AP42 Section:	9.2.1
Background Ch	4
Reference:	26
Title:	B. W. Roch and N. M. Scott, "Sulphur Em... o Sulphur in So... *Pro...rnational Symposium on Sulphur Emissions and the Environment*, 1:242-254, 1979.

The cover sheet to this reference is incorrect. It should read, "ATMOSPHERIC SULPHUR THE AGRONOMIC ASPECTS, Technical Bulletin Number 23, by GL Terman. March 1978.

Sect 4
#26

ATMOSPHERIC SULPHUR— THE AGRONOMIC ASPECTS

by

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Technical Bulletin Number 23

The Sulphur Institute
1725 K Street, N.W., Washington, D.C. 20006

March 1978

PREFACE

Sulphur dioxide—to most people this brings to mind a picture of a noxious gas, harmful to plants and animals. It is a paradox that this same gas, when present in low concentrations, can in some cases, be essential to plants.

In many areas, atmospheric sulphur is an important source of this essential plant nutrient. As antipollution regulations are being enforced, less sulphur dioxide will be permitted to escape to the atmosphere from electric utilities, smelters, and other sources. At the same time, crop yields are being boosted by higher rates of fertilizer use and other improved farming practices. As the yields go up, so does the crop's need for sulphur. In many areas of the U.S., sulphur must already be included in the fertilizer program to ensure maximum crop yields. As less sulphur is emitted to the atmosphere, these areas will become more numerous and widespread.

The Sulphur Institute is pleased to have the opportunity of publishing this review of the agronomic importance of atmospheric sulphur, authored by Gilbert L. Terman, a distinguished scientist at the Tennessee Valley Authority's National Fertilizer Development Center.

Russell Coleman
President
The Sulphur Institute

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1.0 INTRODUCTION

Sulphur (S) is usually termed a secondary nutrient, but should be considered one of the major nutrients essential for plant growth, along with N, P, and K; crop requirements are similar to those for P. Sulphur is needed for the synthesis of certain amino acids, and hence for proteins, including enzymes and glucosides.

If S is moderately deficient, growth is stunted and the foliage is light green in color. If S is extremely deficient, growth is very stunted and the foliage is yellow to yellow-white in color (74). Growth rates and yields may also be reduced at low plant concentrations of S without visual deficiencies being apparent. Deficiencies of S and N are frequently confused because of the similarity of symptoms.

In addition to permitting high crop yields, adequate S results in higher crop protein content and quality, higher Vitamin A content, better baking quality of bread flour, and darker green color of turf grasses and conifers. Sulphur deficiency results in lower feed intake in cattle, and may result in lower milk and meat production (1,29).

As shown in Figures 1 and 2, the S and N cycles among the atmosphere, plants, animals, soil, and water have marked similarities. The greatest proportion of N exists in the atmosphere as N_2, which is not directly available to plants. Various microorganisms, however, fix N_2 as amino-N (NH_2-N) which is utilized by plants. The atmosphere contains only a small fraction of the S supply; a much greater proportion is in bodies of water, soil organic matter, and minerals (8). Kellog et al. (44), Buckman and Brady (10), Burns (12), and others have also described the S cycle.

It is well known that high concentrations of SO_2 in air are not good for plants or animals, including man. However, these harmful effects are emphasized much more often than are the beneficial effects of moderate amounts. Kamprath (43), Oppold et al. (59), and others have discussed beneficial aspects of SO_2 in the atmosphere, and a discussion group of the U.K. Department of the Environment and the National Environment Research Council (80) surveyed both beneficial and detrimental aspects of atmospheric S.

Ross (68), Grennard and Ross (31), and Megonnell (52) in particular, have questioned the importance of the SO_2 problem. They even suggest that it is as much a problem of legislation as it is of emission. Grennard and Ross reported increases in high-level (high stack) SO_2 emissions in England since 1950 but actual decreases in low- and medium-level emissions. This has been accompanied by increased leaf spot diseases of roses grown in urban gardens, which were controlled by higher ground-level SO_2 concentrations (53).

