and possibly other cations to form insoluble sulphides (Ponnamperuma, 1972). When excessive amounts of sulphur are added to soils low in active iron, or other cations, some sulphide will remain in solution. This soluble sulphide can injure the roots of rice plants and cause the physiological disease termed 'Akiochi' or late summer disease (Mitsui, 1956; Tisdale and Nelson, 1966). This disease has been found to occur in sandy soils in Japan and Korea which are normally low in cations, but can also occur in soils as a result of cation depletion due to many years of continuous rice cultivation (Shioiri, 1943; Tisdale and Nelson, 1966).

Okajima and Takagi (1953, 1955, 1956) investigated the mechanisms of injury caused by hydrogen sulphide and found that the efficiency of nutrient absorption was impaired, the translocation of inorganic nutrients in the plant was inhibited, and the formation and translocation of carbohydrate was lowered. Other workers have also shown that hydrogen sulphide depressed nutrient absorption and yield of rice crops (Hashimoto *et al*., 1948; Mitsui *et al*., 1951; Yamane *et al*., 1956; Baba, 1958; Takijima, 1963).

Suzuki and Shiga (1956) attempted to relate the production of hydrogen sulphide in soils with the severity of the disease. They found an average of <0.05, 0.23, and 0.54 mgS as hydrogen sulphide formed when 30 mg of S as sulphate per 100 g soil (dry basis) was incubated with normal, weakly degraded, and strongly degraded soils, respectively. Yoneda (1958) and Shiga and Suzuki (1964) found that approximately 2.5 mgS was sufficient to kill rice plants.

There does seem to be some disagreement as to whether hydrogen sulphide is the real cause of Akiochi disease. However, many farmers have decided to reduce the risk by substituting ammonium chloride for ammonium sulphate in their fertilizer programme for rice (Tisdale and Nelson, 1966).

Soils which produce hydrogen sulphide when wet will become more acid as they are dried because of the oxidation of the sulphide to sulphuric acid.

E. Soil amendment with gypsum and other sulphur materials

Sulphur plays a number of roles in crop production; it is required as a plant nutrient, and it is used as a soil amendment, particularly on saline, alkali, saline–alkali, and calcareous soils. On these soils crops grow poorly, or not at all, because of the high salt content and the unavailability of nutrients or poor soil structure. These soils occur in many of the arid and semi-arid areas of the world which are used for irrigated agriculture. The main points of difference between these four classes of soil have been described by Richards (1954) and Stromberg and Tisdale (1979) and are summarized in Table 3.13. The arbitrary exchangeable sodium percentage (ESP) value of 15 which is used to differentiate soil classes (Table 3.13) has been modified by a number of people on the basis of morphological and experimental evidence. Bernstein (1974) proposed on ESP value of 10 for fine-textured, and 20 for coarse-

Table 3.13 Some properties of saline, saline–alkali, and calcareous soils

	Electrical conductivity of saturation extract (mS[a] cm^{-1})	Exchangeable sodium percentage[b]	pH
Saline	>4	<15	<8.2
Alkali (or sodic)	<4	>15	>8.5
Saline–alkali	>4	>15	>8.5
Calcareous	<4	<10	7.5–8.2

[a] Millisiemens.

[b] Ratio of exchangeable sodium to cation-exchange capacity.

textured soils. Australian experience suggests that an ESP value of 15 or 10 is too high. Northcote and Skene (1972) suggested an ESP of 6 as a better boundary value and this was supported by Loveday and Pyle (1973). McIntyre (1979) presents results which show that 5 would be more relevant for certain plastic soils from eastern Australia. Exchangeable magnesium also affects the swelling and dispersion of soils (e.g. Bakker *et al.*, 1973; Bakker and Emerson, 1973; Emerson and Bakker, 1973; Emerson, 1977) and probably should be taken into account when setting a critical ESP value.

The main requirements for the reclamation of these soils are reduced salinity, improvement in physical characteristics (which impede water penetration, root development, and seedling emergence), lowering of pH (and improvement in nutrient availability), and removal of toxic amounts of boron (Loveday, 1975; Miyamoto *et al.*, 1975; Stromberg and Tisdale, 1979). On some alkaline and calcareous soils many crops suffer from nutrient deficiencies; under these conditions the plant cannot assimilate some nutrients such as phosphorus, iron, copper, manganese, and zinc. The availability of these nutrients is markedly increased by adjusting the pH from 8 to 7 (Stromberg and Tisdale, 1979).

Salinity is usually lowered by leaching; if the soil contains sufficient soluble calcium to replace sodium on the exchange sites no amendment aside from adequate drainable is required (Kelley, 1951; Loveday, 1975). In the absence of calcium, if sufficient swelling clay is present, a reduction in salt content by leaching will cause the clay to swell and disperse and water penetration will decrease. This can be overcome by addition of calcium to reduce the amounts of sodium on the clay. Gypsum is widely used for this purpose throughout the world (Tisdale, 1970).

To reclaim alkali and saline–alkali soils the excess sodium on the cation-exchange complex must be replaced by calcium. This can be done by applying gypsum, as above, or by applying acid or an acid-forming amendment to dissolve the calcium carbonate that is present in many alkali soils. The amendment must be followed by adequate leaching to remove the soluble salts (Overstreet *et al.*, 1951; McGeorge *et al.*, 1956; Tisdale, 1970; Miyamoto *et al.*, 1975; Miyamoto and Stroehlein, 1975; Stromberg and Tisdale, 1979).

Materials which have been used for this purpose include gypsum, elemental sulphur, sulphuric acid, sulphur dioxide, ammonium bisulphite, iron sulphate, ammonium polysulphide, and calcium polysulphide (Thomas, 1936; Thorup, 1972; Mohammed *et al.*, 1979; Stromberg and Tisdale, 1979). Many of these compounds have an acidifying effect on high pH soils; when the pH is lowered the availability to plants of phosphorus and micronutrients such as zinc, iron, and manganese is improved (e.g. McGeorge and Greene, 1935; Thorne, 1944; Mitchell *et al.*, 1952; Mortvedt and Giordano, 1973; Clement, 1978; Stromberg and Tisdale, 1979). The use of sulphuric acid on these soils has been studied in detail (Thorne, 1944; Miyamoto *et al.*, 1974; Ryan and Stroehlein, 1974), but little work has been done with other sulphur sources (Clement, 1978). Elemental sulphur must be oxidized to sulphuric acid before any reaction with calcium carbonate, soil phosphorus, or micronutrients can occur (Clement, 1978).

The choice of a soil amendment depends on the availability and cost of the amendment, the presence or absence of calcium carbonate in the soil, and soil temperature. Materials other than gypsum are generally required in smaller amounts, resulting in economies of storage, handling, and application. The acid-forming materials also have the dual ability of increasing water penetration and nutrient availability (Stromberg and Tisdale, 1979). Some of them, however, have undesirable properties.

The amount of material required for a response is dependent on the acid-forming properties of the compound used, the amount of calcium carbonate present in the soil, the crop species, and soil texture (Miyamoto *et al.*, 1975; Stromberg and Tisdale, 1979). It ranges from 2–6 tonnes ha^{-1} for improving moderately affected soils to 6–12 tonnes ha^{-1} for reclaiming severely affected soils (Miyamoto *et al.*, 1975).

Sodium-affected soils are a serious problem in agriculture (Nyborg, 1978). The full extent of salt-affected soils throughout the world is not accurately known so it is difficult to calculate the possible beneficial effects of amendment with sulphur-containing materials or the possible pollution of groundwaters which might result from these amendments. Approximately 15 million ha of land are affected to some degree by salt in the United States (Beaton and Fox, 1971). Solonetzic soils occupy about 5 million ha in the grass and parkland areas of Alberta and ~3 million ha in Saskatchewan and Manitoba (Cairns and Bowser, 1969; Toews, 1973; Cairns and Beaton, 1976), and 40 million ha in Asia, Africa, Europe, and Oceania (Bohn, 1976). Dr N. I. Bazilevich (pers. comm.) estimates that there are 47 million ha of soil affected by salt to a depth of 2 m in the European part of the USSR and 350 million ha in the whole of the USSR.

Results of laboratory column studies show that addition of sulphuric acid to the surface of arid soils followed by leaching with water is a more effective way of removing toxic amounts of boron than leaching with water alone (Prather and Rhoades, 1975).

There is also the possibility that sulphur could be used to lower high nitrate concentrations in soil water and sewage effluent, thereby reducing nitrate contamination of lakes and streams (Sikora and Keeney, 1976). Mann *et al.* (1972) found that denitrification rates in two soils were higher when sulphur was added to the soils; the nitrate was reduced to nitrogen by the action of the organism *Thiobacillus denitrificans* on the elemental sulphur.

Potentially all of the sulphur that is added as a soil amendment can be leached to contaminate the ground-water. Whether or not pollution occurs depends on the amount and type of acid or acid-forming compounds used, water management, and soil properties. In many areas the sulphur will be leached beyond the root zone but will remain in the soil profile.

According to Miyamoto (1977) 24.2 cm of water completely dissolved the calcium sulphate that had precipitated on the soil surface after acid application of <5 tonnes ha^{-1}, yielding soluble salts approximately equal to 100×10^3 eq ha^{-1}. The salts originally present in the same layer amounted to 126×10^3 eq ha^{-1}. Thus the acid application nearly doubled the salt load of the leaching water.

On the positive side, sulphur dioxide produced from the burning of coal or from the recovery of minerals by smelting could be used for the reclamation of salt-affected soils instead of being discharged into the atmosphere. In the south-western region of the United States there is a surplus production of sulphuric acid which lowers the pH. The pH of the natural precipitation, therefore, depends on the relative amounts of the various acidic and basic salt-affected soils. Further increases in the production of sulphuric acid are projected in the near future (McKee, 1969; Jones, 1972; Miyamoto, 1977).

3.3.2 Acid Rain

Rain-water in equilibrium with carbon dioxide at normal concentrations and pressures has a pH of 5.7 at 25 °C (Kramer, 1978). However, other substances which enter the atmosphere locally can raise or lower the pH. For example, in regions with calcareous soils, incorporation of dust can raise the pH of rain as will the volatilization of ammonia from grazing animals. Sulphur dioxide from sources such as volcanoes is oxidized in the atmosphere to sulphuric acid which lowers the pH. The pH of the natural precipitation, therefore, depends on the relative amounts of the various acidic and basic substances which enter the atmosphere and react with the rain-water (Kramer, 1978; Likens *et al.*, 1979).

Precipitation which fell before the Industrial Revolution, and is preserved in glaciers and continental ice-sheets, normally has a pH above 5. For example, Gjessing and Gjessing (1973) found a mean pH of 6.32 for a snow profile in Antarctica. Man's activities, particularly the burning of fossil fuels and the smelting of sulphide ores, has changed this. The oxides of sulphur and nitrogen emitted during these practices are converted into strong acids in the atmosphere and returned to the ground in precipitation. These strong acids (sulphuric and nitric) completely dissociate in water and lower the pH to less than 5.6 (Likens *et al.*, 1979). On an annual basis rain and snow over large regions of the world are now from 5 to 30 times more acid than the rain from unpolluted areas. In large areas of the eastern United States, south-eastern Canada and western Europe the annual average pH of precipitation ranges from 4 to 4.5 (Likens, 1972; Hornstrom *et al.*, 1973; Cogbill and Likens, 1974; Likens *et al.*, 1979). With normal concentrations of CO_2 in the atmosphere the amount of sulphur required to form sufficient sulphuric acid to lower the pH of rainfall to 4.0 is only 1.5 ppmS (Terman, 1978). Sulphuric is the dominant species in acid precipitation, although nitric appears to be responsible for about 30% of the acidity.

The increase in acidity is accompanied by increases in sulphate concentration in the rain-water. Although sulphur produces visible damage to soil and vegetation close to emission sources (McGovern, 1972; McGovern and Balsillie, 1973; Hutchinson and Whitby, 1976) there are no direct toxic effects from sulphate on flora and fauna. In many areas of the world the sulphate is beneficial because it corrects a sulphur deficiency in the soil. Correction of the pollution problem by controlling the emission of sulphur dioxide will eventually mean a greater requirement for sulphur fertilizers throughout the agricultural areas in Europe and North America.

The effects of acid precipitation on soils and vegetation may be insidious, and Malmer (1974) and McFee *et al.* (1976) suggest that periods of the order of a century may be required to cause irreversible effects. At the present time acute effects of acid precipitation on soils and vegetation have been clearly identified only under extreme conditions, for example very close to sources of air pollution (Overrein, 1978).

Acid rain may affect the soil environment by slightly intensifying the natural weathering processes which causes leaching of bases and development of acid soils. These processes result in dissolution of carbonates (calcite, dolomite), oxides (iron, aluminium, manganese), and aluminosilicates, adsorption of hydrogen ions on oxides, silicate minerals, and organic matter, and mobilization of metal ions (Kramer, 1978; Overrein, 1978). Deposition of acid rain causes exchange of hydrogen ions for calcium, magnesium, sodium, and potassium on clay minerals. Whether or not this will result in immediate marked acidification of soils depends on the buffering capacity of the soil. Calcareous soils show very little immediate effect from deposition of acid rain, and it has been concluded that the most adverse effects of acid precipitation are to be expected in soil types that are transitional between brown earths and podzols (Wiklander, 1973; Malmer, 1974). Overrein (1972) found that the pH of the precipitation had to be below 4 to make a significant effect on the leaching of calcium from soil and on the pH of ground-water.

Natural ecosystems are extremely complex with numerous interactions at all organizational levels; evaluating the effects of acid precipitation on these systems is difficult and expensive (Likens *et al.*, 1979). It is also very difficult to separate out the effect of sulphuric acid brought down in rainfall and that caused by dry deposition of sulphur dioxide. As far as pollution effects are concerned the actual causative agent is not important. Close to sources the bulk of the sulphur comes from direct absorption of sulphur dioxide by the soil or vegetation. This has been shown by setting out potted soils of known sulphur contents at a number of sites downwind from a source (Johansson, 1959; Cox, 1975; Siman and Jansson, 1976b; Nyborg *et al.*, 1977). More sulphur was absorbed from the air than was gained in rainfall (Johansson, 1959).

