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INTERNATIONAL FERTILIZER DEVELOPMENT CENTER

SULFUR IN THE TROPICS

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PREFACE

Signs of sulfur deficiencies are being reported with increasing frequency in many parts of the world's tropical agricultures. This trend can be partly attributed to the increasing use of high-analysis fertilizers that do not contain sulfur. Because many tropical soils contain only minimal reserves of sulfur, the importance of chemical fertilizers as a source of plant nutrient sulfur is expected to grow during the coming years. Recognition of these factors has stimulated renewed interest in research aimed at expanding our current knowledge of the mechanisms controlling efficient utilization of sulfur.

This document summarizes much of the previous research that has been done in sulfur nutrition and highlights some problem areas that should merit the attention of agriculturalists concerned with improved sulfur utilization for crop production. The report was prepared by Dr. Graeme Blair at IFDC during a sabbatical leave from the University of New England, Armidale, Australia. Preparation of the manuscript was jointly supported by The Sulphur Institute and the International Fertilizer Development Center.

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SUMMARY

Soils of the tropics generally have low levels of organic S, and often adsorbed S is the major reserve of this element. The addition of lime or phosphate to soils decreases sulfate adsorption and may significantly reduce their S status.

Responses to sulfur are widespread in the tropics and have been recorded in 40 tropical countries with 23 different crops. Suggested reasons for the widespread nature of the deficiencies are presented.

From published information, no association could be found between S deficiency and soil or climatic factors that would be useful for predicting areas of likely deficiency.

The major problem encountered in examining published data on soil and tissue tests was that of chemical methodology. While soil and tissue tests for sulfur have been used extensively in temperate areas and on some tropical crops, care is needed in deriving acceptable criteria for diagnostic purposes, and a suggested approach to this problem is presented.

INTRODUCTION

Although the essentiality of sulfur (S) as a plant nutrient has been known for more than 100 years, this element has received relatively little attention in laboratory, greenhouse, and field research in comparison to that received by the "big three"--nitrogen (N), phosphorus (P), and potassium (K). This is explained in part by the fact that, in many instances, the use of N and P fertilizers containing S has masked a deficiency of sulfur. Moreover, given the current state of the art, sulfur analysis in biological material is comparatively difficult.

In general, plants contain as much S as P, with an average content of approximately 0.25%. The ratio of N:S in plant protein is generally considered to be relatively constant at a value of 15:1.

A deficiency of S retards plant growth because this element is required for:

1. Synthesis of three amino acids--cystine, cysteine, and methionine--which are essential components of protein and which contain approximately 90% of the S found in plants;

2. Formation of chlorophyll;

3. Activation of certain proteolytic enzymes such as the papainases;

4. Synthesis of certain vitamins (biotin, thiamine, and vitamin B_1), glutathione, and coenzyme A;

5. Formation of the glucoside oils found in onions, garlic, and cruciferous plants;

6. Formation of certain disulfide linkages which are associated with the structural characteristics of protoplasm (the concentration of sulfhydryl (-SH) groups in plant tissues has also been shown to be related to increased cold and drought resistance in some species);

7. Formation of ferredoxin, an iron-containing plant protein that functions as an electron carrier in photosynthetic processes;

8. Formation of a ferredoxin-like compound which is involved in the fixation of N by root nodule bacteria and free living N-fixing soil bacteria; and

9. Activity of ATP sulfurylase, an enzyme that functions in the metabolism of S.

Sulfur deficiencies affect not only plant yield but also protein quality through their effects on the synthesis of the amino acids--cystine, cysteine, and methionine. Since methionine is an essential amino acid for humans, decreases in grain methionine levels as a result of sulfur deficiency may have serious implications for human nutrition and health. Zake (1972) found that sulfur fertilization increased the methionine level of finger millet such that the quantity needed to meet the daily S amino acid requirement of an adult was reduced from 1,325 g/day to 725 g/day.

Sulfur present in soils as the anion SO_4^{-2} undergoes many reactions, similar to those of NO_3^- and $H_2PO_4^-$, and its strength of adsorption to surfaces is intermediate between these two ions.