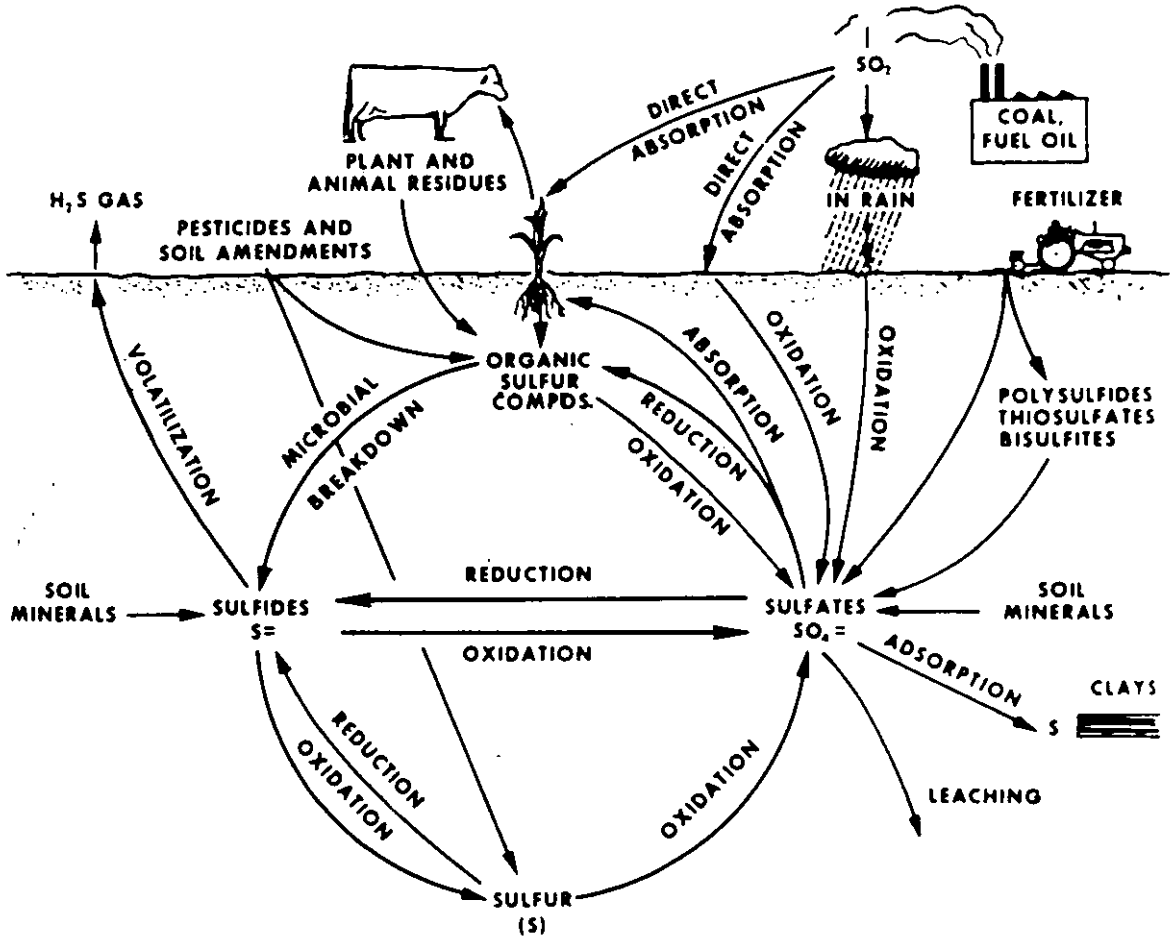

Fig. 1: The sulphur cycle (10).

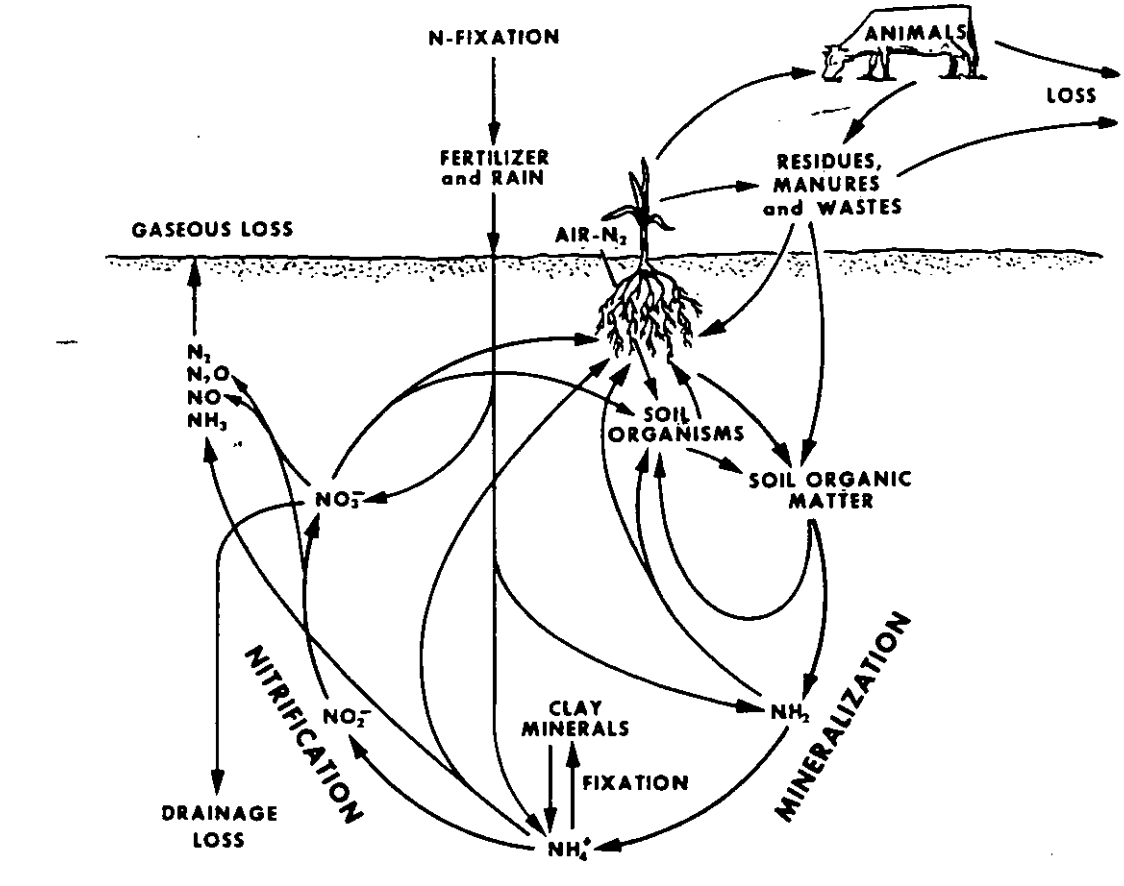

Fig. 2: The nitrogen cycle (10).

2.0 SULPHUR REQUIREMENTS OF CROPS

The amounts of S absorbed by moderate yields of crops range from about 9 to 39 kg/ha (19), and are similar to the amounts of P absorbed. Amounts of S absorbed by the current higher crop yields (Table 1) range from a low of 13 kg/ha for rice to a high of 96 kg/ha for sugarcane. Crops such as grasses, corn, and small grains use the lowest amounts of S; and cabbage, turnips, alfalfa, and surgarcane the most.

The estimated U.S. total land use for 10 principal crops harvested in 1973 was about 113 million ha. Assuming an average crop removal (for grain, hay, cotton, and tobacco) of 18.5 kg of S/ha, these 10 crops would require about 2.1 million tons of S. This S is currently supplied by the soil, from atmospheric S, organic wastes, fertilizers, and other sources.

An amount equivalent to about 1.0 million tons of S is applied in fertilizers annually in the U.S. The potential annual consumption of plant-nutrient S in the U.S. is between 2.5 and 4 million tons, depending on the methods and assumptions used (4, 5). In many industrialized areas the burning of fossil fuels now supplies more than enough S for crop needs. If this source of SO_2 emissions into the atmosphere is greatly reduced, the need for applying fertilizer S for satisfactory crop yields will increase.

Table 1. Sulphur content of crops.