A number of workers have studied the spatial accumulation of sulphate in soils and the acidification of soils around smelters and other industrial concerns. They have found that the sulphate content of the soil falls off rapidly with distance from the source and that the acidification effect also decreases with distance (Katz *et al*., 1939; Gorham and Gordan, 1960a,b; Gordan and Gorham, 1963; Bohn, 1972; Cox, 1975; Moss, 1975; Baker *et al.*, 1977). This reflects the similar trends observed in precipitation.

Vegetation may also be affected adversely by acid precipitation or by direct absorption of sulphur dioxide. Damage in the vicinity of emission sources has been observed for many years but, recently, concern has been expressed that damage to forests far from emission sources may also be occurring (Tamm, 1976).

3.3.3 Effect of Coal and Mineral Mining on Soils

The wastes from coal and heavy metal mining and treatment plants are primarily effluent water, chemicals, and tailings. The coarse residue from mining operations is usually piled high to form large dumps and the fine residues or slimes are usually pumped as a slurry to storage areas or dams where the solid materials settle out and the water can be evaporated or reused (Craze, 1980). In some mining areas these dumps are enormous; for example, at Magna, Utah, the tailings covered an area greater than 2000 ha and material was being added at the rate of 0.11 Tg day^{-1} (Nielson and Peterson, 1972). Solids dumps and slime dams are not only unsightly but are also sources of air and water pollution (Craze, 1980).

Chemical pollution as a result of mining operations is caused by exposing sulphide minerals to oxidation and leaching, resulting in the production of drainage waters that are extremely high in sulphate, acid, and heavy metals. Barton (1978) found that sulphate in the effluent from coal and zinc mine drainage, a uranium tailings pile and a copper smelting acid plant scrubber ranged from 490 to 63 000 ppm, while the pH of the effluents varied from 1.8 to 2.7. Some of the sulphide minerals involved in pollution caused by mining activities are pyrite (FeS_2), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and galena (PbS).

The sequence proposed for the oxidation of pyrite with the formation of acid and sulphate (Temple and Delchamps, 1953) has already been described in section 3.3.2.

In summary, the reactions involved are

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4 \qquad (9)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad (10)$$

$$Fe_2(SO_4)_3 + FeS_2 \rightarrow 3FeSO_4 + 2S \qquad (11)$$

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad (12)$$

Ferric sulphate is a powerful oxidant and thus chalcopyrite, sphalerite, and galena can be oxidized to form sulphuric acid along with soluble copper and zinc sulphates and insoluble lead sulphate (Craze, 1980).

$$CuFeS_2 + 2Fe_2(SO_4)_3 + 2H_2O + 3O_2 \rightarrow CuSO_4 + 5FeSO_4 + 2H_2SO_4 \qquad (13)$$

$$2ZnS + 2Fe_2(SO_4)_3 + 2H_2O + 3O_2 \rightarrow 2ZnSO_4 + 4FeSO_4 + 2H_2SO_4 \qquad (14)$$

$$2PbS + 2Fe_2(SO_4)_3 + 2H_2O + 3O_2 \rightarrow 2PbSO_4 + 4FeSO_4 + 2H_2SO_4 \qquad (15)$$

All these reactions except (11) require an abundant supply of oxygen, and water is also required for most of them to proceed. Because of this, three zones have been observed in aged slime dumps; (1) an oxidized zone, out of which zinc, copper, and lead are removed; (2) a cemented hard-pan where due to oxygen depletion, iron oxides, copper, zinc, and lead are deposited; and (3) a reduced zone where the composition of the dump is unchanged and pHs are in the range of 6–7 (Boorman and Watson, 1976).

A number of factors in additon to oxygen and water are reported to have an affect on the overall dissolution rate of the minerals: e.g. pH, ferric ion concentration, catalytic agents such as bacteria or specific ions, and inhibitors such as bactericides or alkali (Hanna *et al.*, 1963).

Plants will not establish on these mine dumps or on areas affected by drainage waters from the mines or dumps because of the high salt contents or the increased solubility of toxic elements such as aluminium and manganese caused by increased acidity (Blevins *et al.*, 1970; Hoyt and Nyborg, 1972; Nyborg, 1978; Craze, 1980).

Many miles of streams and rivers, reservoirs, and large areas of land have been affected by mining activity.

3.4 SULPHUR BUDGET FOR THE PEDOSPHERE

It has not been possible to calculate the global content of soil sulphur because of lack of data on the sulphur content and mass of the many different soil types.

Bolin *et al.* (1979) presented data for total carbon contents of soil organic matter in world ecosystems. Using their data and C : S ratios of 200 : 1 for natural grassland and forest soils, 130 : 1 for peats, and 100 : 1 for cultivated soils (see above), we calculate the total organic sulphur content to be 1.1×10^4 TgS.

On the basis of annual mineralization of 1–3% of the soil organic matter, the conversion of soil organic sulphur to inorganic forms would amount to $1.1–3.3 \times 10^2$ TgS. Most of this sulphur will be released in the surface 10–15 cm of the profile and may be subject to leaching. However, leaching, should it occur, may not necessarily remove all of this sulphur from the soil, since this will be determined by factors such as rainfall intensity and adsorption reactions. Kilmer *et al.* (1974) estimates a leaching and erosion loss from arable soils of 3 kg ha^{-1} year^{-1} which would result in a global loss of 4.8 TgS.

A suggested sulphur budget for the pedosphere based on these calculations and published data is presented in Table 3.14. Clearly there are many gaps and inaccuracies and more research and data is essential.

Table 3.14 Sulphur budget for the pedosphere

Reservoirs		Total mass (TgS)	Reference
Soil organic matter		1.1×10^4	
Land plants		600	Friend (1973), Till (1980)
Biosphere		6×10^4	Wedepohl (1978)
Fluxes	Local (kg ha^{-1} year^{-1})	Global (TgS year^{-1})	Reference
Internal			
Mineralization of soil organic matter (1–3% year)		$1.1–3.3 \times 10^2$	
Cycled through plants		14	Till (1980)
Inputs			
Amendments for saline soils	$2–12 \times 10^3$		
Fertilizer		26	Friend (1973)
		29	Nriagu (1978)

Table 3.14 (continued)

Fluxes	Local (kg ha^{-1} year^{-1})	Global (TgS year^{-1})	Reference
Weathering			
Magma		5	Granat *et al.* (1976)
Igneous and sedimentary		33	Granat *et al.* (1976)
Pesticides (<1% of fertilizer)		<0.26	Coleman (1966)
Rainfall		43–86	Kellogg *et al.* (1972)
Dry deposition		10–20	Junge (1963) Robinson and Robbins (1968) Friend (1973)
Outputs			
Erosion	47–113		Barrows and Kilmer (1973)
Leaching	0–319		
Volatilization			
Dimethyl sulphide			
Fresh leaves		0.01	Hitchcock (1977)
Senescent leaves		0.53	
Soils		1.5–4.9	
Carbonyl sulphide			
Natural and agricultural fires		0.2–0.3	Crutzen *et al.* (1979)
Soils		0.5	Adams *et al.* (1979)

REFERENCES

Abeles, F. B., Cracker, L. E., Forrence, L. E., and Leather, G. R. (1971) Fate of air pollutants: removal of ethylene, sulfur dioxide, and nitrogen dioxide by soil. *Science* (Wash. DC), **173**, 194–916.

Adams, D. F., Farwell, S. O., Pack, M. R., and Bamesburger, W. L. (1979) Preliminary measurements of biogenic sulfur-containing gas emissions from soils. *J. Air Pollut. Control Assoc.*, **29**, 380–383.

Adams, F., and Hajak, B. F. (1978) Effects of solution sulfate, hydroxide, and potassium concentrations on the crystallization of alunite, basaluminite and gibbsite from dilute aluminum solutions. *Soil Sci.*, **126**, 169–173.

Adams, F., and Rawajfih, Z. (1977) Basaluminite and alunite: a possible cause of sulfate retention by acid soils. *Soil Sci. Soc. Am. J.*, **41**, 686–691.

Aderikhin, P. G., and Tikhova, E. P. (1969) Sulphur in chernozems and grey forest soils of the Central Chermozemic Zone. *Agrokhimiya*, No. 11, 121–127 [in Russian].

Ahmed, S., and Jha, K. K. (1969) Sulphur status of Bihar soils. *J. Indian Soc. Soil. Sci.*, **17**, 197–202.

Aiyar, S. P. (1945) A chlorosis of paddy (*Oryza sativa*) due to sulphate deficiency. *Curr. Sci.*, **14**, 10–11.

Alexander, M. (1961) *Introduction to Soil Microbiology*. Wiley, New York, 472 pp.

Allison, F. E. (1973) *Soil Organic Matter and its Role in Crop Production*. Elsevier, Amsterdam, 637 pp.

Almy, L. H., and James, L. H. (1926) A method for the study of the formation of volatile sulfur compounds by bacteria. *J. Bacteriol.*, **12**, 319–331.

Alway, F. J., Marsh, A. W., and Methley, W. J. (1937) Sufficiency of atmospheric sulfur for maximum crop yields. *Soil Sci. Soc. Am. Proc.*, **2**, 229–238.

Aneja, V. P., Overton, J. H., Cupitt, L. T., Durham, J. L., and Wilson, W. E. (1979) Carbon disulphide and carbonyl sulphide from biogenic sources and their contributions to the global sulphur cycle. *Nature (Lond.)*, **282**, 493–496.

Aylmore, L. A. G., Karim, M., and Quirk, J. P. (1967) Adsorption and desorption of sulfate ions by soil constituents. *Soil. Sci.*, **103**, 10–15.

Baba, I. (1958) Nutritional studies on the occurrence of *Helminthosporium* leaf spot and akiochi of rice plant. *Bull. Nat. Inst. Agric. Sci.*, Ser. D, **7**, 1–157.

Baker, J., Hocking, D., and Nyborg, M. (1977) Acidity of open and intercepted precipitation in forests and effects on forest soils in Alberta, Canada. *Water Air Soil Pollut.*, **7**, 449–460.

Baker, J. L., Campbell, K. L., Johnson, H. P., and Hanway, J. J. (1975) Nitrate phosphorus and sulfate in subsurface drainage water. *J. Environ. Qual.*, **4**, 406–412.

Bakker, A. C., and Emerson, W. W. (1973). The comparative effects of exchangeable calcium, magnesium, and sodium on some physical properties of red–brown earth subsoils. III. The permeability of Shepparton soil and comparison of methods. *Aust. J. Soil Res.*, **11**, 159–165.

Bakker, A. C., Emerson, W. W., and Oades, J. M. (1973) The comparative effects of exchangeable calcium, magnesium, and sodium on some physical properties of red–brown earth subsoils. I. Exchange reactions and water contents for dispersion of Shepparton soil. *Aust. J. Soil Res.*, **11**, 143–150.

Balyanın, M. I., and Evstigneeva, L. T. (1974) Sulphur content in chenozems of the Pre-Urals in the Tatar ASSR. In: Kosloskova, A. V. *Physico-chemical Properties of Soils and Fertilizer Application*, pp. 13–18. Izd. Kazan Univ., Kazan [in Russian]

Banwart, W. L., and Bremner, J. M. (1974) Gas chromatographic identification of sulfur gases in soil atmospheres. *Soil Biol. Biochem.*, **6**, 113–115.

Banwart, W. L., and Bremner, J. M. (1975a) Identification of sulfur gases evolved from animal manures. *J. Environ. Qual.*, **4**, 363–366.

Banwart, W. L., and Bremner, J. M. (1975b) Formation of volatile sulfur compounds by microbial decomposition of sulfur-containing amino acids in soils. *Soil Biol. Biochem.*, **7**, 359–364.

Banwart, W. L., and Bremner, J. M. (1976a) Volatilization of sulfur from unamended and sulfate-treated soils. *Soil Biol. Biochem.*, **8**, 19–22.

Banwart, W. L., and Bremner, J. M. (1976b) Evolution of volatile sulfur compounds from soils treated with sulfur-containing organic materials. *Soil Biol. Biochem.*, **8**, 439–443.

Barjac, H. de (1952) Metabolism of sulfur-containing amino acids, especially of methionine in the soil *Ann. Inst. Pasteur (Paris)*, **82**, 623–628.

Barker, H. A. (1961) Fermentations of nitrogenous organic compounds. In: Gunsalus, I. C. and Stanier, R. Y. (eds), *The Bacteria*, Vol. 2. Academic Press, New York, pp. 151–207.

Barrow, N. J. (1960) A comparison of the mineralization of nitrogen and of sulfur from decomposing organic materials. *Aust. J. Agric. Res.*, **11**, 960–969.

Barrow, N. J. (1961) Studies on mineralization of sulfur from soil organic matter. *Aust. J. Agric. Res.*, **12**, 306–319.

Barrow, N. J. (1966) The residual value of the phosphorus and sulphur components of superphosphate on some Western Australian soils. *Aust. J. Exp. Agric. Anim. Husb.*, **6**, 9–16.

Barrow, N. J. (1967a) Studies on extraction and availability to plants of adsorbed plus soluble sulfate. *Soil Sci.*, **104**, 242–249.

Barrow, N. J. (1967b) Studies on the adsorption of sulfate by soils. *Soil Sci.*, **104**, 342–349.

Barrow, N. J. (1967c) Some aspects of the effects of grazing on the nutrition of pastures. *J. Aust. Inst. Agric. Sci.*, **33**, 254–262.

Barrow, N. J. (1969a) The accumulation of soil organic matter under pasture and its effect on soil properties. *Aust. J. Exp. Agric. Anim. Husb.*, **9**, 437–444.

Barrow, N. J. (1969b) Effects of adsorption of sulfate by soils on the amount of sulfate present and its availability to plants. *Soil Sci.*, **108**, 193–201.