While some complete studies of sulfur have been conducted in temperate areas of the world, little research is available on sulfur in the tropics. The purpose of this paper is to review the research which has been done on sulfur in tropical agriculture.

SULFUR IN THE TROPICS

Soils of the Humid Tropics

There is great variation in the age and character of soil parent materials in the tropics, and this gives rise to a wide range of soil types. The intensity of weathering is generally high under humid tropical conditions because of the high intensity rainfall and high and relatively constant soil temperatures. The annual variation in temperature at 50 cm depth is often less than 5°C (Buol, 1973) and remains high (>20°C) throughout the year. The effect of weathering on soil depends on the intensity of leaching which is high throughout the year in the rainy and humid-seasonal climatic regions and also during the wet season in the wet-dry region. As weathering takes place, the silica in the clay minerals, being more soluble than the iron and aluminum oxides, is lost from the minerals.

This leaching of bases and silica leaves the exchange complex dominated by Al^{3+}, Fe^{3+}, H^{+}, and a large amount of reactive Fe and Al oxides. These have important implications for soil sulfates in tropical soils (Ensminger, 1954) because of their ability to adsorb this ion.

Being highly weathered, soils from the tropics largely contain 1:1-type clays (kaolinite and halloysite) which have a low cation exchange capacity and generally high oxide content. The majority of these soils are the Oxisols and Ultisols, which cover some 71% of the humid tropics (table 1). The pH is generally acid with the most acid soils being found in the rainy regions of the area. Soils of the low rainfall or wet/dry areas, in general, have higher pH's. This is partly because the organic matter is generally higher in soils from the latter area, and the bases from this source help to maintain soil pH levels. As cropping depletes the level of soil organic matter, the supply of bases declines as does the soil pH.

Since soils of the humid tropics are formed under conditions of high moisture percolation, there is a rapid removal of bases from the profile. As they are leached from the profile, they carry with them the anions Cl^{-}, NO_3^{-}, and SO_4^{-2}. In the experiments conducted by Pearson et al. (1962), 90% of the water-soluble bases were leached as sulfates from the acid Latosol and Red-Yellow Podzol profiles, while chlorides and nitrates accounted for only about 6% and 1%, respectively.

Soil Sulfur

Soils vary widely in their total content of S. As with phosphorus, soils of the temperate region show a decline in total S content with the degree of weathering. Jordan and Reisenauer (1957) report average values of 540 ppm total S for Mollisol and 210 ppm for Alfisol surface soils from the temperate areas. Generally, the total S content of tropical soils is lower because of their lower organic matter content. A summary of data on total S contents of topsoils from tropical areas is given in table 2. Although the range is very great, the mean (106 ppm) is well below the average values for temperate soils given by Jordan and Reisenauer (1957).

Sulfur is found in soils as a variable mixture of the following:

Table 1. Estimated Area of Major Soil Groups Found in the Humid Tropics (President's Science Advisory Committee, 1967)

Soil Groups	Tropical Climatic Regions			
	Rainy	Humid-Seasonal	Wet-Dry	Total
	- - - - - - '000,000 ha - - - - - -			
Dark-colored soils; base rock (Chernozemic, Grumusols, Rendzina, Brown Forest), Mollisols and Vertisols	23	56	119	198
Moderately weathered and leached soils (Noncalcic--Brown, Ando), Alfisols and Andepts - Inceptisols	4	34	90	128
Highly weathered and leached soils (Latosols, Lateritic, Red-Yellow Podzolic), Oxisols and Ultisols	931	1,084	474	2,489
Shallow soils and dry sands (Lithisols and Regosols) Entisols	81	105	170	356
Alluvial soils, Entisols	146	124	71	341
Total	1,185	1,403	924	3,512