Crops	Yield Tons/ha	Total S Content kg/ha
Grain and oil crops		
Barley (*Hordeum vulgare* L.)	5.4	22
Corn (*Zea Mays* L.)	11.2	34
Grain sorghum (*Sorghum bicolor* L. Moench)	9.0	43
Oats (*Avena sativa* L.)	3.6	22
Rice (*Oryza sativa* L.)	7.8	13
Wheat (*Triticum aestivum* L.)	5.4	22
Peanuts (*Arachis hypogaea* L.)	4.5	24
Soybeans (*Glycine max Merr.*)	4.0	28
Hay crops		
Alfalfa (*Medicago sativa* L.)	17.9	45
Clover-grass	13.4	34
Bermudagrass (*Cynodon dactylon* L.)		
Common	9.0	17
Coastal	22.4	50
Bromegrass (*Bromus inermis Leyss.*)	11.2	22
Orchardgrass (*Dactylis glomerata* L.)	13.4	39
Pangolagrass (*Digitaria decumbens Stent*)	26.4	52
Timothy (*Phleum pratense* L.)	9.0	18
Cotton and tobacco		
Cotton (lint + seed) (*Gossypium hirsutum* L.)	4.3	34
Tobacco (*Nicotiana tabacum* L.)		
Burley	4.5	21
Flue cured	3.4	50
Fruit, sugar, and vegetable crops		
Beets		
Sugar (*Beta saccharifera*)	67	50
Table (*Beta vulgaris* L.)	56	46
Cabbage (*Brassica oleracea*)	78	72
Irish potatoes (*Solanum tuberosum* L.)	56	27
Onions (*Allium cepa* L.)	67	41
Oranges (*Citrus* sp.)	52	31
Pineapple (*Ananas comosus*)	40	16
Sugarcane (*Saccharum officinarum* L.)	224	96

Estimates by Potash/Phosphate Institute of North America.

3.0 NON-ATMOSPHERIC SOURCES OF S

3.1 Soils and Irrigation Water

In humid regions most of the S in soils is present in the proteins of soil organic matter, as sulphate ion in the soil solution, or is held by the clay fraction. Soils having medium to high contents of organic matter seldom respond to applied S because of release from this source. The SO_4-S may be reduced to H_2S and partially lost to the atmosphere by volatilization if the soil is flooded for long periods, such as in swamps or rice paddies.

The S in organic matter is gradually released as SO_4-S for crop growth as a result of decomposition (oxidation) by organisms. Freney et al. (26) found the HI-reducible organic S in 15 soils amounted to about 50% of the total. The remaining organic S was in the form of amino acids. The average ratio of total C, N, and S in a wide range of soils is about 140:10:1.3 (10). Apparently, few measurements of the release of S from soil organic matter have been made. Experiments with ^{15}N have shown only 2 to 3% annual release of immobilized N. Assuming a similar maximum release of S, about 18 kg of S/ha/year might be released from a soil containing 5% organic matter. A corresponding value for a soil containing 1% organic matter is 3.6 kg/ha/year. Thus, only soils naturally high in organic matter or those receiving large amounts of crop residues can supply total crop needs for S from organic matter decomposition.

Table 2. Sulphur-deficient areas (74).

UNITED STATES	CANADA	SOUTH AND CENTRAL AMERICA
Alabama	Alberta	Argentina
Alaska	British Columbia	Brazil
Arkansas	Manitoba	Chile
California	Ontario	Costa Rica
Colorado	Saskatchewan	Honduras
Florida		Venezuela
Georgia	**EUROPE**	Windward Islands
Hawaii	Czechoslovakia	
Idaho	France	
Indiana	Germany	
Iowa	Iceland	**AFRICA**
Kansas	Ireland	Ghana
Louisiana	Netherlands	Kenya
Maryland	Norway	Malawi
Michigan	Poland	Nigeria
Minnesota	Spain	Senegal
Mississippi	Sweden	South Africa
Missouri	Yugoslavia	Tanzania
Montana		Uganda
Nebraska	**AUSTRAL-ASIA**	Upper Volta
North Carolina	Australia	Zambia
North Dakota	Fiji, Solomon Islands	
Ohio	New Guinea	**ASIA**
Oklahoma	New Zealand	Ceylon
Oregon		India
South Carolina		Japan
South Dakota		
Tennessee		
Texas		
Virginia		
Washington		
Wisconsin		

Sulphate is readily leached from sandy soils. However, some soils having sandy surface horizons have fine-textured layers in lower horizons which adsorb SO_4 (40). Many such soils occur in the Atlantic and Gulf Coastal Plains of the U.S. Such soils may be S deficient for early growth of cotton or other crops, but may be adequate in S as the roots penetrate to clay horizons. Deep sandy soils, however, may be S deficient throughout the growing season.

The amount of available S in soils is commonly determined by extraction with phosphate solutions or 0.5 *M* $NaHCO_3$ solution at pH 8.5 (18). Retention of SO_4-S is greatest in soils high in sesquioxides and is greater by kaolinitic than by montmorillonitic clays. Application of phosphate fertilizers tends to decrease SO_4-S retention by soils (17). Retention increases with increase in acidification (33). In general, predominantly sand- and silt-textured soils in humid areas, especially in areas of high winter rainfall, retain applied soluble SO_4-S one year or less (51).

In arid regions, SO_4-S tends to accumulate in subsoils as gypsum because of insufficient rainfall to leach through the profile. Drainage water from soils in these areas may contain high concentrations of SO_4-S. Irrigation water in arid regions usually supplies adequate or more than adequate amounts of S for crops. Coal mine spoils and a few soils may contain pyrites which supply S.

3.2 Fertilizers

Prior to about 1950, commercial fertilizers were based primarily on ordinary superphosphate, which contains S as gypsum [OSP, 18-20% P_2O_5 (8-9% P) and 14% S]. Ammonium sulphate (AS, 21% N and 24% S) was a leading source of N. Use of these low-analysis fertilizers generally supplied adequate S for the crops. More recently, the contents of N, P, and K in fertilizers have been increased greatly relative to S, and in most high-analysis grades, little or no S is present. Numerous cropping areas have now been identified as having soils which are S deficient (Table 2).