Barrow, N. J. (1975) Reactions of fertilizer sulphate in soils. In: McLachlan, K. D. (ed.), *Sulphur in Australasian Agriculture*. Sydney University Press, Sydney, pp. 50–57.

Barrow, N. J., and Lambourne, L. J. (1962) Partition of excreted nitrogen, sulphur and phosphorus between the faeces and urine of sheep being fed pasture. *Aust. J. Agric. Res.*, **13**, 461–471.

Barrow, N. J., and Spencer, K. (1959) Lateral movement of fertilizer sulphur. *J. Aust. Inst. Agric. Sci.*, **25**, 208–209.

Barrow, N. J., Spencer, K., and McArthur, W. M. (1969) Effects of rainfall and parent material on the ability of soils to adsorb sulfate. *Soil Sci.*, **108**, 120–126.

Barrows, H. L., and Kilmer, V. J. (1963) Plant nutrient losses from soils by water erosion. *Adv. Agron.*, **15**, 303–315.

Barton, P. (1978) The acid mine drainage. In: Nriagu, J. O. (ed.), *Sulfur in the Environment*, Pt II. Wiley, Chichester, pp. 313–358.

Bassett, H., and Goodwin, T. H. (1949) The basic aluminum sulfates. *J. Chem. Soc. (Lond.)*, 2239–2279.

Baver, L. D. (1956) *Soil Physics*. Wiley, New York, 489 pp.

Beaton, J. D., and Fox, R. L. (1971) Production, marketing and use of sulfur products. In: Olson, R. A., Army, T. J., Hanway, J. J. and Kilmer, V. J. (eds), *Fertilizer Technology and Use*. Soil Sci. Soc. Am., Madison, Wisconsin, pp. 335–379.

Beattie, J. A., and Haldane, A. D. (1958) The occurrence of palygorskite and barytes in certain parna soils of the Murrumbidgee region New South Wales. *Aust. J. Sci.*, **20**, 274–275.

Begheijn, L. Th., van Breemen, N., and Velthorst, E. J. (1978) Analysis of sulfur compounds in acid sulfate soils and other recent marine soils. *Commun. Soil Sci. Plant Anal.*, **9**, 873–882.

Belot, Y., Bourreau, J. C., Dubois, M. L., and Pauly, C. S. (1974) Use of sulfur-34 to measure the absorption rate of sulfur dioxide on the leaves of plants. Isotope ratios as pollutant source and behaviour indicators. *Proc. Symp.*, 18–22 Nov. 1974 Vienna (IAEA – SM-191-18), 403–416 [in French].

Berg, W. A., and Thomas, G. W. (1959) Anion elution patterns from soils and soil clays. *Soil Sci. Soc. Am. Proc.*, **23**, 348–350.

Bernstein, L. (1974) Crop growth and salinity. In: Schilfgaarde, J. van (ed.), *Drainage for Agriculture*, Agronomy 17. Amer. Soc. Agron., Madison, pp. 39–54.

Bettany, J. R., Saggar, S., and Stewart, J. W. B. (1980) Comparison of the amounts and forms of sulfur in soil organic matter fractions after 65 years of cultivation. *Soil Sci. Soc. Am. J.*, **44**, 70–75.

Bettany, J. R., Stewart, J. W. B., and Halstead, E. H. (1973) Sulfur fractions and carbon, nitrogen, and sulfur relationships in grassland, forest and associated transitional soils. *Soil Sci. Soc. Am. Proc.*, **37**, 915–918.

Bettany, J. R., Stewart, J. W. B., and Saggar, S. (1979) The nature and forms of sulfur in organic matter fractions of soils selected along an environmental gradient. *Soil Sci. Soc. Am. J.*, **43**, 981–985.

Bhan, C., and Tripathi, B. R. (1973) The forms and contents of sulphur in some soils of U.P. *J. Indian Soc. Soil Sci.*, **21**, 499–504.

Bhardwaj, S. P., and Pathak, A. N. (1969) Fractionation of sulphur in soils of Uttah Pradesh and its relation to phosphorus. *J. Indian Soc. Soil Sci.*, **17**, 285–289.

Biederbeck, V. O. (1978) Soil organic sulfur and fertility. In: Schnitzer, M. and Khan, S. U. (eds), *Soil Organic Matter*. Elsevier, Amsterdam, pp. 273–310.

Birch, H. F. (1960a) Nitrification in soils after different periods of dryness. *Plant Soil*, **12**, 81–96.

Birch, H. F. (1960b) Soil drying and soil fertility. *Trop. Agric.*, **37**, 3–10.

Bird, P. R. (1971) Sulphur metabolism and excretion studies in ruminants. II. Organic and inorganic sulphur excretion by sheep after intraruminal or intraduodenal infusions of sodium sulphate. *Aust. J. Biol. Sci.* **24**, 1329–1339.

Bird, P. R., and Hume, I. D. (1971) Sulphur metabolism and excretion studies in ruminants. IV. Cystine and sulphate effects upon the flow of sulphur from the rumen and upon sulphur excretion by sheep. *Aust. J. Agric. Res.*, **22**, 443–452.

Bird, P. R., and Moir, R. J. (1972) Sulphur metabolism and excretion studies in ruminants. VIII. Methionine degradation and utilization in sheep when infused into the rumen or abomasum. *Aust. J. Biol. Sci.*, **25**, 835–848.

Blair, G. J. (1971) The sulphur cycle. *J. Aust. Inst. Agric. Sci.*, **37**, 113–121.

Blair, G. J., Mamaril, C. P., Pangerang Umar, A., Momuat, E. O., and Momuat, C. (1979a) Sulfur nutrition of rice. I. A survey of soils of South Sulawesi, Indonesia. *Agron. J.*, **71**, 473–477.

Blair, G. J., Momuat, E. O., and Mamaril, C. P. (1979b) Sulfur nutrition of rice. II. Effect of source and rate of S on growth and yield under flooded conditions. *Agron. J.*, **71**, 477–480.

Blenkhorn, H. D. (1974) Effect of sulphur and magnesium on silage corn in Ontario. *Sulphur Inst. J.*, **10**, 10–12.

Blevins, R. L., Bailey, H. H., and Ballard, G. E. (1970) The effect of acid mine water on floodplain soils in the western Kentucky coalfields. *Soil Sci.*, **110**, 191–196.

Bloomfield, C. (1969) Sulphate reduction in waterlogged soils. *J. Soil. Sci.*, **20**, 207–221.

Bohn, H. L. (1972) Soil absorption of air pollutants. *J. Environ. Qual.*, **1**, 372–377.

Bohn, H. L. (1976) Estimate of organic carbon in world soils. *Soil Sci. Soc. Am. J.*, **40**, 468–470.

Bolin, B., Degens, E. T., Duvigneaud, P., and Kempe, S. (1979) The global biogeochemical carbon cycle. In: Bolin, B., Degens, E. T., Kempe, S. and Ketner, P. (eds), *The Global Carbon Cycle*. Wiley, Chichester, pp. 1–56.

Boorman, R. S., and Watson, D. M. (1976) Chemical processes in abandoned sulphide tailings dumps and environmental implication for Northeastern New Brunswick. *CIM. Bulletin*, **69**, 86–96.

Bouchard, R., and Conrad, H. R. (1973a) Sulfur requirement of lactating dairy cows. I. Sulfur balance and dietary supplementation. *J. Dairy Sci.*, **56**, 1276–1282.

Bouchard, R., and Conrad, H. R. (1973b) Sulfur requirement of lactating dairy cows. II. Utilization of sulfates, molasses, and lignin-sulfonate. *J. Dairy Sci.*, **56**, 1429–1434.

Bremner, J. M. (1977) Role of organic matter in volalization of sulfur and nitrogen from soils. In; *Proc. Symp. Soil Organic Matter Studies*, Vol. II. Braunschweig. Federal Republic of Germany 1976. International Atomic Energy Agency, Vienna, pp. 229–240.

Bremner, J. M., and Banwart, W. L. (1974) Identifying volatile S compounds by gas chromatography. *Sulphur Inst. J.*, **10**, 6–9.

Bremner, J. M., and Banwart, W. L. (1976) Sorption of sulfur gases by soils. *Soil Biol. Biochem.*, **8**, 79–83.

Bremner, J. M., and Steele, C. G. (1978) Role of microorganisms in the atmospheric sulfur cycle. *Adv. Microb. Ecol.*, **2**, 155–201.

Bromfield, A. R. (1972) Sulphur in Northern Nigeria soils. 1. The effects of cultivation and fertilizers on total S and sulphate patterns in soil profiles. *J. Agric. Sci.*, **78**, 465–470.

Brümmer, G., Grunwaldt, H.-S., and Schroeder, D. (1971) Contributions to the genesis and classification of marsh soils. III. Contents, oxidation states and bonding mechanisms of sulphur in polder soils. *Z. Pflanzenernaehr. Dueng Bodenk D.*, **129**, 92–108.

Buchner, A. (1958) The sulphur supply for agriculture in West Germany. *Landwirtsch. Forsch.*, **11**, 79–92 [in German].

Burbano, O. H., and Blasco, L. M. (1975) Volcanic soils of Nicaragua. II. Sulphur distribution and content. *Turrialba*, **25**, 429–435.

Burnett, W. E. (1969) Air pollution from animal wastes. Determination of malodors by gas chromatographic and organoleptic techniques. *Environ. Sci. Technol.*, **3**, 744–749.

Cadle, R. D. (1975) The sulfur cycle. In: Parker, H. S. (ed.), *Sulphur in the Environment*. Missouri Botanical Garden and Union Electric Company, St Louis, Missouri, pp. 1–13.

Cairns, R. R., and Beaton, J. D. (1976) Improving a solonetzic soil by nitrogen–sulphur materials. *Sulphur Inst. J.*, **12**, 10–12.

Cairns, R. R., and Bowser, W. E. (1969) *Solonetzic Soils and their Management.* Canada Dept. Agr. Pub. 1391. Ottawa, Ontario, 24 pp.

Carlson, D. A., and Gumerman, R. C. (1966) Hydrogen sulfide and methyl mercaptan removal with soil columns. In: *Proceedings of the 21st Industrial Waste Conference.* Purdue University, Lafayette, Indiana, pp. 177–191.

Carlson, D. A., and Leiser, C. P. (1966) Soil beds for the control of sewage odors. *J. Water Pollut. Control Fed.*, **38**, 829–840.

Chae, Y. M., and Lowe, L. E. (1980) Distribution of lipid sulphur and total lipids in soils of British Columbia. *Can. J. Soil. Sci.*, **60**, 633–640.

Chang, M. L., and Thomas, G. W. (1963) A suggested mechanism for sulfate adsorption by soils. *Soil Sci. Soc. Am. Proc.*, **27**, 281–283.

Chao, T. T., Harward, M. E., and Fang, S. C. (1962a) Movement of S35 tagged sulfate through soil columns. *Soil Sci. Soc. Am. Proc.*, **26**, 27–37.

Chao, T. T., Harward, M. E., and Fang, S. C. (1962b) Adsorption and desorption phenomena of sulfate ions in soils. *Soil Sci. Soc. Am. Proc.*, **26**, 234–237.

Chao, T. T., Harward, M. E., and Fang, S. C. (1962c). Soil constituents and properties in the adsorption of sulfate ions. *Soil Sci.*, **94**, 276–283.

Chao, T. T., Harward, M. E., and Fang, S. C. (1963) Cationic effects on sulfate adsorption by soils. *Soil Sci. Soc. Am. Proc.* **27**, 35–38.

Chao, T. T., Harward, M. E., and Fang, S. C. (1964) Iron and aluminium coatings in relation to sulfate adsorption characteristics of soils. *Soil Sci. Soc. Am. Proc.*, **28**, 632–635.

Chaudhry, I. A., and Cornfield, A. H. (1967a) Effect of moisture content during incubation of soil treated with organic materials on changes in sulphate and sulphide levels. *J. Sci. Food Agric.*, **18**, 38–40.

Chaudhry, I. A., and Cornfield, A. H. (1967b) Effect of temperature of incubation on sulphate levels in aerobic and sulphide levels in anaerobic soils. *J. Sci. Food Agric.*, **18**, 82–84.

Chow, W. T., and Ng, S. K. (1969) A preliminary study on acid sulphate soils in West Malaysia. *Malays. Agric. J.*, **47**, 253–267.

Clark, J. S., Gobin, C. A., and Sprout, P. N. (1961) Yellow mottles in some poorly drained soils of the lower Fraser Valley, British Columbia. *Can. J. Soil Sci.*, **41**, 218–227.

Clement, L. (1978) Sulphur increases availability of phosphorus in calcareous soils. *Sulphur in Agric.*, **2**, 9–12.

Cogbill, C. V., and Likens, G. E. (1974) Acid precipitation in northeastern United States. *Water Resour. Res.*, **10**, 1133–1137.

Coleman, R. (1966) The importance of sulfur as a plant nutrient in world crop production. *Soil Sci.*, **101**, 230–239.

Cook, L. J. (1939) Further results secured in 'top dressing' poor south-eastern pasture lands with phosphatic fertilizers. *J. Agric. South Aust.*, **42**, 791–865.

Cooper, P. J. M. (1972) Arylsulphatase activity in northern Nigerian soils. *Soil Biol. Biochem.*, **4**, 333–337.

Cormis, L. de (1968a) Contribution à l'étude de l'absorption du soufre par les plantes soumises à une atmosphère contenant due dioxyde de soufre. *Ann. Physiol. Veg. Univ. Brux.*, **10**, 99–112.

Cormis, L. de (1968b) Dégagement d'hydrogène sulfuré par des plantes soumises à une atmosphère contenant de l'anhydride sulfureux. *C. R. Hebd. Séances Acad. Sci., Ser D*, **226**, 683–685.

Cowling, D. W., and Jones, L. H. P. (1970). Deficiency in soil sulfur supplies for perennial ryegrass in England. *Soil Sci.*, **110**, 340–348.

Cox, G. L. (1975) Effects of smelter emissions on the soils of the Sudbury area. M.Sc. Thesis, University of Guelph, Guelph, Ontario.