Table 2. Total S-Values for a Range of Soils from Tropical Regions

Location	No. Soils	Total S (ppm) Mean	Range	Reference
Malawi	14	66	35-139	Laurence et al. (1976)
Nigeria	3	43	38-52	Bromfield (1972)
W. Indies	8	248	110-510	Haque and Walmsley (1973)
N. Cameroon, Chad, Ivory Coast	31	70	20-300	Dabin (1972)
Brazil (virgin)	4	103	40-251	McClung et al. (1959)
Brazil (cropped)	6	49	27-67	McClung et al. (1959)
Nigeria		-	18-132	Watson (1964)
Zambia and Rhodesia	-	-	60-100	Grant et al. (1964)
Brazil	6	166	43-298	Neptune et al. (1975)
Mean		106		

primary minerals,
sulfate ions in solution,
adsorbed sulfate,
organically bound ester sulfates, and
organic sulfur compounds.

Primary Minerals

The original sources of most soil sulfate are the metal sulfides of plutonic rocks which undergo oxidation during weathering. The earth's crust contains an average of 0.06% sulfur (Tisdale and Nelson, 1975), but the distribution is variable, ranging in field soils from zero (Ensminger, 1958) to above 500 ppm (Starkey, 1950).

Sulfate Ions in Solution

Although the level of soluble sulfate in the soil of humid regions is generally below 10 ppm, considerable fluctuations may occur. These changes are the net result of mineralization from organic matter, leaching of soluble sulfate, uptake by plants (Williams, 1968), and sulfate additions from rainfall and irrigation water and applied fertilizer.

Adsorbed Sulfate

The surfaces of Fe and Al oxides and weathered edges of clay particles contain ions that are not fully coordinated in the lattice. These ions complete their coordination shell with OH groups and water molecules, and the presence of H^+ ions favors the development of net positive charges at these sites. Such a positive charge attracts anions in the same way as surface negative charges attract cations. This phenomenon is known as "anion adsorption."

The sulfate adsorption capacity of soils varies widely and is dependent on several soil properties, the most important of which are the nature and extent of active oxide surfaces (Harward et al., 1962; Barrow, 1976), clay content (Ensminger, 1954), clay type, and pH. The adsorption reaction is reversible and concentration dependent.

The type and amount of clay present in a soil determines the number of weathered-edge adsorption sites. Harward et al. (1962) found that the amount of S retained by reference clays was in the

order kaolinite > illite > montmorillonite. Aylmore et al. (1967) have shown that sulfate adsorbed to iron and aluminum oxides is held more firmly than that adsorbed to kaolinites.

Nitrate and chloride anions do not have a specific affinity for the surface atoms and are adsorbed in proportion to their concentration in solution. Sulfate ions have a specific affinity for adsorption, and their presence almost completely prevents the adsorption of nonspecific NO_3^- and Cl^-.

Since fully dissociated anions (SO_4^{-2}) cannot adsorb onto negative or uncharged surfaces, the amount of adsorption is dependent on the amount of positive charge on the surface and, hence, pH (Kamprath et al., 1956). On the other hand, the adsorption of undissociated ions such as $H_2PO_4^-$ does not depend on the presence of a net positive charge and consequently they are readily adsorbed to surfaces. In addition, phosphate ions are very effective, both in displacing adsorbed sulfate and in reducing the capacity of the surface to adsorb additional sulfate. This was shown by Aylmore et al. (1967) who found that solutions containing KH_2PO_4 desorbed some 20% more sulfate from clay and oxide surfaces than did water. Once the sulfate ions are desorbed from the surface and enter the soil solution, they can be easily leached from the profile.

Adsorbed sulfate is not free to move to plant roots by convective flow and diffusion; therefore, in soils where there is not significant moisture movement through the profile, the availability of sulfate is lower in an adsorbing than a nonadsorbing soil. Hence, sulfate in the soil solution, which is available to plants, is a balance between adsorption and leaching losses.

Organically Bound Ester Sulfates

Ester sulfate is believed to consist largely, if not entirely, of organic sulfate-containing ester linkages (e.g., choline sulfate, phenolic sulfates, and sulfated polysaccharides). This fraction of soil S can be reduced by hydriodic acid and alkali (Freney, 1967).