As a result, some states require that S be added to fertilizers. For example, Alabama requires that all mixed fertilizers sold in the State contain a minimum of 3% S. Sources of S added to fertilizers include AS, OSP, elemental S, sulphuric acid, gypsum, potassium sulphate (18% S), and potassium magnesium sulphate (23% S). Thiosulphates or polysulphides are also added to fluid fertilizers. Bixby and Beaton (7) provide a more detailed discussion of S in fertilizers.

3.3 Pesticides

Finely ground elemental S for dusting and lime-elemental S mixtures for dusting and spraying were once used extensively as fungicides. These materials provided adequate and even excessive amounts of S for needs of the crops on which they were used. In more recent years more effective organic pesticides have been developed, largely replacing those containing elemental S. Some organic formulations also contain small amounts of S, but total S application rates are much lower than with older pesticides.

4.0 ATMOSPHERIC SOURCES OF S

Sulphur exists in the atmosphere as SO_2, as SO_4-S in aerosols, H_2SO_4, particulate matter, as H_2S, and methylmercaptan (CH_3SH).

4.1 Burning of Fossil Fuels

Large-scale burning of coal and fuel oil in steam electric generating plants, heating plants, other industrial activities, transportation, and for home heating is now recognized as a major source of SO_2 in the atmosphere. The amounts of S introduced into the atmosphere estimated by Robinson and Robbins (66) are shown in Table 3.

Only about one-third of atmospheric S is estimated to be of man-made origin. The sources of SO_2 are considered to be 70% from burning of coal, 16% from petroleum combustion, 4% from petroleum refining, and 10% from smelting of ores. Other estimates of total release of S to the atmosphere range up to 405 million tons annually (21).

Global circulation of atmospheric pollutants has been discussed by Newell (57) and others. It has been estimated (48) that 70% of the atmospheric S over Sweden is from anthropogenic sources and that 77% of this originates outside Sweden. Kellog et al. (44) estimated that man is contributing half as much atmospheric S now as is nature, but will contribute equally as much by A.D. 2000.

Table 3. Emissions of sulphur to the atmosphere (66).

	Annual emissions of S, tons × 10^6		
Source	Northern	Southern	Total
SO_2 sources	68	5	73
Biological H_2S			
Land	49	19	68
Marine	13	17	30
Sea spray	19	25	44
Total	149 (69%)	66 (31%)	215

4.2 SO_2 Abatement

The U.S. Congress, the U.S. Environmental Protection Agency (EPA), and state agencies have decreed that present SO_2 emissions in the U.S. must be reduced. The chief continuing questions are by how much and at what cost.

Potential SO_2 emission abatement in the U.S. in 1975 was estimated from EPA data (11) to be equivalent to 6.7 million tons of S from fossil-fueled power plants alone. Throwaway methods involving scrubbing of stack gases in slurries of crushed limestone (15, 71) now seem to be the most feasible for reducing SO_2 emissions from existing and some new fossil fuel-fired power plants. For older plants the cost may be too high for continued profitable operation. In addition, huge amounts of spent limestone slurry are generated. The slurry, which contains $CaSO_3 \cdot 0.5\ H_2O$, fly ash, and unreacted $CaCO_3$, creates a major disposal problem (about 15 cm/ha/year/MW of generating capacity). Fluidized bed boilers, which show promise for new plants to reduce SO_2 emissions, produce an anhydrous granular waste containing $CaSO_4$ and unreacted CaO or MgO. Research results (77) indicate that the waste has some value as a source of S for crops and for liming acid soils.

Recovery of SO_2 as H_2SO_4 or $(NH_4)_2SO_4$ from power plant emissions by processes similar to those used by the steel and smelter industries has been proposed, but recovery from the relatively low SO_2 concentrations is expensive. For example, one estimate of the cost of SO_2 abatement is $250 per ton of SO_2 (48). In Europe the total cost of reducing the present 60 million tons of annual SO_2 emissions to a "tolerable" level is estimated at $8.75 billion annually. Corresponding cost of reducing U.S. SO_2 emissions by half is $4 billion annually.

Very high costs are certain from either recovery or throwaway methods for SO_2 abatement ($50-100 capital costs/kW of installed capacity + $10-20/dry ton of scrubber wastes—about 4 tons/ton of S abatement). Expected increased operating costs for 65% abatement recovery as H_2SO_4 is about 2.5 mils/kWh (11).

Abatement has recently been termed a billion-dollar solution to a million-dollar problem (56).

Power companies advocate a combination of high stacks for wide dispersion of pollutant emissions, together with burning of low-S coal during adverse weather, instead of the much higher cost proposals for abatement to very low emission levels (59).

4.3 Smelters

It has long been known that excessive release of SO_2 into the atmosphere from certain types of industrial plants may lead to complete denudation of the surrounding area. Notorious examples of this include the Copper Basin of southeastern Tennessee, where a 9,300 ha area was denuded from about 1850-1905 by a combination of SO_2 from copper smelting, forest removal, and over-grazing. More recently, the SO_2 has been recovered on site as H_2SO_4, and considerable progress has been made in revegetating this denuded area. A recent study (78) indicates that liming and fertilization with N and P, together with erosion control, are necessary for satisfactory growth of grass in the Copper Basin area.

Nonferrous smelters have also denuded areas surrounding smelters in several western states. Most smelters now have SO_2 recovery systems (55). Bohn (9) reported that SO_2 emissions (775 tons of S/day) from a smelter in Arizona acidified the previously calcareous surface soil to pH 5.5. Smelters at Sudbury, Ontario, are estimated to emit about 1.8 million tons of S each year (48).

4.4 Fly Ash

Most of the coal mined in the Eastern U.S. contains more than 3% S, largely as pyrites, and has a low content of calcium (Ca). As a result, most of the S is emitted as SO_2 gas from stacks without scrubbers; the fly ash is very low in SO_4 (< 1%) and Ca (< 2%). In contrast, most northern plains lignites contain less than 2% S and are higher in Ca content. As a result, stack emis-

sions of SO_2 from these lignites are low and SO_4 in the fly ash is much higher (3-13%), as is Ca content (11-35%). On the average, eastern coals retain about 5% of the coal S in ash under laboratory tests, while western coal ash retains 23-32%, with values as high as 90% for lignite (72).