Craze, B. (1980) Problems on the revegetation of mine spoil dumps. In: Freney, J. R. and Nicolson, A. J. (eds), *Sulfur in Australia.* Australian Academy of Science, Canberra, pp. 256–264.

Cregan, P. D., Sykes, J. A., and Dymock, A. J. (1979) Pasture improvement and soil acidification. *Agric. Gaz. N. S. W.*, **90**, 33–35.

Crutzen, P. J., Heidt, L. E., Krasnec, J. P., Pollock, W. H., and Seiler, W. (1979) Biomass burning as a source of atmospheric gases CO, H_2, N_2O, NO, CH_3Cl and COS. *Nature (Lond.)*, **282**, 253–256.

Dabin, B. (1972) Preliminary results of a survey of the sulphur contents of the soils of tropical Africa. Int. Symp. Sulphur in Agriculture. *Ann. Agron.*, **72**, 113–136 [in French].

Davidesco, D., and Palovski, G. (1965) Considerations on the sulfur content of soils in the Rumanian People's Republic. *Agrochimica*, **9**, 178–182.

Delver, P. (1962) Properties of saline soils in Iraq. *Neth. J. Agric. Sci.*, **10**, 194–210.

Doak, B. W. (1949) The fate of nitrogenous constituents in animals excreta when voided on soil. In: *Plant and Animal Nutrition in Relation to Soil and Climatic Factors.* British Commonwealth Scientific Specialist Conference, Australia, pp. 418–423.

Donald, C. M., and Williams, C. H. (1954) Fertility and productivity of a podzolic soil as influenced by subterranean clover (*Trifolium subterraneum* L.) and superphosphate. *Aust. J. Agric. Res*., **5**, 664–687.

Doneen, L. D. (1966) Effect of soil salinity and nitrates on tile drainage in San Joaquin Valley, California. University of California, Davis, Dept. Water Sci. Eng., Paper 4002, 48 pp.

Doyle, P. T. and Moir, R. J. (1979) Sulfur and methionine metabolism in sheep. III. Excretion and retention of dietary and supplemented sulfur and production responses to intraruminal infusions of DL-methionine. *Aust. J. Agric. Res.*, **30**, 1185–1196.

Dutil, P., and Ballip, J. L. (1979) Biochemical oxidation of different forms of sulphur in chalk soils of Champagne. *C.R. Hebd. Séances Acad. Agric. Fr.*, **65**, 370–375.

Elliott, L. F., and Travis, T. A. (1973) Detection of carbonyl sulfide and other gases emanating from beef cattle manure. *Soil Sci. Soc. Am. Proc.*, **37**, 600–702.

Emerson, W. W. (1977) Physical properties and structure. In: Russell, J. S. and Greacen, E. L. (eds), *Soil Factors in Crop Production in a Semi-Arid Environment*. University of Queensland Press, Brisbane, pp. 78–104.

Emerson, W. W., and Bakker, A. C. (1973) The comparative effects of exchangeable calcium, magnesium and sodium on some physical properties of red–brown earth subsoils. II. The spontaneous dispersion of aggregates in water. *Aust. J. Soil. Res.*, **11**, 151–157.

Ensminger, L. E. (1954) Some factors affecting the adsorption of sulfate by Alabama soils. *Soil Sci. Soc. Am. Proc.*, **18**, 259–264.

Eriksson, E. (1963) The yearly circulation of sulfur in nature. *J. Geophys. Res.*, **68**, 4001–4008.

Evans, C. A., and Rost, C. O. (1945) Total organic sulfur and humus sulfur of Minnesota soils. *Soil Sci.*, **59**, 125–136.

Faller, N. N. (1968) Der Schwefeldioxydgehalt der Luft als Koomponente der Schwefelversorgung der Pflanze. Diss. Doktorgrades, Inst. Pflanzenernährung, Justus Liebig Univ., Giessen, 120 pp.

Fedorov, M. V. (1954) *Soil Microbiology*. Izdatel'stvo Sovetskaya Nauka [in Russian].

Fleming, J. F., and Alexander, L. T. (1961) Sulfur acidity in South Carolina tidal marsh soils. *Soil Sci. Soc. Am. Proc.*, **25**, 94–95.

Flemons, K., and Siman, A. (1970) Goulburn lucerne failures linked with induced manganese toxicity. *Agric. Gaz. N.S.W.*, **81**, 664–687.

Fowler, D. (1976) Uptake of sulfur dioxide by crops and soil. Ph.D. Thesis, University of Nottingham.

Fowler, D. (1978) Dry deposition of SO_2 on agricultural crops. *Atmos. Environ.*, **12**, 369–373.

Fowler, D., and Unsworth, M. H. (1974) Dry deposition of sulphur dioxide on wheat. *Nature (Lond.)* **249**, 389–390.

Fox, R. L., Flowerday, A. D., Hosterman, F. W., Rhoades, H. F., and Olson, R. A. (1964a) Sulfur fertilizers for alfalfa production in Nebraska. *Nebr. Agric. Exp. Stn. Bull. 214*, 37 pp.

Fox, R. L., Olson, R. A., and Rhoades, H. F. (1964b) Evaluating the sulfur status of soils by plant and soil tests. *Soil Sci. Soc. Am. Proc.*, **28**, 243–246.

Frederick, L. R., Starkey, R. L., and Segal, W. (1957) Decomposability of some organic sulfur compounds in soil. *Soil Sci. Soc. Am. Proc.*, **21**, 287–292.

Freney, J. R. (1958) Determination of water-soluble sulfate in soils. *Soil Sci.*, **86**, 241–244.

Freney, J. R. (1961) Some observations on the nature of organic sulphur compounds in soil. *Aust. J. Agric. Res.* **12**, 424–432.

Freney, J. R., Barrow, N. J., and Spencer, K. (1962) A review of certain aspects of sulphur as a soil constituent and plant nutrient. *Plant Soil*, **17**, 295–308.

Freney, J. R., Melville, G. E., and Williams, C. H. (1969) Extraction, chemical nature, and properties of soil organic sulphur. *J. Sci. Food Agric.*, **20**, 440–445.

Freney, J. R., Melville, G. E., and Williams, C. H. (1970) The determination of carbon bonded sulfur in soil. *Soil Sci.*, **109**, 310–318.

Freney, J. R., Melville, G. E., and Williams, C. H. (1971) Organic sulphur fractions labelled by addition of ^{35}S-sulphate to soil. *Soil Biol. Biochem.*, **3**, 133–141.

Freney, J. R., Melville, G. E., and Williams, C. H. (1975) Soil organic matter fractions as sources of plant-available sulphur. *Soil Biol. Biochem.*, **7**, 217–221.

Freney, J. R., and Spencer, K. (1960) Soil sulphate changes in the presence and absence of growing plants. *Aust. J. Agric. Res.*, **11**, 339–345.

Freney, J. R., Stevenson, F. J., and Beavers, A. H. (1972) Sulfur-containing amino acids in soil hydrolysates. *Soil Sci.*, **114**, 468–476.

Freney, J. R., and Williams, C. H. (1980) Forms and amounts of sulfur in soils. In: Freney, J. R. and Nicolson, A. J. (eds), *Sulfur in Australia*. Australian Academy of Science, Canberra, pp. 170–175.

Fried, M. (1948) The absorption of sulfur dioxide by plants as shown by the use of radioactive sulfur. *Soil Sci. Soc. Am. Proc.*, **13**, 135–138.

Friend, J. P. (1973) The global sulfur cycle. In: Rasool, S. I. (ed.), *Chemistry of the Lower Atmosphere*. Plenum Press, New York, pp. 177–201.

Fuhr, I., Bransford, A. V., and Silver, S. D. (1948) Sorption of fumigant vapors by soil. *Science* (Wash. D.C.), **107**, 274–275.

Gachon, L. (1972) Sulphur losses by drainage. Intern. Symp. on Sulphur in Agriculture. *Ann. Agron.*, **72**, 11–21.

Galbally, I. E. (1980) Sulfur dioxide uptake at the Earth's surface. In: Freney, J. R. and Nicolson, A. J. (eds.), *Sulfur in Australia*. Australian Academy of Science, Canberra, pp. 71–74.

Galbally, I. E., Garland, J. A., and Wilson, M. J. G. (1979) Sulphur uptake from the atmosphere by forest and farmland. *Nature (Lond.)*, **280**, 49–50.

Gallagher, P. A. (1969) The effect of sulphur in fertilizers, rainwater and soils on crop nutrition. *Sci. Proc. R. Dublin Soc.*, **2B**, 191–204.

Galoppini, C. (1964) Lo zolfo nei depositi alluvionali della Toscana e la sua distribuzione in alcuni terreni tipici. *5^e Symp. Intern. Agrochimica*, Palermo, 225–233.

Garland, J. A. (1977) The dry deposition of sulphur dioxide to land and water surfaces. *Proc. R. Soc.* (*Lond.*) Ser. A, **354**, 245–268.

Garland, J. A. (1978) Dry and wet removal of sulphur from the atmosphere. *Atmos. Environ.*, **12**, 349–362.

Garland, J. A., and Branson, J. R. (1977) The deposition of sulphur dioxide to pine forest assessed by a radioactive method. *Tellus*, **29**, 445–454.

Ghiorse, W. C., and Alexander, M. (1976) Effect of microorganisms on the sorption and fate of sulfur dioxide and nitrogen dioxide in soil. *J. Environ. Qual.*, **5**, 227–230.

Gillman, G. P. (1973) Studies on some deep sandy soils in Cape York Peninsula, North Queensland. 3. Losses of applied phosphorus and sulphur. *Aust. J. Exp. Agric. Anim. Husb.*, **13**, 418–422.

Gjessing, Y. T., and Gjessing, E. T. (1973) Chemical composition of an Antarctic snow profile. *Vatten*, **3**, 233–237.

Gordan, A. G., and Gorham, E. (1963) Ecological aspects of air pollution from an iron-sintering plant at Wawa, Ontario. *Can. J. Bot.*, **41**, 1063–1078.

Gorham, E., and Gordan, A. G. (1960a) Some effects of smelter pollution N.E. of Falconbridge, Ontario. *Can. J. Bot.*, **38**, 307–312.

Gorham, E., and Gordan, A. G. (1960b) Influence of smelter fumes upon surrounding vegetation. *Can. J. Bot.*, **38**, 477–487.

Granat, L., Rodhe, H., and Hallberg, R. O. (1976) The global sulphur cycle. In: Svensson, B. H. and Söderlund, R. (eds), *Nitrogen, Phosphorus and Sulphur–Global Cycles.* SCOPE Report 7. *Ecol. Bull (Stockholm)*, **22**, 89–134.

Grant, R. C. N., Hughes, E. W., Moerman, J., and Colzer, D. T. (1964) Soil chemistry. In: *Ann. Rep. Agric. Research Council Central Africa*, pp. 15–21.

Green, V. E. Jr. (1957) The culture of rice on organic soils – a world survey. *Agron. J.*, **49**, 468–472.

Greenwood, D. J., and Lees, H. (1956) Studies on the decomposition of amino acids in soils. 1. A preliminary survey of techniques. *Plant Soil*, **7**, 253–262.

Gregg, P. E. H., and Goh, K. M. (1978) Field studies with radioactive sulphur-labelled gypsum fertilizer. I. Soil factors affecting the movement of fertilizer sulphur. *N.Z. J. Agric. Res.*, **21**, 593–601.

Gulimov, S., and Mukhanova, V. L. (1976) Content of sulphur and its forms in irrigated soils of Uzbekistan. *Pochvovedenie, No. 11*, 28–32 [in Russian].

Hanna, G. P. Jr., Lucas, J. R., Randles, C. I., Smith, E. E., and Brant, R. A. (1963) Acid mine drainage research potentialities. *J. Water Pollut. Control Fed.*, **35**, 275–296.

Haque, I., and Walmsley, D. (1972) Incubation studies on mineralization of organic sulphur and organic nitrogen. *Plant Soil*, **37**, 255–264.

Haque, I., and Walmsley, D. (1973) Adsorption and desorption of sulphate in some soils of the West Indies. *Geoderma*, **9**, 269–278.

Haque, I., and Walmsley, D. (1974a). Movement of sulphate in two Caribbean soils. *Plant Soil*, **40**, 145–152.

Haque, I., and Walmsley, D. (1974b) Sulphur investigations in some West Indian soils. *Trop. Agric.*, **51**, 253–263.

Harmsen, G. W., Quispel, A., and Otzen, D. (1954) Observations on the formation and oxidation of pyrite in the soil. *Plant Soil*, **5**, 324–348.

Harper, H. J. (1959) Sulfur content of Oklahoma soils, rainfall and atmosphere. *Okla. Agric. Exp. Stn. Bull. B-536*, 18 pp.

Hart, M. G. R. (1959) Sulphur oxidation in tidal mangrove soils of Sierra Leone. *Plant Soil*, **11**, 215–236.

Harter, R. D., and McLean, E. O. (1965) The effect of moisture level and incubation time on the chemical equilibria of a Toledo clay loam soil. *Agron. J.*, **57**, 583–588.

Harward, M. E., Chao, T. T., and Fang, S. C. (1962) The sulfur status and sulfur supplying power of Oregon soils. *Agron. J.*, **54**, 101–106.

Harward, M. E., and Reisenauer, H. M. (1966) Reactions and movement of inorganic soil sulfur. *Soil Sci.*, **101**, 326–335.

Hasan, S. M., Fox, R. L., and Boyd, C. C. (1970) Solubility and availability of sorbed sulfate in Hawaiian soils. *Soil Sci. Soc. Am. Proc.*, **34**, 897–901.

Hashimoto, H., Koda, T., and Mitsui, S. (1948) Effect of the addition of base and silica on degraded paddy soils. *J. Sci. Soil Manure, Tokyo*, **19**, 61–62.

Helyar, K. R. (1976) Nitrogen cycling and soil acidification. *J. Aust. Inst. Agric. Sci.*, **42**, 217–221.