Ester sulfates were found to constitute from 20% to 65% of the total S in a group of six Brazilian soils and from 50% to 62% in six soils from Iowa (Neptune et al., 1975) (figure 1). In a wider range of soils from a temperate area, this fraction has been found to vary between 30%-70% of total S (Williams, 1975). This fraction of soil S is unavailable to plants, but on breaking the

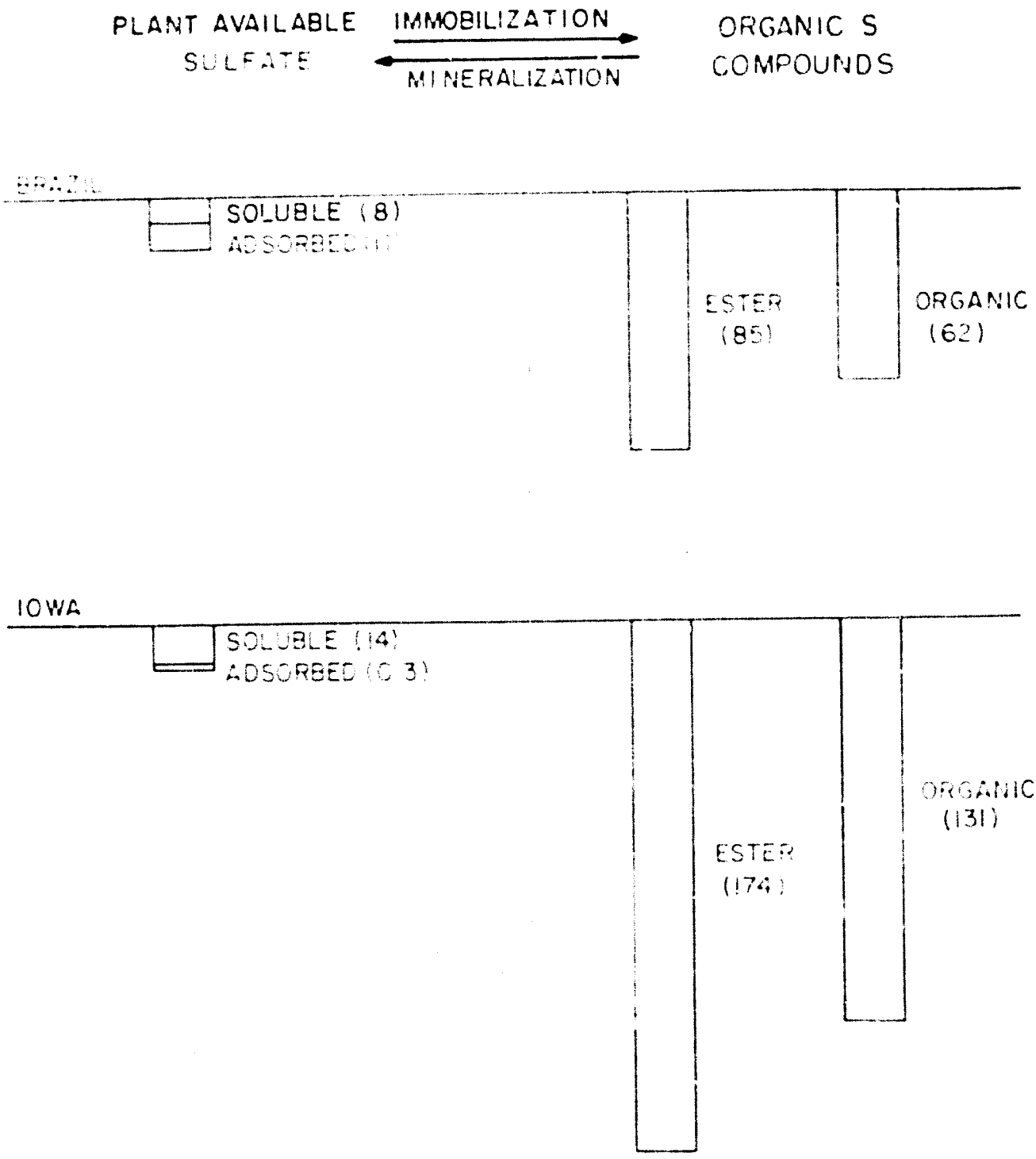

Figure 1. Soil sulfur pools in samples from Iowa (U.S.A.) and Brazil. The numbers in brackets represent kgS/ha (drawn from the data of Septum et al., 1976).

ester linkage, plant-available sulfate is released. Drying the soil breaks this linkage (Barrow, 1961), and this can have dramatic effects on soil test results.