4.5 Natural and Other Sources

Junge and Werby (42) concluded that most of SO_4-S over the oceans originates from sea spray. The oceans contain about 3×10^{15} tons of S as sulphates. They estimated that on a global scale about 30% of the SO_4 brought down in rainfall over land areas was due to human activities.

The production of swamp gas (methane and H_2S) in marshy areas, as a result of anaerobic decomposition of organic materials, contributes to atmospheric S. Kellog et al. (44) observed that SO_2 is not only a product of burning fossil fuels but also of oxidation of H_2S.

Elliott and Travis (16) identified H_2S and carbonyl sulphide emanating from feedlot wastes. Banwart and Bremner (3) identified H_2S, methyl mercaptan, dimethyl sulphide, and carbonyl sulphide from anaerobic decomposition of animal manures. (These compounds have also been identified in emissions from kraft paper mills.) Only dimethyl sulphide could be identified under aerobic conditions, since other organic compounds oxidize to SO_4. Siman and Jansson (70) also found that H_2S was formed during anaerobic decomposition of organic and SO_4-S. The H_2S is oxidized rapidly by atmospheric ozone (65). Such organic S compounds may be important atmospheric pollutants locally.

Volcanoes are major contributors to atmospheric SO_2 and S-containing particulate matter during periods of activity. Kratky et al. (45) found that tomato yields were reduced severely in the Kona district of Hawaii during volcanic activity 75 km away. Forest fires also release large amounts of SO_2.

5.0 ABSORPTION OF ATMOSPHERIC S

5.1 By Lead Peroxide

Lead peroxide (PbO_2) cylinders protected from rainfall have been commonly used to measure absorption of SO_2 from the atmosphere. The SO_2 reacts with PbO_2 to form $PbSO_4$. Amounts of S absorbed increase with concentrations of SO_2 in the atmosphere, temperature, and air movement. Alway et al. (2) measured annual values by PbO_2 absorption ranging from 460 kg/ha in Minneapolis to 3 kg/ha at a rural site in 1937. Seim and Caldwell (unpublished data) made similar measurements in Minnesota for 1962-67. Annual amounts of S absorbed ranged from 41 kg/ha at St. Paul (metropolitan area), to 11 kg at Duluth and an average of 7 kg at two rural sites. Amounts of S in precipitation at these locations were 16, 9, and 7 kg/ha. Much more S was absorbed at St. Paul during winter months, but slightly more was absorbed at a rural location (Park Rapids) during summer. The difference was attributed to greater amounts of fossil fuels burned in winter at St. Paul and to a higher contribution of H_2S or volatile organic compounds from decaying organic matter at the rural site.

Jordan et al. (41) reported amounts of S absorbed by PbO_2 in Alabama and Virginia in 1956. These ranged from 6 to 30 kg/ha (average of 14 kg) at 7 locations in the Muscle Shoals, Alabama, area within 5 km of the Colbert power plant (estimated emission of 37,000 tons of S as SO_2 in 1955 and 73,000 in 1956). This indicates a general dispersion (as measured on a monthly basis) of the SO_2 emissions at sites even less than 5 km from the power plant stacks. In Virginia amounts of S absorbed as SO_2 in 1955 were 61 kg/ha at Norfolk and from 14 to 39 at 15 other sites (average of 23 kg). Much more SO_2 was absorbed during winter months than in other seasons (50). Corresponding average amounts of S in the precipitation were also 14 kg/ha for the 7 sites in Alabama and 21 kg for the 15 Virginia sites.

Hoeft et al. (36) reported annual SO_2 absorption by PbO_2 in 1969-71 of 380 kg of S/ha for a site 2 km east of an industrial source and 80 m above the emitting stack. Toxicity symptoms were noted on alfalfa and birch near this site. Averages were 28 kg for 9 urban sites and 14 kg/ha for 13 rural sites. Amounts were higher in winter than during summer months at urban and rural sites, but not at the industrial site. Corresponding amounts of S measured in precipitation were 168, 42, and 16 kg/ha at the industrial, urban, and rural sites, respectively.

Although somewhat limited, the available data indicate that in urban areas or near industrial sites SO_2 absorption by PbO_2 is much higher than the amounts of S measured in rainfall. In rural areas, SO_2 is widely diffused and the amounts measured by PbO_2 and in precipitation are similar. This may not be true in drier climates, but comparative data are lacking.

5.2 By Soil

Seim (69) found in a laboratory study that significant amounts of SO_2 were absorbed by five Minnesota soils from a flow of air containing from 0.75 to 5,250 μg SO_2/liter. Both dry and moist soils absorbed SO_2, largely in the surface 0-2 cm layer. Removal of SO_2 from the air stream ranged from 60 to 100%. No SO_2 was found in the exposed soil, but large increases in extractable SO_4-S were measured.

Earlier investigators also reported that SO_2 was absorbed by soils. Roberts and Koehler (64) found that SO_2 injected into an eastern Washington S-deficient soil was equal to gypsum as a source of S for wheat up to 500 ppm of S. However, 2,500 ppm as SO_2 reduced growth, and 5,000 ppm was lethal to the plants soon after emergence.

Alway et al. (2) reported 22% as much absorption of SO_2 by soil as by equal surface areas of lead peroxide (PbO_2) candles. Johansson (37) found that S added directly to soil as SO_2 decreased greatly with distance from an oil-burning plant in Sweden, while S added in precipitation decreased only slightly (Fig. 3).

Yee et al. (83) found that SO_2 absorption by calcareous soils increased with SO_2 concentration and moisture in the air and with specific surface and moisture in the soil. Soils also absorb H_2S and organic S compounds.

Adverse effects of absorption of low concentrations of atmospheric S by soils in general are minor; however, some investigators (49), consider them more serious. The adverse effects of excessive absorption of SO_2 by soil and vegetation from extremely large smelter emissions are, of source, obvious.