Hesse, P. R. (1957) Sulphur and nitrogen changes in forest soils of East Africa. *Plant Soil*, **9**, 86–96.

Hilder, E. J. (1964) The distribution of plant nutrients by sheep at pasture. *Proc. Aust. Soc. Anim. Prod.*, **5**, 241–248.

Hingston, F. J. (1959) The loss of applied phosphorus and sulphur from soils under pasture in W. A. *J. Aust. Inst. Agric. Sci.*, **25**, 209–213.

Hitchcock, D. R. (1977) Biogenic contributions to atmospheric sulfate levels. In: Cecil, L. K. (ed.), *Proceedings of the Second National Conference on Complete*

WateReuse. Water's Interface with Energy Air and Solids. American Institute of Chemical Engineers, New York, pp. 291–310.

Hollingworth, S. E., and Banister, F. A. (1952) Basaluminite and hydrobasaluminite; two new minerals from Northamptonshire. *Mineral Mag.*, **29**, 1–17.

Hörnstrom, E., Ekström, C., Miller, U., and Dickson, W. (1973) Effects of the acidification of lakes in the Swedish west coast region. *Statens Naturvårdsverk*, 1973: **7**, Vallingby, Sweden, 97 pp.

Houghton, C., and Rose, F. A. (1976) Liberation of sulfate from sulfate esters by soils. *Appl. Environ. Microbiol.*, **31**, 969–976.

Hoyt, P. B., and Nyborg, M. (1972) Use of dilute calcium chloride for the extraction of plant-available aluminium and manganese from acid soil. *Can. J. Soil Sci.*, **52**, 163–167.

Hsu, P. H., and Bates, T. F. (1964) Formation of X-ray amorphous and crystalline aluminium hydroxides. *Mineral. Mag.*, **33**, 749–768.

Hutchinson, G. E. (1957) *A Treatise on Limnology*, vol. 1. Wiley, New York, 1015 pp.

Hutchinson, T. C., and Whitby, L. M. (1976) The effects of acid rainfall apd heavy metal particulates on a boreal forest ecosystem near the Sudbury smelting region of Canada. U.S. Department of Agriculture, Forest Service. *Tech. Rept. NE-23*, pp. 745–766.

Ismunadji, M., and Zulkarnaini, I. (1978) Sulphur deficiency of lowland rice in Indonesia. *Sulphur Agric.*, **2**, 17–19.

Ivanov, M. V. (1968) *Microbiological Processes in the Formation of Sulfur Deposits.* Israel Program for Scientific Translations, 298 pp.

Jackman, R. H. (1964) Accumulation of organic matter in some New Zealand soils under permanent pasture. I. Patterns of change of organic carbon, nitrogen, sulphur, and phosphorus. *N.Z. J. Agric. Res.*, **7**, 445–471.

Jenny, H. (1941) *Factors of Soil Formation.* McGraw-Hill, New York, 278 pp.

Johansson, O. (1959) On sulfur problems in Swedish agriculture. *K. Lantbrukshogsk. Ann.*, **25**, 57–169.

Jones, H. R. (1972) *Pollution Control in the Nonferrous Metals Industry*. Noyes Data Corp., Park Ridge, NJ, 201 pp.

Jones, L. H. P., Cowling, D. W., and Lockyer, D. R. (1972) Plant-available and -extractable sulfur in some soils of England and Wales. *Soil Sci.*, **114**, 104–114.

Jones, M. B., Martin, W. E., and Williams, W. A. (1968) Behavior of sulfate sulfur and elemental sulfur in three California soils in lysimeters. *Soil Sci. Soc. Am. Proc.*, **32**, 535–540.

Jones, M. B., Williams, W. A., and Martin, W. E. (1971) Effect of waterlogging and organic matter on the loss of applied sulfur. *Soil Sci. Soc. Am. Proc.*, **35**, 343–346.

Jones, M. B., and Woodmansee, R. G. (1979) Biogeochemical cycling in annual grassland ecosystems. *Bot. Rev.*, **45**, 111–114.

Jorgensen, B. B., Hansen, M. H., and Ingvarson, K. (1978) Sulfate reduction in coastal sediments and the release of H_2S to the atmosphere. In: Krumbein, W. E. (ed.), *Environmental Biogeochemistry and Geomicrobiology*, vol. 1. Ann Arbor Science, Michigan, pp. 245–253.

Junge, C. E. (1963) Sulfur in the atmosphere. *J. Geophys. Res.*, **68**, 3975–3976.

Kadota, H., and Ishida, Y. (1972) Production of volatile sulfur compounds by microorganisms. *Annu. Rev. Microbiol.*, **26**, 127–138.

Kamprath, E. J., Nelson, W. L., and Fitts, J. W. (1956) The effect of pH, sulfate and phosphate concentrations on the adsorption of sulfate by soils. *Soil Sci. Soc. Am. Proc.*, **20**, 463–466.

Kanivets, V. I. (1970) Reaction of hydrogen, methane, and hydrogen sulfide with the mineral part of the soil. *Pochvovedenie*, No. 5, 52–59.

Kanwar, J. S., and Takkar, P. N. (1964) Distribution of sulphur forms in tea soils of the Punjab. *J. Res. Punjab Agric. Univ.*, **1**, 1–15.

Katz, M., Wyatt, F. A., and Atkinson, H. J. (1939) The hydrogen ion concentration, base-exchange capacity and sulfate content of soils. In: *Effects of SO_2 on Vegetation* (National Research Council, Report No. 815), Ch. 5. NRC, Ottawa, pp. 131–164.

Kelley, W. P. (1951) *Alkali Soils, their Formation, Properties, and Reclamation*, Reinhold, New York, 176 pp.

Kellogg, W. W., Cadle, R. D., Allen, E. R., Lazrus, A. L., and Martell, E. A. (1972) The sulfur cycle. *Science* (Wash. D.C.), **175**, 587–596.

Kelly, D. P. (1972) Transformations of sulphur and its compounds in soils. *Symp. Internat. sur le Soufre in Agric.* Versailles (1970), pp. 217–232.

Kennedy, P. M., and Siebert, B. D. (1972) The utilization of spear grass (*Heteropogon contortus*). II. The influence of sulphur on energy intake and rumen and blood parameters in cattle and sheep. *Aust. J. Agric. Res.*, **23**, 45–56.

Kennedy, P. M., Williams, E. R., and Siebert, B. D. (1975) Sulfate recycling and metabolism in sheep and cattle. *Aust. J. Biol. Sci.*, **28**, 31–42.

Kilmer, V. J., Gilliam, J. W., Lutz, J. F., Joyce, R. T., and Eklund, C. D. (1974) Nutrient loss from fertilized grassed watersheds in western North Carolina. *J. Environ. Qual.*, **3**, 214–219.

Kodama, H., and Singh, S. S. (1972) Hydroxy aluminum sulfate–montmorillonite complex. *Can. J. Soil Sci.*, **52**, 208–218.

Kohn, G. D., Osborne, G. J., Batten, G. D., Smith, A. N., and Lill, W. J. (1977) The effect of topdressed superphosphate on changes in nitrogen : carbon : sulphur : phosphorus and pH on a red earth soil during a long term grazing experiment. *Aust. J. Soil Res.*, **15**, 147–158.

Kondo, M. (1923) The production of mercaptan from l-cystine by bacteria. *Biochem. Z.*, **136**, 198–202.

Korkman, J. (1973) Sulphur status of Finnish cultivated soils. *Maataloustiet Aikak.*, **45**, 121–215.

Kovda, V. A. (1973) *The Principles of Pedology. General Theory of Soil Formation*, vol. 2. Nauka, Moscow, pp. 421–425 [in Russian].

Kramer, J. R. (1978) Acid precipitation. In: Nriagu, J. O. (ed.), *Sulfur in the Environment.* Wiley, New York, pp. 325–370.

Krouse, H. R. (1977) Sulphur isotope abundance elucidate uptake of atmospheric sulphur emissions by vegetation. *Nature (Lond.)*, **265**, 45–46.

Krupskii, N. K., and Mamontova, E. G. (1974) Sulphur in typical thick chernozems of the Ukrainian SSR. *Trans. 10th Int. Congress Soil Sci.*, **II**, 168–173 [in Russian].

Krupskii, N. K., Mamontova, E. G., and Batsula, A. A. (1971) Sulfur content in humic and fulvic acids of some Ukranian soils. *Pochvovedenie*, No. 10, 37–41 [in Russian].

Kuhn, H., and Weller, H. (1977) Six-year studies on sulphur inputs from precipitation and losses by leaching (in lysimeters). *Z. Pflanzenernaehr. Dueng Bodenk D.*, **140**, 431–440 [in German].

Langlands, J. P., Sutherland, H. A. M., and Playne, M. J. (1973) Sulfur as a nutrient for Merino sheep. 2. The utilization of sulphur in forage diets. *Br. J. Nutr.*, **30**, 537–543.

Laurence, R. C. N., Gibbons, R. W., and Young, C. T. (1976) Changes in the yield, protein, oil and maturity of groundnut cultivars with application of sulphur fertilizers and fungicides. *J. Agric. Sci.*, **86**, 245–250.

Leeper, G. W. (1952) *Introduction to Soil Science*. 2nd edn, Melbourne University Press, Melbourne, 222 pp.

Lewis, J. A., and Papavizas, G. C. (1970) Evolution of volatile sulfur-containing compounds from decomposition of crucifers in soils. *Soil Biol. Biochem.*, **2**, 239–246.

Li, P., and Caldwell, A. C. (1966) The oxidation of elemental sulfur in soil. *Soil Sci. Soc. Am. Proc.*, **30**, 370–372.

Lichtenwalner, D. C., Flenner, A. L., and Gordon, N. E. (1923) Adsorption and replacement of plant food in colloidal oxides of iron and aluminum. *Soil Sci.*, **15**, 157–165.

Likens, G. E. (1972) *The Chemistry of Precipitation in the Central Finger Lakes Region.* Cornell University, Water Resource and Marine Science Center Tech. Rept. T50, Ithaca, N.Y., 47 pp.

Likens, G. E., Wright, R. F., Galloway, J. N., and Butler, T. J. (1979) Acid rain. *Sci. Am.*, **241**, 39–47.

Lipsett, J., and Williams, C. H. (1971) The sulphur status of wheat in red-brown earths in southern New South Wales. *Aust. J. Exp. Agric. Anim. Husb.*, **11**, 59–63.

Little, R. C. (1957) Sulphur in soils. II. Determination of the total sulphur content of soil. *J. Sci. Food Agric.*, **8**, 271–279.

Lockyer, D. R., Cowling, D. W., and Fenlon, J. S. (1978) Laboratory measurements of dry deposition of sulphur dioxide on to several soils from England and Wales. *J. Sci. Food Agric.*, **29**, 739–746.

Lotero, J., Woodhouse, W. W. Jr., and Petersen, R. G. (1966) Local effect on fertility of urine voided by grazing cattle. *Agron. J.*, **58**, 262–265.

Loveday, J. (1975) The use of sulphur and its compounds in soil amendment. In: McLachlan, K. D. (ed.), *Sulphur in Australasian Agriculture.* Sydney University Press, Sydney, pp. 163–171.

Loveday, J., and Pyle, J. (1973) The Emerson dispersion test and its relation to hydraulic conductivity. Aust. CSIRO Div. Soils, Tech. Paper. No. 15.

Lovelock, J. E., Maggs, R. J., and Rasmussen, R. A. (1972) Atmospheric dimethyl sulphide and the natural sulphur cycle. *Nature (Lond.)*, **237**, 452–453.

Lowe, L. E. (1964) An approach to the study of the sulfur status of soils and its application to selected Quebec soils. *Can. J. Soil Sci.*, **44**, 176–179.

Lowe, L. E. (1965) Sulfur fractions of selected Alberta soil profiles of the chernozemic and podzolic orders. *Can. J. Soil Sci.*, **45**, 297–303.

Lowe, L. E. (1969) Sulfur fractions of selected Alberta profiles of the gleysolic order. *Can. J. Soil Sci.*, **49**, 375–381.

Lowe, L. E., and De Long, W. A. (1963) Carbon bonded sulphur in selected Quebec soils. *Can. J. Soil Sci.*, **43**, 151–155.

McClung, A. C., De Freitas, L. M. M., and Lott, W. L. (1959) Analyses of several Brazilian soils in relation to plant responses to sulphur. *Soil Sci. Soc. Am. Proc.*, **23**, 221–224.

McFee, W. W., Kelly, J. M., and Beck, R. H. (1976) Acid precipitation effects on soils in the humid temperature zone. US Department of Agriculture, Forest Service. *Tech. Rept. NE-23*, pp. 725–736.

McGeorge, W. T., Breazeale, E. L., and Abbott, J. L. (1956) Polysulfides as soil conditioners. *Ariz. Agric. Exp. Stn Bull. 131*, 3–29.

McGeorge, W. T., and Green, R. A. (1935) Oxidation of sulfur in Arizona soils and its effect on soil properties. *Ariz. Agric. Exp. Stn Bull. 59*, 299–325.

McGovern, P. C. (1972) *Sulphur Dioxide Levels and Environmental Studies in the Sudbury Area during 1971*. Ministry of the Environment, Air Quality Branch, Sudbury, Ontario, 33 pp.

McGovern, P. C., and Balsillie, D. (1973) *Sulphur Dioxide (1972) – Heavy Metal (1971) Levels and Vegetative Effects in the Sudbury area.* Ministry of the Environment, Air Quality Branch, Sudbury, Ontario, 50 pp.

McIntyre, D. S. (1979) Exchangeable sodium, subplasticity and hydraulic conductivity of some Australian soils. *Aust. J. Soil Res.*, **17**, 115–120.

McKee, A. G. (1969) *Systems Study for Control of Emissions. Primary Nonferrous*

Smelting Industry. Final report US National Technical Information Service PB184884. Washington, DC, 190 pp.

McKell, C. M., and Williams, W. A. (1960) A lysimeter study of sulfur fertilization of an annual-range soil. *J. Range Manage.*, **13**, 113–117.