Organic Sulfur Compounds

Little is known of the chemical nature of soil organic sulfur compounds, but the S-containing amino acids--cystine, cysteine and methionine--have been isolated and may constitute up to 30% of the total organic sulfur (Freney et al., 1972). Although the C:N:S ratio of soil approximates an average of 108:8:1 between groups of soils (Whitehead, 1964; Williams, 1967a), there can be considerable differences within each group. Dabin (1972) found a range in N:S ratios of from 4:1 to 36:1 in soils from Africa, and Neptune et al. (1975) found a variation of from 3.4:1 to 12:1 in Brazilian soils.

Evidence that a major portion of sulfur in some tropical soils is associated with organic matter is reported by Dabin (1972) who studied soils of Africa (figure 2) and by Neptune et al. (1976) who found a correlation coefficient of 0.99 between organic S and total S in six Brazilian soils.

Organic sulfur is a reserve for plants but must undergo mineralization to sulfate before becoming available. Many factors are known to affect the rate of mineralization of organic S compounds (Freney and Swaby, 1975). Since the mineralization process is primarily microbial, factors that influence the growth of the micro-organisms will influence the rate of conversion of organic S to plant available sulfate. The major factors affecting the mineralization of organic sulfur are:

Temperature--Optimum approximately 40°C (Williams, 1976).

Soil Moisture--Optimum at approximately 60% of field capacity (Chaudhry and Cornfield, 1967).

Presence of Plants--Mineralization of S was found to be higher in the presence of plants than in bare soil (Freney and Spencer, 1960), presumably because of the greater number of micro-organisms present in the rhizosphere.

S-Content of Organic Matter--Stewart et al. (1966) have shown that S mineralization occurred only when the S content of the straw was above 0.15%.