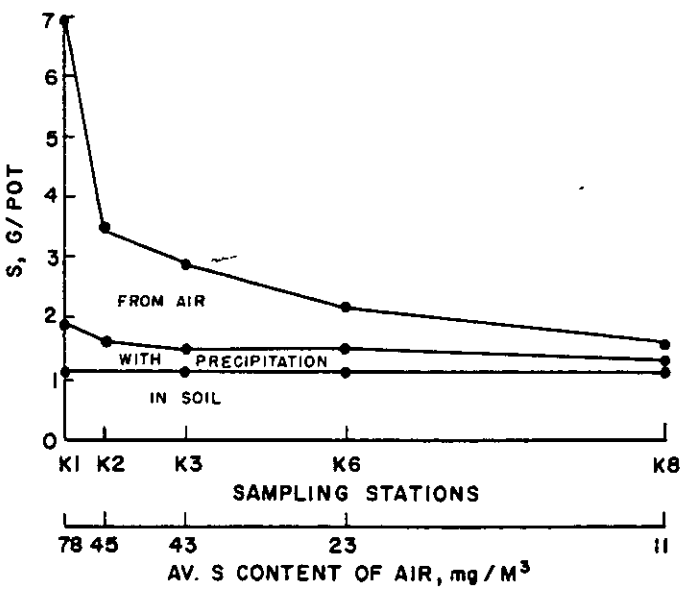

Fig. 3: Amounts of S added to uncropped soil over a 6-year period in precipitation and by direct absorption from the air at various distances from a shale oil plant in Sweden (37).

5.3 By Plants

Numerous investigators, both in North America and Europe, have reported that atmospheric SO_2 is absorbed directly by plant foliage. At low concentrations, SO_2 can partially substitute for SO_4-S absorbed by the roots to supply this nutrient for plant growth (58). At high concentrations, absorbed SO_2 can interfere with photosynthesis and cause characteristic chlorotic or necrotic

injury symptoms on various plant species. A severe exposure can be lethal to some plants. Concentrations of SO_2 that cause visible injury vary rather widely, depending on various conditions of temperature, light, humidity, water content of the plant, duration of the exposure dose (time x concentration), plant species and variety, and other factors. It is possible that some plant toxicity attributed to SO_2 is actually due to ozone and other associated pollutants.

Atmospheric SO_2 can enter leaf stomata directly or be absorbed in moisture on the leaves. In either case, SO_3-S and then SO_4-S are soon formed. In general, varying degrees of injury may occur on sensitive species at SO_2 concentrations above about 0.2 ppm, but more commonly at concentrations above 0.5 ppm for 1 hour. Fried (27) proved conclusively by use of ^{35}S-labeled SO_2 that direct plant utilization of SO_2 occurs.

Olsen (58) showed that cotton plants supplied with adequate SO_4 in solution still absorbed about 30% of their S from the atmosphere. In a S-deficient solution, up to 90% was absorbed from the atmosphere, containing 0.01-0.05 ppm of SO_2. Absorption of SO_2 entirely from the air was not adequate for satisfactory growth. Siman and Jansson (70) found that oats and rape grown with ^{35}S-labeled fertilizer absorbed about 50% of their S directly from the air at low soil S supply, but much less at high S supply. Faller (23, 24) also reported that atmospheric SO_2 was a major source for plant growth, that tobacco plants could utilize atmospheric SO_2 as their only source of plant-nutrient sulphur, and that this source was fully equivalent to SO_4 nutrition through the root system.

It has been estimated that about 2.1×10^{11} tons of dry photosynthate is produced worldwide per year. Assuming an S content of 0.2%, about 4.2×10^8 tons of S could be absorbed per year. Thus, perhaps half of the S needs could be absorbed from the atmosphere (22). Hill (35) found that absorption of atmospheric SO_2 by vegetation increased with wind velocity above the plants, height of the canopy, and temperature.

Emissions of SO_2 over Britain during the 1940's were estimated at 4.5 million tons per year, of which 3.5 million were deposited on land. Of this amount, 0.6 million tons were accounted for in precipitation. Most of the remaining 2.9 million tons were believed to be absorbed by vegetation (73). In the U.S., all of the estimated 16.6 million tons of S emitted in 1970, if absorbed uniformly by the 770 million ha of land in the contiguous 48 states, would provide about 21 kg of S/ha. Unknown amounts would, of course, be absorbed by lakes and rivers or carried elsewhere by atmospheric currents.

It is obvious that vegetation, soils, and water surfaces are almost unlimited sinks for S compounds in the atmosphere. The residence times for various S compounds in the atmosphere are no more than a few days.

6.0 AMOUNTS OF S IN PRECIPITATION

In contrast to most other atmospheric pollutants, SO_2 is quite soluble in water (11.3 g/100 ml at 20C) and SO_3-S is highly soluble. The resulting product is dilute H_2SO_4 or sulphate salts.

Several reports on S in precipitation were published prior to 1950, but most do not appear pertinent to today's conditions. The amounts of S reported varied widely. Some recorded amounts were in cities where they were affected by nearby heating and industrial sources of SO_2. In addition, in some early studies, the rain gauges were made of corrodible metal with which SO_2 reacted, contributing to high values of S brought down in precipitation. Much of the early data were summarized by Eriksson (20).

Reports since 1950 of S found in precipitation in several states are summarized in Table 4. The most extensive survey was of southern states summarized by Jordan et al. (41). Amounts of S recorded for 1953-55 in states bordering the Gulf and southern Atlantic coasts at points not affected appreciably by local industry were usually less than 6 kg of S/ha/year. Amounts record-

Table 4. Amounts of sulphur found in precipitation in various states.