Mackenzie, A. F., De Long, W. A., and Ghanem, I. S. (1967) Total sulfur, acetate-extractable sulfur and isotopically exchangeable sulfate in some eastern Canadian soils. *Plant Soil*, **27**, 408–414.

McLachlan, K. D., and De Marco, D. G. (1975) Changes in soil sulphur fractions with fertilizer additions and cropping treatments. *Aust. J. Soil Res.*, **13**, 169–176.

McLaren, R. G., and Swift, R. S. (1977) Changes in soil organic sulphur fractions due to the long term cultivation of soils. *J. Soil Sci.*, **28**, 445–453.

Malmer, N. (1974). *On the Effects on Water, Soil and Vegetation of an increasing Atmospheric Supply of Sulphur*. National Swedish Environmental Protection Board SNVPM 402E, Solna, 125 pp.

Mamaril, C. P., Pangerang Umar, A., Manwan, I., and Momuat, C. J. S. (1976) *Sulphur Response of Lowland Rice in South Sulawesi, Indonesia.* Contrib. Cent. Res. Inst. Agric. Bogor, 22 pp.

Mann, L. D., Focht, D. D., Joseph, H. A., and Stolzy, L. H. (1972) Increased denitrification in soils by additions of sulfur as an energy source. *J. Environ. Qual.*, **1**, 329–332.

Massoumi, A., and Cornfield, A. H. (1964) Total sulphur and water-soluble sulphate contents of soils and their relation to other soil properties. *J. Sci. Food Agric.*, **15**, 623–625.

Massoumi, A., and Cornfield, A. H. (1965) Sulphate levels in soil of varying pH during incubation with organic materials. *J. Sci. Food Agric.*, **16**, 565–568.

May, P. F., Till, A. R., and Downes, A. M. (1968) Nutrient cycling in grazed pastures I. A preliminary investigation of the use of (^{35}S) gypsum. *Aust. J. Agric. Res.*, **19**, 531–543.

Metson, A. J., and Blackmore, L. C. (1978) Sulphate retention by New Zealand soils in relation to the competitive effect of phosphate. *N.Z. J. Agric. Res.*, **21**, 243–253.

Misra, R. D. (1938) Edaphic factors in the distribution of aquatic plants in English lakes. *J. Ecol.*, **26**, 411–451.

Mitchell, J., Dehn, J. E., and Dion, H. G. (1952) The effect of small additions of elemental sulphur on the availability of phosphate fertilizers. *Sci. Agric.*, **32**, 311–316.

Mitsui, S. (1956) *Inorganic Nutrition, Fertilization and Soil Amelioration of Lowland Rice*, 3rd edn, Yokendo, Tokyo, Japan, 107 pp.

Mitsui, S., Aso, S., and Kumazawa, K. (1951) Dynamic studies on nutrient uptake by crop plant. Pt 1. The nutrient uptake of rice root as influenced by hydrogen sulfide. *J. Sci. Soil Manure, Tokyo*, **22**, 46–52.

Miyamoto, S. (1977) Predicting effects of sulfuric acid on qualities of irrigation and drainage waters in calcareous soils. *J. Environ. Qual.*, **6**, 12–18.

Miyamoto, S., Bohn, H. L., Ryan, J., and Yee, M. S. (1974) Effect of sulfuric acid and sulfur dioxide on the aggregate stability of calcareous soils. *Soil Sci.*, **118**, 299–303.

Miyamoto, S., Ryan, J., and Stroehlein, J. L. (1975) Potentially beneficial uses of sulfuric acid in south western agriculture. *J. Environ. Qual.*, **4**, 431–437.

Miyamoto, S., and Stroehlein, J. L. (1975) Sulfuric acid for increasing water penetration into some Arizona soils. *Prog. Agric. Ariz.*, **27**, 13–16.

Mohammed, E. T. Y., Letey, J., and Branson, R. (1979) Sulphur compounds in water treatment – effect on infiltration rate. *Sulphur Agric.*, **3**, 7–11.

Moje, W., Munnecke, D. E., and Richardson, L. T. (1964) Carbonyl sulphide, a volatile fungitoxicant from nabam in soil. *Nature (Lond.)*, **202**, 831–832.

Moormann, F. R. (1963) Acid sulfate soils (cat-clays) of the tropics. *Soil Sci.*, **95**, 271–275.

Morozov, A. Z. (1972) Effects of sulfur feed supplements on the productivity of ewes. *Tr. Alma-At. Zoovet. Inst.*, **24**, 185–187.

Mortimer, C. H. (1941) The exchange of dissolved substances between mud and water in lakes. *J. Ecol.*, **29**, 280–329.

Mortvedt, J. J., and Giordano, P. M. (1973) Grain sorghum response to iron in a ferrous sulfate–ammonium thiosulfate–ammonium polyphosphate suspension. *Soil Sci. Soc. Am. Proc.*, **37**, 951–955.

Moser, U. S., and Olson, R. V. (1952) Sulfur oxidation in four soils as influenced by moisture tension and bacteria. *Soil Sci.*, **76**, 251–257.

Moss, M. R. (1975) Spatial patterns of sulphur accumulation by vegetation and soils around industrial centres. *J. Biogeography*, **2**, 205–222.

Muller, F. B. (1975) Sulphur received in rainfall and leached from a yellow brown loam. *N.Z. J. Sci.*, **18**, 243–252.

Munnecke, D. E., Domsch, K. H., and Eckert, J. W. (1962) Fungicidal activity of air passed through columns of soil treated with fungicides. *Phytopathology*, **52**, 1298–1306.

Nakayama, F., and Scott, A. D. (1962) Gas sorption by soils and clay minerals 1. Solubility of oxygen in moist materials. *Soil Sci.*, **94**, 106–110.

Neller, J. R. (1959) Extractable sulfate sulfur in soils of Florida in relation to amount of clay in the profile. *Soil Sci., Soc. Am. Proc.*, **23**, 346–348.

Neptune, A. M. L., Tabatabai, M. A., and Hanway, J. J. (1975) Sulfur fractions and carbon–nitrogen–phosphorus–sulfur relationships in some Brazilian and Iowa soils. *Soil Sci. Soc. Am. Proc.*, **39**, 51–55.

Nicolson, A. J. (1970) Soil sulphur balance studies in the presence and absence of growing plants. *Soil Sci.*, **109**, 345–350.

Nielson, R. F., and Peterson, H. B. (1972) Treatment of mine tailings to promote vegetative stabilization. *Utah Agric. Exp. Stn. Bull.* **485**, 22 pp.

Nikolov, N. (1964) Total sulphur content of the basic soil types of Bulgaria. *Rozteniev Nauki*, **1**, 23–30 [in Bulgarian].

Northcote, K. H., and Skene, J. K. M. (1972) *Australian Soils with Saline and Sodic Properties.* CSIRO Aust. Soil Publ. No. 27, 62 pp.

Nriagu, J. O. (1978) Production and uses of sulfur. In: Nriagu, J. O. (ed.), *Sulfur in the Environment*, Pt I. Wiley, New York, pp. 1–21.

Nyborg, M. (1978) Sulfur pollution and soils. In: Nriagu, J. O. (ed.), *Sulfur in the Environment*, Pt II. Wiley, New York, pp. 359–390.

Nyborg, M., Crepin, J., Hocking, D., and Baker, J. (1977) Effect of sulphur dioxide on precipitation and on the sulphur content and acidity of soils in Alberta, Canada. *Water Air Soil Pollut*, **7**, 439–448.

Ødelien, M. (1965) Investigations on the leaching of sulphate from soil. *Forsk. Fors. Landbruket*, **16**, 39–76.

Odynets, R. N., Perelygina, V. S., and Mossorova, R. (1972) Use of sulfur preparations in the feeding of sheep. *Izv. Akad. Nauk. Kirg. SSR*, Ser. Biol. Nauk, No. 5, 46–52 [in Russian].

Ogoleva, V. P., and Vershinina, G. A. (1976) Sulphur content and its distribution in soils of the Volgogrod Region. *Agrokhimiya*, No. 3, 89–91 [in Russian].

Okajima, H., and Takagi, S. (1953) Physiological behavior of hydrogen sulfide in the rice plant. Part 1. Effect of hydrogen sulfide on the absorption of nutrients. *Sci. Rep. Res. Inst. Tôhoku Univ.*, Ser. D, **5**. 21–31.

Okajima, H., and Takagi, S. (1955) Physiological behaviour of hydrogen sulfide in the rice plant. Part 2. Effect of hydrogen sulfide on the content of nutrients in the rice plant. *Sci. Rep. Res. Inst. Tôhoku Univ. Ser. D*, **6**, 89–99.

Okajima, H., and Takagi, S. (1956) Physiological behaviour of hydrogen sulfide in the rice plant. Part 4. Effect of hydrogen sulfide on the distribution of radioactive P^{32} in the rice plant. *Sci. Rep. Res. Inst. Tôhoku Univ, Ser. D*, **7**, 107–113.

Oke, O. L. (1967) The sulphur status of Nigerian soils. *J. Indian Soc. Soil. Sci.*, **15**, 207–208.

Olivero, C. (1960) Reserves of organic-sulphur compounds in Italian soils. *Ann. Stn Chim. Agrar. Sper. Roma*, Ser. 3, No. 179, 1–5 [in Italian].

Olsen, R. A. (1957) Absorption of sulphur dioxide from the atmosphere by cotton plants. *Soil Sci.*, **84**, 107–111.

Osborne, G. J., Wright, W. A., and Sykes, J. (1978). Increasing soil acidity threatens farming system. *Agric. Gaz. N.S.W.*, **89**, 21.

Overrein, L. N. (1972) Sulfur pollution patterns observed; leaching of calcium in forest soil determined. *Ambio*, **1**, 145–147.

Overrein, L. N. (1978) Changes in soil productivity through acidification. *Trans. 11th Congress Intern. Soil Sci. Soc.*, **3**, 260–278.

Overstreet, R., Martin, J. C., and King, H. M. (1951) Gypsum, sulfur and sulfuric acid for reclaiming an alkali soil of the Fresno Series. *Hilgardia*, **21**, 113–127.

Owers, M. J., and Powell, A. W. (1974) Deposition velocity of sulphur dioxide on land and water surfaces using a ^{35}S tracer method. *Atmos. Environ.*, **8**, 63–68.

Pallotta, U., Sandri, G., and Rossi, N. (1964) Sulphur in the soils of Emilia, *5ᵉ* Symp. Intern. Agrochimica. Palermo, 276–290 [in Italian].

Patrick, W. H., and Mikkelsen, D. S. (1971) Plant nutrient behaviour in flooded soil. In: Olson, R. A., Army, T. J., Hanway, J. J., and Kilmer, V. J. (eds), *Fertilizer Technology and Use.* Soil Sci. Soc. Am., Madison, pp. 187–215.

Paul, E. A., and Schmidt, E. L. (1961) Formation of free amino acids in rhizosphere and nonrhizosphere soil. *Soil Sci. Soc. Am. Proc.*, **25**, 259–362.

Payrissat, M., and Beilke, S. (1975) Laboratory measurements of the uptake of sulphur dioxide by different European soils. *Atmos. Environ.*, **9**, 211–217.

Petersen, R. G., Lucas, H. L., and Woodhouse, W. W. Jr. (1956) Distribution of excreta by freely grazing cattle and its effect on pasture fertility 1. Excretal distribution. *Agron. J.*, **48**, 440–444.

Piper, C. S., and de Vries, M. P. C. (1964) The residual value of superphosphate on a red–brown earth in South Australia. *Aust. J. Agric. Res.*, **15**, 234–272.

Ponnamperuma, F. N. (1972) The chemistry of submerged soils. *Adv. Agron.*, **24**, 29–96.

Prather, R. J., and Rhoades, J. D. (1975) Sulphuric acid as an amendment for reclaiming soils high in boron. *Agron. Abs.*, **121.**

Probert, M. E. (1974) The sulphur status of some North Queensland soils. In: McLachlan, K. D. (ed.), *Handbook on Sulphur in Australian Agriculture*. CSIRO, Melbourne, pp. 64–68.

Probert, M. E. (1976) Studies of 'available' and isotopically exchangeable sulphur in some North Queensland soils. *Plant Soil*, **45**, 461–475.

Probert, M. E. (1977) The distribution of sulphur and carbon–nitrogen–sulphur relationships in some north Queensland soils. Aust CSIRO Div. Soils Tech. Paper No. 31, 20 pp.

Probert, M. E. (1980) Effect of soil forming processes on the distribution of sulfur in soils. In: Freney, J. R. and Nicolson, A. J. (eds), *Sulfur in Australia*, Australian Academy of Science, Canberra, pp. 158–169.

Pund, W. A. (1969) Sulphur improves urea-treated corn silage. *Sulphur Inst. J.*, **5**, 7–9.

Putnam, H. D., and Schmidt, E. L. (1959) Studies on the free amino acid fractions of soils. *Soil Sci.*, **87**, 22–27.

Ralph, B. J. (1980) Weathering of sulfur in rocks. In: Freney, J. R. and Nicolson, A. J. (eds), *Sulfur in Australia*. Australian Academy of Science, Canberra, pp. 146–157.

Rasmussen, K. H., Taheri, M., and Kabel, R. L. (1975) Global emissions and natural processes for removal of gaseous pollutants. *Water Air Soil Pollut.*, **4**, 33–64.

Reddy, C. S., and Mehta, B. V. (1970) Relationship of carbon, nitrogen and sulphur in Gujarat soils. *Indian J. Agric. Sci.*, **40**, 630–633.

Rehm, G. W., and Caldwell, A. C. (1968) Sulfur supplying capacity of soils and the relationship to soil type. *Soil Sci.*, **105**, 355–361.

Rendig, V. V., and Weir, W. C. (1957) Evaluation by lamb feeding tests of alfalfa hay grown on a low-sulphur soil. *J. Anim. Sci.*, **16**, 451–461.