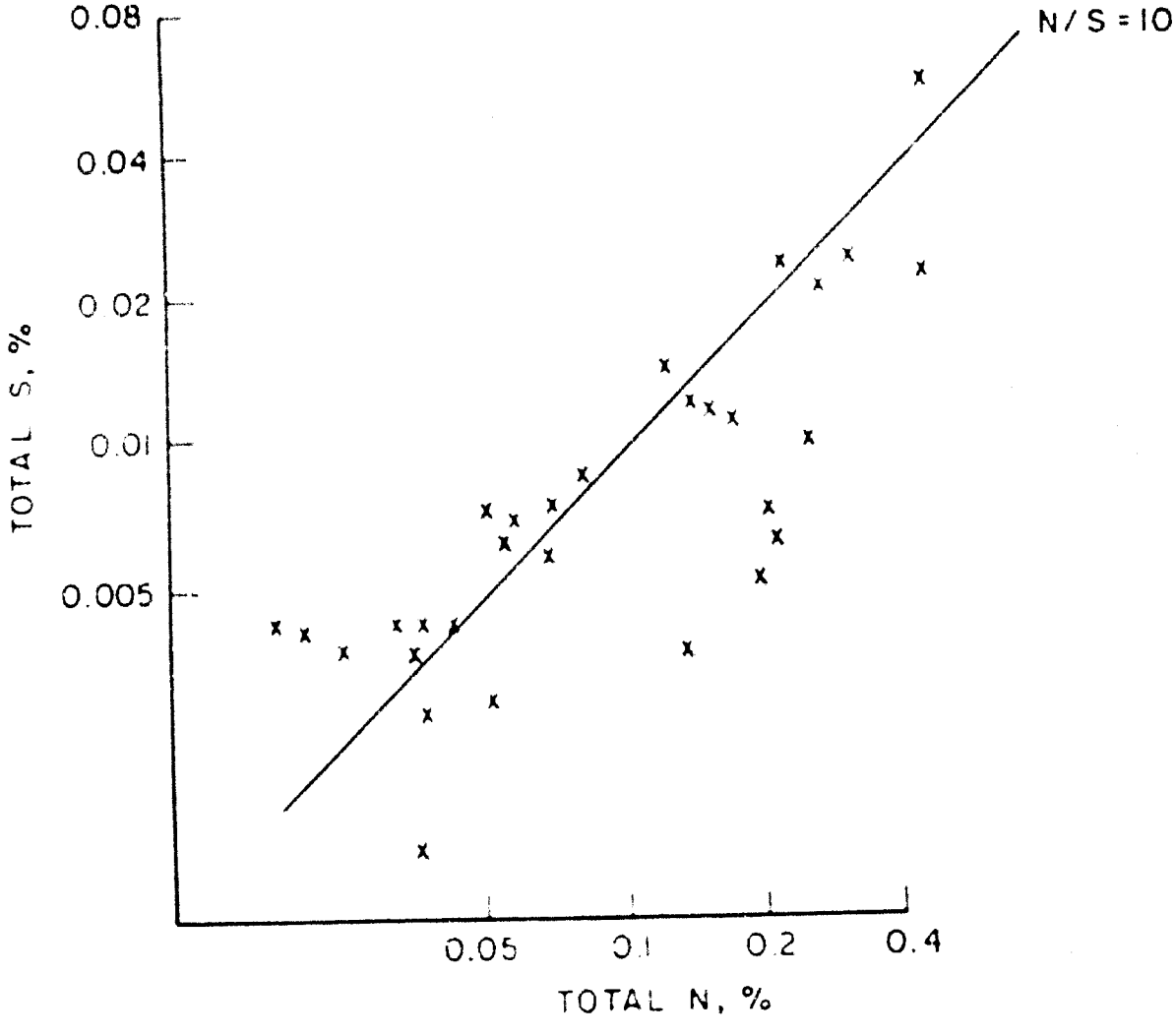

Figure 2. The relationship between total N and total S content of surface soils of tropical Africa (Dabin, 1971).

The most obvious differences in sulfur contents between tropical and temperate soils may be summarized as follows:

1. Adsorbed S is generally higher in tropical soils (figure 1). In this state it cannot be leached from the profile.

2. Organic S and ester sulfate, which may be thought of as "reserve S," are generally lower in tropical soils.

3. Environmental conditions in the tropics are generally conducive to a rapid mineralization of organic matter which leads to high turnover rates of S. An exception to this rule is the volcanic soils (Andepts) in which adsorption of organic matter on the particles of allophane retards mineralization.

Sulfur Deficiencies in the Tropics

In his review of sulfur in world crop production, Coleman (1966) reported sulfur deficiencies in 12 tropical countries and noted that the incidence of sulfur deficiency was increasing. The major reasons for this increasing incidence in tropical countries are:

1. The increasing use of high-analysis, low sulfur-containing fertilizers.

2. The increased S demand brought about by increases in yields obtained as a result of other technological advances.

3. A greater number of experiments have been conducted where sulfur has been studied as a nutrient in its own right. In many early experiments, responses to fertilizers such as ammonium sulfate, potassium sulfate, zinc sulfate, and single superphosphate have been attributed to the N, K, Zn, and P components of the fertilizer, thereby ignoring the potential response to S.

Responses to S have been reported in 40 tropical countries (table 3). Table 3 does not give an exhaustive tabulation of all responses recorded within a country. Where many responses have been reported in a particular country, those on different crops have been selected for presentation. In this summary responses have been recorded for some 23 different crop species. This