State	Location in state		Years	Major Source	Amounts/year Range	Average	Reference
Southern States							
Alabama	Prattville	1	1954-55	General	3.4- 4.0	3.7	(41)
	Muscle Shoals	19	1954	General	3.1- 6.8	5.4	
	Muscle Shoals	20	1955	Steam Plant	6.4-16.2	11.9	
	Muscle Shoals	23	1956	Steam Plant	6.5-16.6	11.0	
Arkansas	NW and SE	2	1954-55	General	2.6- 5.3	3.7	
Florida	Cantonment	1	1953-55	Industry	14.8-52.6	33.5	
	Gainesville	1	1953-55	Urban	8.0- 9.6	8.8	
	Others	5	1953-55	General	1.8- 4.4	3.2	
Georgia	Various	6	1954-55	General	2.8-13.9	7.7	
Kentucky	Various	6	1954-65	General	4.1-22.3	13.1	
Louisiana	Various	5	1954-55	General	2.1-13.9	9.0	
Mississippi	Various	7	1953-55	General	0.8-10.1	5.0	
North Carolina	Statesville	1	1953-55	Industry	12.7-19.4	15.5	
	Others	15	1953-55	General	3.1-14.6	6.0	
	Clyde	1	1969-73	Industry	10.6-43.3	22.1	V. J. Kilmer, unpub. data, TVA
Oklahoma	Stillwater	1	1927-42	General	6.9-14.2	9.7	(32)
South Carolina	Various	4	1953-55	General	3.1-17.7	7.5	(41)
Tennessee	Various	7	1955	General	10.5-21.4	14.2	
	Various	5	1971-72	General	13.9-20.0	17.1	(39)
Texas	Beaumont	1	1954-55	Industry	10.0-14.1	12.1	(41)
	Others	4	1954-55	General	3.1- 7.5	5.7	
Virginia	Norfolk	1	1954-55	Industry	33.4-37.0	35.2	
	Others	14	1954	General	8.4-26.9	15.0	
	Others	17	1955	General	13.3-34.5	21.2	
	Various	16	1953-56	General	14.2-37.5	21.4	(50)
Northern States							
Indiana	Gary	1	1946-47	Industry	—	142.2	(6)
	Others	10	1946-47	General	22.4-37.0	30.0	
Michigan	Various	5	1959-60	Industry	9.0-14.0	11.3	(14)
Minnesota	St. Paul	1	1962-67	Urban and Industry	—	16.5	Seim, E.C., and A.C. Caldwell, unpub. data, University of Minn.
	Others	3	1962-67	Urban and Industry	4.1-10.1	7.7	
Nebraska	Various	7	1953-54	General	2.6-15.9	7.2	(25)
New York	Ithaca	1	1931-49	Urban and Industry	34.7-76.2	54.9	(46)
Wisconsin	Industrial Site	1	1969-71	Industry	—	168.0	(36)
	Urban	9	1969-71	Urban	—	42.0	
	Rural	13	1969-71	General	—	16.0	

ed near local industries and generally over northern Alabama, Kentucky, Tennessee, and Virginia were much higher (10 to 30 kg/ha/year). Presumably, the higher amounts of S for these four states result largely from emissions of SO_2 from fossil-fueled power plants, which burn largely coal high in S, plus contributions from local heating plants, combustion engine exhausts, and industries. Data from 19 locations in the Muscle Shoals, Alabama, area show a doubling of S in precipitation after startup of the TVA Colbert steam plant in 1955. There was no apparent relationship between distance from the plant and amount of S recorded. This indicates wide dispersion of SO_2 from the stacks. Accretions of S in the rainfall are correlated to some extent with frequency of rains, since oxidation of SO_2 to SO_4 is rather rapid, so that a moderate rainfall (1.5 cm) removes most or all of the S from the lower atmosphere. Siman and Jansson (70) found that S in rainwater near an oil-fired heating plant was 3 times higher than at 32 km from the plant; plant S content was 2.5 times higher near the plant.

Hoeft et al. (36) recorded amounts of S in precipitation at 20 locations in Wisconsin during 1969-71. Average annual S measured 2 km from an industrial site was 168 kg/ha, 4 times that at 9 urban sites (42 kg/ha), and 10 times that at 13 rural sites (16 kg/ha). At 5 km from the industrial site, amounts of S decreased to rural levels. Tabatabai and Laflen (75, 76) found that amounts of SO_4-S added annually in precipitation ranged from 13 kg/ha in northeastern to 17 kg in northcentral Iowa.

7.0 THE ACID RAIN PROBLEM

Oxidation of SO_2 to SO_3 occurs rather rapidly (13) and SO_3 is absorbed by moisture to form SO_4 aerosols. Gartrell et al. (30) found oxidation rates of 0.1-2% per minute in plumes at varying distances downwind from stacks of a coal-burning power plant. The oxidation rate increased with moisture in the air.

Very small amounts of S oxidized to H_2SO_4 drastically lower the pH of unbuffered rainwater. With normal CO_2 concentrations in the atmosphere, the amount of S required to form enough H_2SO_4 to lower the pH of rainfall to 4.0 (the maximum average acidity) is only about 1.5 ppm (3.0 ppm of SO_2) or 1.5 g/m^3 of water.

Water in equilibrium with the normal partial pressure of CO_2 in the atmosphere has a pH of 5.6. The pH of water saturated with CO_2 is 3.8 which might occur at some emitting stacks. Thus, the pH of rainwater falling near highly industrialized sites could range between these values with only CO_2 emissions (that is, without any SO_2 emission). Nitrogen oxides (NO_X) are another source of rainfall acidity.

Jones (39) measured average SO_4-S concentrations of 1.6 to 2.1 ppm in rainfall in 1971-72 at 5 sites around the TVA Cumberland power plant in west central Tennessee prior to its initial operation. The corresponding pH range of the precipitation was 3.6-6.8.

Fly ash emissions from stacks are usually alkaline. If appreciable amounts are brought down in the precipitation, the acid may be neutralized and the resulting pH may be only slightly acid, or even above pH 7.0. It is likely that the rainfall pH values reported by Jones and others are the result of varying amounts of SO_X, NO_X, and fly ash. Reuss (61) concluded that net titratable acidity of the precipitation was more meaningful than was pH. Galloway, Likens, and Edgerton (28) concluded that the acidity of precipitation in rural, forested areas of the northeastern U.S. was dominated by H_2SO_4 and HNO_3, as determined by titrations of total acidity.

Richardson and Merva (62) found that pH of precipitation ranged from 4.7 to 8.5 (average of 6.3) in Michigan in 1972-74. They concluded that CO_2 controlled precipitation pH over most of the State. Likens and Bormann (49) found that the pH of precipitation in New England ranged from 2.1 to 5.0, with an average of 4.0. Acidity increased about 20 years ago, possibly because of increased particulate removal from stack emissions. Tabatabai and Laflen (75, 76) found that the average pH of precipitation in Iowa in 1971-73 was about 6.0, and that pH was not related to SO_4-S concentrations. Li (47) found that precipitation pH was increased after installation of cooling towers near a Maryland power plant. He attributed low pH values to SO_2 and NO_X emissions from combustion of coal.