Rhoades, J. D., and Bernstein, L. (1971) Chemical, physical and biological characteristics of irrigation and soil water. In: Ciaccio, L. L. (ed.), *Water and Water Pollution Handbook*, vol. 1. Marcel Dekker, New York, pp. 141–222.

Rhue, R. D., and Kamprath, E. J. (1973) Leaching losses of sulphur during winter months when applied as gypsum, elemental S or prilled S. *Agron. J.*, **65**, 603–605.

Richards, L. A. (1954) *Diagnosis and Improvement of Saline and Alkali Soils*. Handbook No. 60, US Department of Agriculture, 160 pp.

Richardson, H. L. (1938) The nitrogen cycle in grassland soils with especial reference to the Rothamsted Park grass experiment. *J. Agric. Sci.*, **28**, 73–121.

Roberts, B. R. (1974) Foliar absorption of atmospheric SO_2 by woody plants. *Environ. Pollut.*, **7**, 133–140.

Robinson, E., and Robbins, R. C. (1968) *Sources, Abundance and Fate of Gaseous Atmospheric Pollutants*. Final Report, Project PR-6755, Stanford Research Institute, Menlo Park, California, 110 pp.

Roy, A. B., and Trudinger, P. A. (1970) *The Biochemistry of Inorganic Compounds of Sulphur*. Cambridge University Press, Cambridge, UK, 400 pp.

Ruhal, D S., and Paliwal, K. V. (1978) Status and distribution of sulphur in soils of Rajasthan. *J. Indian Soc. Soil Sci.*, **26**, 352–358.

Russell, E. J. (1973) *Soil Conditions and Plant Growth*, 10th edn. Longman, London, 849 pp.

Russell, J. S. (1960) Soil fertility changes in the long term experimental plots at Kybybolite, South Australia. 1. Changes in pH, total nitrogen, organic carbon and bulk density. *Aust. J. Agric. Res.*, **11**, 902–926.

Ryan, J., and Stroehlein, J. L. (1974) Use of sulfuric acid on phosphorus deficient Arizona soils. *Prog. Agric. Ariz.*, **25**, 11–13.

Saalbach, E. (1965/66) The influence of sulfur on the yield of forage crops in West Germany. *Sulphur Inst. J.*, **1**, 7–9.

Saalbach, E. (1966) Sulphur fertilization and protein quality. *Sulphur Inst. J.*, **2**, 2–5.

Sachdev, M. S., and Chhabra, P. (1974) Transformations of ^{35}S-labelled sulfate in aerobic and flooded soil conditions. *Plant Soil*, **41**, 335–341.

Salsbury, R. L., and Merricks, D. L. (1975) Production of methanethiol and dimethyl sulfide by rumen microorganisms. *Plant Soil*, **43**, 191–209.

Saran, A. B. (1949) Some observations on an obscure disease of paddy, *Oryza sativa*. *Curr. Sci.*, **18**, 378–379.

Schalscha, E. B., Estrada, C., and Galindo, G. G. (1972) Sulphur status of some volcanic ash derived soils in Chile. *Agrochimica*, **16**, 77–82.

Schwertmann, U. (1961) The occurrence and origin of jarosite (maibolt) in marshy soil. *Naturwissenschaften*, **48**, 159–160.

Scott, N. M. (1976) Sulphate contents and sorption in Scottish soils. *J. Sci. Food Agric.*, **27**, 367–372.

Scott, N. M., and Anderson, G. (1976) Sulphur, carbon and nitrogen contents of organic fractions from acetylacetone extracts of soils. *J. Soil. Sci.*, **27**, 324–330.

Sears, P. D., Goodall, V. C., and Jackman, R. H. (1965) Pasture growth and soil fertility. IX. Repeated cropping of a soil previously under high-quality permanent pasture. *N.Z. J. Agric. Res.*, **8**, 497–510.

Seim, E. C. (1970) Sulfur dioxide absorption by soil. Ph.D. Thesis. University of Minnesota, 138 pp.

Sen, A. T. (1938) Further experiments on the occurrence of depressed yellow patch of paddy in the Mandalay farm. *Burma Dept. Agric. Rept. 1937–1938*, pp. 35–36.

Shedd, O. M. (1928) Influence of sulfur and gypsum on the solubility of potassium in soils and on the quantity of this element removed by certain plants. *Soil Sci.*, **22**, 335–354.

Shepherd, J. G. (1974) Measurements of the direct deposition of sulphur dioxide onto grass and water by the profile method. *Atmos. Environ.*, **8**, 69–74.

Shiga, H., and Suzuki, S. (1964) Studies on the behavior of hydrogen sulfide in water-logged soils. Part 8. Influence of free hydrogen sulfide in soils on the growth of rice plants. *Bull. Chugoku Nat. Agric. Exp. Stn.*, Ser. **A10**, 113–130.

Shioiri, M. (1943) *Chemistry of Paddy Soils*. Japanese Agricultural Society, Dai Nihon Nokai, Tokyo, 64 pp.

Shkonde, E. I. (1957) The role of sulphur in plant nutrition. *Dokl. Vses Akad. SKH. Nauk*, No. 2, 22–25 [in Russian].

Shukla, U. C., and Gheyi, A. K. (1971) Sulphur status of some Rajasthan soils. *Indian J. Agric. Sci.*, **41**, 247–253.

Sikora, L. J., and Keeney, D. R. (1976) Evaluation of a sulfur–*Thiobacillus denitrificans* nitrate removal system. *J. Environ. Qual.*, **5**, 298–303.

Siman, G., and Jansson, S. L. (1976a) Sulphur exchange between soil and atmosphere, with special attention to sulphur release directly to the atmosphere. 1. Formation of gaseous sulphur compounds in soil. *Swed. J. Agric. Res.*, **6**, 37–45.

Siman, G., and Jansson, S. L. (1967b) Sulphur exchange between soil and atmosphere, with special attention to sulphur release directly to the atmosphere. 2. The role of vegetation in sulphur exchange between soil and atmosphere. *Swed. J. Agric. Res.*, **6**, 135–144.

Simon-Sylvestre, G. (1965) Annual evolution of sulphur in soil compared to that of nitrogen. *C.R. Hebd. Séances Acad. Agric. Fr.*, 426–431 [in French].

Simon-Sylvestre, G. (1967a) Observations on the annual cycle of sulphur in soil under a moderately wet climate. *Agrochimica*, **12**, 60–68 [in French].

Simon-Sylvestre, G. (1967b) New observations on the annual cycle of sulphur and nitrogen in soil. *C.R. Hebd. Séances Acad. Agric. Fr.*, 90–96 [in French].

Simon-Sylvestre, G. (1969a) Soluble sulphates in soil. *Ann. Agron.*, **20**, 435–447 [in French].

Simon-Sylvestre, G. (1969b) First results of a survey on the total sulphur content of arable soils in France. *Ann. Agron.*, **20**, 609–625 [in French].

Simon-Sylvestre, G. (1972) Sulphur in soils – Its evolution. Int. Symp. on Sulphur in Agriculture, Versailles, 3–4 Dec. 1970. *Ann. Agron.*, **72**, 181–199 [in French].

Singh, B. R., Uriyo, A. P., and Kilasara, M. (1979) Sorption of sulphate and distribution of total sulphate and mineralisable sulphur in some tropical soil profiles in Tanzania. *J. Sci. Food Agric.*, **30**, 8–14.

Singh, S. S. (1967) Sulfate ions and ion activity product (Al) $(OH)^3$ in Wyoming suspensions. *Soil Sci.*, **104**, 433–438.

Singh, S. S., and Brydon, J. E. (1967) Precipitation of aluminium by calcium hydroxide in the presence of Wyoming bentonite and sulfate ions. *Soil Sci.*, **103**, 162–167.

Singh, S. S., and Brydon, J. E. (1969) Solubility of basic aluminium sulfates at equilibrium in solution and in the presence of montmorillonite. *Soil Sci.*, **107**, 12–16.

Sklodovski, P. (1969) Sulphur distribution in the profiles of some soil types in Poland. *Rocz. Glebozn.*, **19**, 99–119 [in Polish].

Smith, K. A., Bremner, J. M., and Tabatabai, M. A. (1973) Sorption of gaseous atmospheric pollutants by soils. *Soil Sci.*, **116**, 313–319.

Smith, M. S., Francis, A. J., and Duxbury, J. M. (1977) Collection and analysis of organic gases from natural ecosystems: application to poultry manure. *Environ. Sci. Technol.*, **11**, 51–55.

Smittenberg, J., Harmsen, G. W., Quispel, A., and Otzen, D. (1951) Rapid methods for determining different types of sulphur compounds in soil. *Plant Soil*, **3**, 353–360.

Sowden, F. J. (1955) Estimation of amino acids in soil hydrolysates by the Moore and Stein method. *Soil Sci.*, **80**, 181–188.

Sowden, F. J. (1956) Distribution of amino acids in selected horizons of soil profiles. *Soil Sci.*, **82**, 491–496.

Sowden, F. J. (1958) The forms of nitrogen in the organic matter of different horizons of soil profiles. *Can. J. Soil Sci.*, **38**, 147–154.

Spálený, J. (1977) Sulphate transformation to hydrogen sulphide in spruce seedlings. *Plant Soil*, **48**, 557–563.

Spedding, D. J. (1969a) Uptake of sulphur dioxide by barley plants at low sulphur dioxide concentrations. *Nature (Lond.)*, **224**, 1229–1231.

Spedding, D. J. (1969b) Sulphur dioxide uptake by limestone. *Atmos. Environ.*, **3**, 683.

Spek, J. van der (1950) Katteklei. *Versl. Landbouwkd. Onderz.*, **56**(2), 1–40.

Spencer, K. (1975) Sulphur requirements of plants. In: McLachlan, K. D. (ed.), *Sulphur in Australasian Agriculture*. Sydney University Press, Sydney, pp. 98–109.

Stace, H. C. T., Hubble, G. D., Brewer, R., Northcote, K. H., Sleeman, J. R., Mulcahy, M. J., and Hallsworth, E. G. (1968) *A Handbook of Australian Soils*. Rellim, Glenside, SA, 435 pp.

Stallings, J. H. (1957) *Soil Conservation*. Prentice-Hall, Englewood Cliffs, NJ. 575 pp.

Starkey, R. L. (1966) Oxidation and reduction of sulfur compounds in soils. *Soil. Sci.*, **101**, 297–306.

Stepanov, D. G., and Yakimchuk, E. F. (1973) Effect of sulfur containing compounds on the live weight and wool productivity of Ascanian fine wooled ewe lambs. *Trudy Kishinev. SKH. Inst.*, **113**, 72–78 [in Russian].

Stevenson, F. J. (1956) Isolation and identification of some amino compounds in soils. *Soil Sci. Soc. Am. Proc.*, **20**, 201–208.

Stewart, B. A., Porter, L. K., and Viets, F. G. Jr. (1966a) Effect of sulfur content of straws on rates of decomposition and plant growth. *Soil Sci. Soc. Am. Proc.*, **30**, 355–358.

Stewart, B. A., Porter, L. K., and Viets, F. G. Jr. (1966b) Sulfur requirements for decomposition of cellulose and glucose in soil. *Soil Sci. Soc. Am. Proc.* **30**, 453–456.

Stewart, B. A., and Whitfield, C. J. (1965) Effect of crop residue soil temperature and sulfur on the growth of winter wheat. *Soil Sci. Soc. Am. Proc.*, **29**, 752–755.

Stotzky, G., and Norman, A. G. (1961) Factors limiting microbial activities in soil. II. The effect of sulfur. *Arch. Mikrobiol.*, **40**, 370–382.

Stromberg, L. K., and Tisdale, S. L. (1979) Treating irrigated arid-land soils with acid-forming sulphur compounds. *Tech. Bull. 24*. The Sulphur Institute, Washington, 26 pp.

Suzuki, S., and Shiga, H. (1956) Studies on physical and chemical characteristics of Akiochi paddy soils. Part 2. Relation between production of free hydrogen sulfide and Akiochi degree. *Bull. Chugoku Nat. Agric. Exp. Stn.*, **3**, 69–80.

Swaby, R. J., and Fedel, R. (1973) Microbial production of sulphate and sulphide in some Australian soils. *Soil Biol. Biochem.*, **5**, 773–781.

Swanson, C. O., and Latshaw, W. L. (1922) Sulfur as an important fertility element. *Soil Sci.*, **14**, 421–430.

Sylvester, R. O., and Seabloom, R. W. (1962) *A Study on the Character and Significance of Irrigation Return Flows in the Yakima River Basin.* Univ. Washington. Dept. Civil Engineering, 104 pp.

Sylvester, R. O., and Seabloom, R. W. (1963) Quality and significance of irrigation return flow. *J. Irrig. Drain. Div. Am. Soc. Civ. Engrs*, **89**, 1–27.

Tabatabai, M. A., and Bremner, J. M. (1972a) Forms of sulfur, and carbon, nitrogen and sulfur relationships in Iowa soils. *Soil Sci.*, **114**, 380–386.

Tabatabai, M. A., and Bremner, J. M. (1972b) Distribution of total and available sulfur in selected soils and soil profiles. *Agron. J.*, **64**, 40–44.

Takai, Y., and Asami, T. (1962). Formation of methyl mercaptan in paddy soils. 1. *Soil Sci. Pl. Nutr.*, **8**, 40–44.

Takijima, Y. (1963) Studies on behavior of the growth inhibiting substances in paddy soils with special reference to the occurrence of root damage in the peaty paddy field. *Bull. Natn. Inst. Agric. Sci. Ser. B.*, **13**, 117–252.

Tamiya, N. (1951a) Aerobic decomposition of cystine by *Escherichia coli.* I. *J. Chem. Soc. Japan*, **72**, 118–121.

Tamiya, N. (1951b) Aerobic decomposition of cystine by *Escherichia coli.* II. *J. Chem. Soc. Japan*, **72**, 121–124.

Tamm, C. F. (1976) Acid precipitation – biological effects on soil and on forest vegetation. *Ambio* **5**, 235–238.