Wright et al. (82) surveyed lakes in Southern Norway. Lower pH values of the lake water of 5.5 or less were largely associated with the highest concentrations of SO_4-S within a strip along the southern coast. Some species of fish and plankton have disappeared from the acid lakes, all of which occur in areas of acidic granite rocks. Likens (48) surveyed acid precipitation problems in Norway. He published maps showing rather close relationships between SO_4-S concentrations and acidity of precipitation and the acidity of lake waters; also between increases in European fossil fuel consumption, acidity of precipitation, and numbers of barren lakes in Southern Norway. Similar increases in acidity and decreases in fish populations have occurred in lakes in granite areas of the Adirondack Mountains of New York (48). However, it is interesting that Rosenqvist (67) attributed some of the increased acidity in Norway to changes in forest logging and dairy farming practices, and to the acidic properties of forest soil humus. In addition, a discussion group of the U.K. Department of the Environment and the National Environment Research Council (80) did not find the detrimental effects of atmospheric S on U.K. forests and lakes in the Scottish Highlands that have been reported from Norway and Sweden.

A less well known atmospheric S effect is that of darkening and exfoliation of stone in old buildings and in marble statuary. The H_2SO_4 formed from atmospheric S reacts with $CaCO_3$ in the stone surfaces to form gypsum. The resulting increase in volume results in exfoliation (79). Metals are also corroded by SO_2 and acid precipitation.

Soil acidification resulting from atmospheric S is considered to be a minor problem except near smelters. Overrein (60) found that pH of precipitation had to be below 4 to significantly affect leaching of Ca and the pH of ground water. In humid areas it slightly intensifies the natural weathering processes of rainfall, which causes leaching of bases and development of acid soils, as do various biological oxidation processes.

In low rainfall areas some soil acidification may be beneficial since it tends to increase P and micronutrient availability to crops in addition to supplying S (34, 55). Rather large amounts of elemental S, H_2SO_4, and gypsum are used in the reclamation of alkali soils. The object is to provide soluble Ca by addition or by acidification and dissolution; the Ca replaces exchangeable Na in the soil, which can then be leached out by irrigation water. However, water-applied acid or SO_2 at high rates may reduce aggregate stability (54). Uses of H_2SO_4 to reclaim sodium-affected soils and for other benefits have been summarized by Miyamoto et al. (55).

8.0 S-DEFICIENT SOIL AREAS

As indicated previously, S-deficient soils are found almost entirely in areas remote from industrial activity. However, such remote areas may have some soils which are not S deficient because of release of S from organic matter or accumulations of gypsum in the root zone.

The general extent of S-deficient soils in the U.S. was shown in Table 2, Section 3.1 It seems significant that most of the Eastern U.S., except for the Gulf and southern Atlantic coastal plains, have few or no S-deficient soils. This is the region of greatest industrialization, resulting in adequate S being supplied largely from the atmosphere. It is interesting that in colonial times Benjamin Franklin is reported to have "plastered" a pastured hillside in eastern Pennsylvania with gypsum to show its benefits for growth of grass, identified much later as correction of S deficiency. Gypsum was also used extensively for other crops during that period. At present no S-deficient soils are reported in the Northeastern U.S. The apparent reason is deposition from local and distant emissions to the southwest as a result of prevailing winds from the west and southwest (38).

In the southeast and elsewhere sandy soils tend to be most deficient in S. In these nonindustrialized areas, S deficiencies have increased with the increased use of high-analysis fertilizers, unless S is also applied. Sulphur-deficient areas would be expected to increase with SO_2 abatement and continued use of fertilizers low in S.

Areas of S-deficient soils are also widespread in Australia, Canada, and many countries of Africa, Asia, Europe, and South America. Again, the S-deficient soil areas are also remote from industrial activity.

Northern Alabama, apparently included in the S-deficient areas because of Alabama's statewide requirement for S in fertilizers sold in the State, has no known S-deficient soils. Present information in many states having S-deficient soils is not adequate to delineate S-deficient areas very accurately. However, the extent of such areas and the need for S in fertilizers are expected to increase with SO_2 abatement.

No data were found which included all forms of atmospheric S contributions (SO_2 and other S absorption, precipitation, and particulates) at even one site. It is strongly recommended that all sources be measured at each site in future studies.

9.0 SUMMARY AND CONCLUSIONS

Serious consideration of all aspects of SO_2 emissions is particularly appropriate because of the tremendous costs involved in reducing emissions to legislated levels, the resulting increases in electricity rates, and the new problem of disposal of huge tonnages of SO_2 scrubber waste products.

Legitimate concerns have been expressed by environmentalists about the potential adverse effects of anthropogenic contributions to atmospheric S. Some of these effects, especially of high SO_2 concentrations, are real and have been adequately documented. Others, related to lower atmospheric concentrations, are debatable and require further research.

Except for local adverse topographic situations, ground-level concentrations of atmospheric SO_2 from tall stack emissions are not usually high enough to damage plant growth. Exceptions may occur, however, during atmospheric temperature inversions, during which SO_2 and other pollutants cannot diffuse freely into the atmosphere.

Considerable benefits have been shown for atmospheric S as a source of this element for plants. Use of fertilizer S would have to be increased substantially if SO_2 emissions from the burning of fossil fuels were abated.

In view of the benefits derived from atmospheric S, and since adverse effects have been shown to be largely local problems, the emission standards set by the Clean Air Act of 1970 (1.2 lbs of SO_2/million BTU heat input for new sources) and by state pollution control agencies may be unrealistic. It may be essential only to prevent excessive SO_2 concentrations from occurring at ground level in any given area. If SO_2 concentrations near ground level are kept reasonably low, fly ash and smoke are the more obvious and obnoxious pollutants from most industrial stacks. Essentially all of the SO_2 emissions are rather rapidly absorbed by vegetation, soils, and bodies of water, or are brought down in precipitation.

The entire series of problems concerning the need for adequate power supplies in modern society at reasonable cost, the high cost of SO_2 abatement, and the net effects of atmospheric SO_2 on plants and animals (including man) will have to be resolved by trade-offs between costs and the possible ill effects that people are willing to tolerate.

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