Tarr, H. L. A. (1933a) Anaerobic decomposition of 1-cystine by washed cells of *Proteus vulgaris. Biochem. J.*, **27**, 759–763.

Tarr, H. L. A. (1933b) Enzymic formation of hydrogen sulfide by certain heterotrophic bacteria. *Biochem. J.*, **27**, 1869–1874.

Temple, K. L., and Delchamps, E. W. (1953) Autotrophic bacteria and the formation of acid in bituminous coal mines. *Appl. Microbiol.*, **1**, 255–258.

Terman, G. L. (1978) Atmospheric sulphur—the agronomic aspects. *Tech. Bull. No. 23.* The Sulphur Institute, Washington, 15 pp.

Terraglio, F. P., and Manganelli, R. M. (1966) The influence of moisture on the adsorption of atmospheric sulfur dioxide by soil. *Int. J. Air Water Pollut.*, **10**, 783–791.

Thomas, E. E. (1936) Reclamation of black-alkali soils with various kinds of sulfur. *Hilgardia*, **19**, 127–142.

Thomas, M. D., Hendricks, R. H., and Hill, G. R. (1944) Some chemical reactions of sulfur dioxide after absorption by alfalfa and sugar beets. *Plant Physiol.*, **19**, 212–226.

Thomas, M. D., and Hill, G. R. (1937) Relation of sulfur dioxide in the atmosphere to photosynthesis and respiration of alfalfa. *Plant Physiol.*, **12**, 309–383.

Thorne, D. W. (1944) The use of acidifying materials on calcareous soils. *J. Am. Soc. Agron.*, **36**, 815–828.

Thorup, J. T. (1972) Soil sulphur application: a new approach. *Sulphur Inst. J.*, **8**, 16–17.

Till, A. R. (1975) Sulphur cycling in grazed pastures. In: McLachlan, K. D. (ed.), *Sulphur in Australasian Agriculture.* Sydney University Press, Sydney, pp. 68–75.

Till, A. R. (1980) Sulphur cycling in soil–plant–animal systems. In: Freney, J. R. and Nicolson, A. J. (eds), *Sulfur in Australia.* Australian Academy of Science, Canberra, pp. 204–217.

Till, A. R., and McCabe, T. P. (1976) Sulfur leaching and lysimeter characterization. *Soil Sci.*, **121**, 44–47.

Till, A. R., and May, P. F. (1971) Nutrient cycling in grazed pastures. IV. The fate of sulphur-35 following its application to a small area in a grazed pasture. *Aust. J. Agric. Res.*, **22**, 391–400.

Tisdale, S. L. (1970) The use of sulphur compounds in irrigated aridland agriculture. *Sulphur Inst. J.*, **6**, 2–7.

Tisdale, S. L., Davis, R. L., Kingsley, A. F., and Mertz, E. T. (1950) Methionine and cystine content of two strains of alfalfa as influenced by different concentrations of the sulphate ion. *Agron. J.*, **42**, 221–225.

Tisdale, S. L., and Nelson, W. L. (1966) *Soil Fertility and Fertilizers*. Macmillan, New York, 694 pp.

Tiwari, R. C., and Ram, M. (1973) Distribution of different forms of sulphur in soils of Varanasi. *Bhartiya Krishi Anusandhan Patrika*, **1**, 33–38 [in Hindustani].

Toews, B. (1973) Deep plowing solonetzic soils in Alberta. *Proc. 17th Manitoba Soil Sci. Meeting*, Winnipeg, Manitoba, 5–6 Dec., pp. 107–111.

Toxopeus, M. R. J. (1970) Sulphur deficiency in grassland on young soils from volcanic ash and its possible prediction by laboratory tests. *Proc. XI Intern. Grassl. Cong.*, 345–346.

Trudinger, P. A. (1975) The biogeochemistry of sulphur. In: McLachlan, K. D. (ed.), *Sulphur in Australasian Agriculture*, Sydney University Press, Sydney, pp. 11–20.

Tsuji, T. (1975) Sulphur supplying power of Japanese grassland soils. *JARQ*, **9**, 142–147.

Turco, R. P., Whitten, R. C., Toon, O. B., Pollack, J. B., and Hamill, P. (1980) OCS, stratospheric aerosols and climate. *Nature (Lond.)*, **283**, 283–286.

Val'nikov, I. U. (1970) Forms of sulfur in forest–steppe soils of the Tatar ASSR and role of sulfur in soil fertility. *Agrokhimiya, No. 2*, 60–64 [in Russian].

Val'nikov, I. U., Grishin, P. V., and Lomako, E. I. (1971) Sulphur in compact Chuvash chernozems. *Agrokhimiya*, No. 8, 93–96 [in Russian].

Val'nikov, I. U., and Mishin, A. M. (1974) The forms of sulphur in soils of the central Volga. *Agrokhimiya*, No. 12, 112–118 [in Russian].

Vâmos, R. (1964) The release of hydrogen sulphide from mud. *J. Soil Sci.*, **15**, 103–109.

Vandecaveye, S. C., Horner, G. M., and Keaton, C. M. (1936). Unproductivenesss of certain orchard soils as related to lead arsenate spray accumulations. *Soil Sci.*, **42**, 203–215.

Venkateswarlu, J., Subbiah, B. V., and Tamhane, R. V. (1969) Vertical distribution of forms of sulphur in selected rice soils of India. *Indian J. Agric. Sci.*, **39**, 426–431.

Virmani, S. M., and Kanwar, J. S. (1971) Distribution of forms of sulphur in six soil profiles of north-East India. *J. Indian Soc. Soil Sci.*, **19**, 73–77.

Vishniac, W., and Santer, M. (1957) The thiobacilli. *Bacteriol. Rev.*, **21**, 195–213.

Vitolins, M. I., and Swaby, R. J. (1969) Activity of sulphur-oxidising microorganisms in some Australian soils. *Aust. J. Soil Res.*, **7**, 171–183.

Wagnon, K. A., Bentley, J. R., and Green, L. R. (1958) Steer gains on annual-plant range pastures fertilized with sulphur. *J. Range Manage.*, **11**, 177–182.

Walker, P. H. (1972) Seasonal and stratigraphic controls in coastal flood plain soils. *Aust. J. Soil Res.*, **10**, 127–142.

Walker, T. W. (1957) The sulfur cycle in grassland soils. *J. Br. Grassl. Soc.*, **12**, 10–18.

Walker, T. W., and Adams, A. F. R. (1958) Studies on soil organic matter. I. Influence of phosphorus content of parent materials on accumulations of carbon, nitrogen, sulfur and organic phosphorus in grassland soils. *Soil Sci.*, **85**, 307–318.

Walker, T. W., and Adams, A. F. R. (1959) Studies on soil organic matter: 2. Influence of increased leaching at various stages of weathering on levels of carbon, nitrogen, sulfur and organic and total phosphorus. *Soil Sci.*, **87**, 1–10.

Walker, T. W., and Gregg, P. E. H. (1975) The occurrence of sulphur deficiency in

New Zealand. In: McLachlan, K. D. (ed.), *Sulphur in Australasian Agriculture*. Sydney University Press, Sydney, pp. 145–153.

Walker, T. W., Thapa, B. K., and Adams, A. F. R. (1959) Studies on soil organic matter: 3. Accumulation of carbon, nitrogen, sulfur, organic and total phosphorus in improved grassland soils. *Soil Sci.*, **87**, 135–140.

Walton, G. (1966) Agricultural waste water; treatment and recycling for agricultural waste. *Proc. Symp. on Agric. Waste Water*, Davis, Univ. Calif., 6–8 Apr., 1966, pp. 273–281 (Calif. Univ. Water Resources Center. Rep. 10).

Wang, C. H. (1978) Sulphur fertilization of rice. *Sulphur Agric.*, **2**, 13–16.

Wang, C. H., Liem, T. H., and Mikkelsen, D. S. (1976a) Sulfur deficiency—a limiting factor in rice production in the Lower Amazon basin. I. Development of sulfur deficiency as a limiting factor for rice production. *IRI Bull. 47*, New York, 46 pp.

Wang, C. H., Liem, T. H., and Mikkelsen, D. S. (1976b) Sulfur deficiency—a limiting factor in rice production in the Lower Amazon basin II. Sulfur requirement for rice production. *IRI Bull. 48*, New York, 38 pp.

Warth, F. J., and Krishnan, T. S. (1935) Sulfur and sulfate balance experiments with sheep. *Indian J. Vet. Sci. Anim. Husb.*, **5**, 319–331.

Watson, E. R. (1969) The influence of subterranean clover pastures on soil fertility. III. The effect of applied phosphorus and sulphur. *Aust. J. Agric. Res.*, **20**, 447–456.

Watson, K. A. (1964) Fertilizers in Northern Nigeria. Current Utilization and Recommendations for their Use. *Samaru Res. Bull.* 38, 20 pp.

Wedepohl, K. H. (1978) *Handbook of Geochemistry*. Springer-Verlag, Berlin.

Weir, R. G. (1975) The oxidation of elemental sulphur and sulphides in soil. In: McLachlan, K. D. (ed.), *Sulphur in Australasian Agriculture*. Sydney University Press, Sydney, pp. 40–49.

Whitehead, D. C. (1964) Soil and plant-nutrition aspects of the sulphur cycle. *Soils Fert.*, **27**, 1–8.

Widdowson, J. P., and Hanway, J. J. (1974) Available sulfur status of some representative Iowa soils, *Iowa Agric. Exp. Stn Res. Bull.*, No. 579, 714–736.

Wiklander, L. (1973) The acidification of soil by acid precipitation. *Grundforbattring*, **26**, 155–164.

Wiklander, L., and Hallgren, G. (1949) Studies on Gyttja soils. I. Distribution of different sulfur and phosphorus forms and of iron manganese and calcium carbonate in a profile from Kungsängen. *K. Lantbrukshogsk. Ann.*, **16**, 811–827.

Williams, C. (1975a) The distribution of sulphur in the soils and herbage of North West Pembrokeshire. *J. Agric. Sci.*, **84**, 445–452.

Williams, C. H. (1967) Some factors affecting the mineralization of organic sulphur in soils. *Plant Soil*, **26**, 205–223.

Williams, C. H. (1968) Seasonal fluctuations in mineral sulphur under subterranean clover pasture in southern New South Wales. *Aust. J. Soil Res.*, **6**, 131–139.

Williams, C. H. (1974) The chemical nature of sulphur in some New South Wales soils. In: McLachlan, K. D. (ed.), *Handbook on Sulphur in Australian Agriculture*. CSIRO, Melbourne, pp. 16–23.

Williams, C. H. (1975b) The chemical nature of sulphur compounds in soils. In: McLachlan, K. D. (ed.), *Sulphur in Australasian Agriculture*, Sydney University Press, Sydney, pp. 21–30.

Williams, C. H. (1980) Soil acidification under clover pasture. *J. Aust. Inst. Agric. Sci.*, **20**, 561–567.

Williams, C. H., and David, D. J. (1976) Effects of pasture improvement with subterranean clover and superphosphate on the availability of trace metals to plants. *Aust. J. Soil Res.*, **14**, 85–93.

Williams, C. H., and Donald, C. M. (1957) Changes in organic matter and pH in a podzolic soil as influenced by subterranean clover and superphosphate. *Aust. J. Agric. Res.*, **8**, 179–189.

Williams, C. H., and Lipsett, J. (1961) Fertility changes in soils cultivated for wheat in southern New South Wales. *Aust. J. Agric. Res.*, **12**, 612–629.

Williams, C. H., and Steinbergs, A. (1958). Sulphur and phosphorus in some eastern Australian soils. *Aust. J. Agric. Res.*, **9**, 483–491.

Williams, C. H., and Steinbergs, A. (1959) Soil sulphur fractions as chemical indices of available sulphur in some Australian soils. *Aust. J. Agric. Res.*, **10**, 340–352.

Williams, C. H., and Steinbergs, A. (1962) The evaluation of plant-available sulphur in soils: I. *Plant Soil*, **17**, 279–294.

Williams, C. H., and Steinbergs, A. (1964) The evaluation of plant available sulfur in soils. II. *Plant Soil*, **21**, 50–62.

Williams, C. H., Williams, E. G., and Scott, N. M. (1960) Carbon, nitrogen sulphur and phosphorus in some Scottish soils. *J. Soil Sci.*, **11**, 334–346.

Wilson, L. G., Bressan, R. A., and Filner, P. (1978) Light-dependent emission of hydrogen sulfide from plants. *Plant Physiol.*, **61**, 184–189.

Wolt, J. D., and Adams, F. (1979) The release of sulfate from soil-applied basaluminite and alunite. *Soil Sci. Soc. Am. J.*, **43**, 118–121.

Wrenford, M. (1968) Nutritional deficiencies of white clover *Trifolium repens* in improved pastures of New England. M. Rur. Sci. Thesis, Univ. of New England, 175 pp.

Yamane, I., and Sato, I. (1961) Metabolism in muck paddy soil. Part 3. Role of soil organic matter in the evolution of free hydrogen sulfide in water-logged soil. *Sci. Rep. Res. Inst Tôhoku Univ., Ser.* **D12**, 73–86.

Yamane, I., Usami, T., Ikeda, K., and Omukai, S. (1956) Influence of root damange by hydrogen sulfide on the rice growth. *Bull. Tôhoku Nat. Agric. Exp. Str.*, **10**, 134–155.

Yee, M. S., Bohn, H. L., and Miyamoto, S. (1975) Sorption of sulfur dioxide by calcareous soils. *Soil Sci. Soc. Am. Proc.*, **39**, 268–270.

Yoneda, S. (1958) Salt damage and soil (3). *Agr. and Hort.*, **33**, 1337–1342.

Young, A. (1969) Present rate of land erosion. *Nature (Lond.)*, **224**, 851–852.

ZoBell, C. E. (1963) Organic geochemistry of sulfur. In: Breger, I. A. (ed.), *Organic Geochemistry*. Macmillan, New York, pp. 543–578.