Table 3. Crop Responses to Sulfur in Four Regions of the Tropics

Country	Crop	Field or Pot Experiment	Reference
AFRICA			
Cameroon	Cotton	F	Braud (1970)
Cameroon	Banana	F	Braud (1970)
Cent. Afr. Rep.	Cotton	F	Dabin (1972)
Chad	Cotton	F	Braud (1970)
Dahomey	Cotton	F	Dabin (1972)
Ghana	Cereals	F	Bolle-Jones (1964)
Guinea	Pineapple	F	Pye (1964)
Ivory Coast	Oil Palm	F	Ollagnier & Ocho (1972)
Ivory Coast	Oil Palm	F	Calves et al. (1976)
Kenya	Black Wattle	F	Gosnell (1964)
Kenya	Tomato	P	Mehlich (1970)
Kenya	Cotton	F	Dabin (1972)
Kenya	Sugarcane	F	Hill (1963)
Madagascar	Sugarcane	F	Halais & Girault (1973)
Madagascar	Coconut	F	Ollagnier & Ocho (1972)
Mali	Cotton	F	Dabin (1972)
Malawi	Tea	F	Grant & Shaxon (1970)
Nigeria	Peanut	F	Watson (1964)
Nigeria	Soybean	F	Watson (1964)
Nigeria	Rice	P	Osiname & Kang (1975)
Nigeria	Peanut	F	Greenwood (1951)
Nigeria	Corn	P	Erwezor (1976)
Nyasaland	Tea	F	Story & Leach (1933)
Nyasaland	Tea	F	Forbes (1942)
Rhodesia	Corn	F	Vogt (1966)
Rhodesia	Coffee, Maize	F	Bolle-Jones (1964)
Rhodesia	Sugarcane	F	Gosnell & Lone (1969)
Senegal	Peanut	F	Brockelee-Morvan & Martin (1966)
Tanzania	Tea	F	Child (1975)
Togo	Cotton	F	Dabin (1972)
Uganda	Tea	F	Child (1957)
Upper Volta	Cotton	F	Dabin (1972)
Upper Volta	Peanut	F	Brockelee-Morvan & Martin (1966)
CENTRAL AND SOUTH AMERICA			
Brazil	Sorghum	P	McClung et al. (1959)
Brazil	Corn	F	Mikkelsen et al. (1964)
Brazil	Pasture	F	McClung & Quinn (1959)
Brazil	Coffee	F	DeFreitas et al. (1972)
Brazil	Rice	P, F	Wang et al. (1976a, b)
Brazil	Coffee	F	Lott et al. (1960)
Chile	-	P	Schenkel et al. (1974)
Colombia	Ryegrass	P	Pedraza & Lora (1974)
Costa Rica	-	-	Martin (1968)
Costa Rica	Pineapple	P, F	Fitts (1970)

Table 3. Crop Responses to Sulfur in Four Regions of the Tropics (Continued)

Country	Crop	Field or Pot Experiment	Reference
El Salvador	-	-	Muller (1965)
El Salvador	Coffee	F	Fitts (1970)
Guatemala	-	P	Fitts (1970)
Honduras	Banana	F	Benton (1966)
Puerto Rico	Sugarcane	F	Bornet (1967)
Puerto Rico	Pineapple	F	Cibes & Samuels (1958)
Puerto Rico	Pineapple	F	Samuels & Diaz (1960)
West Indies	Brassica	P	Haque & Walmsley (1973)
West Indies	Banana	F	Messing (1970)
ASIA			
Bangladesh	Rice	P	Karim & Majlish (1958)
Bangladesh	Rice	P	Karim et al. (1970)
Bangladesh	Rice	P	Alam & Karim (1972)
Burma	Rice	F	Sen (1938)
Burma	Rice	F	Aiyar (1945)
India	Rice	P	Acharya (1973)
India	Rice	F	Saran (1949)
India	Tea	F	Ferguson et al. (1957)
India	Tea	F	Child (1957)
India	Corn	F	Das & Datta (1973)
India	Sugarcane	F	Dutt (1962)
India	Peanut	F	Dungarwal et al. (1974)
India	Jute	F	Dutt (1962)
Indonesia	Rice	P	Yoshida & Chaudry (1970)
Indonesia	Rice	P	Leijder & Aldjabri (1972)
Indonesia	Rice	P	Ismunadji et al. (1975)
Indonesia	Rice	F	Mamaril et al. (1977)
Indonesia	Tea	F	Pronk (1955)
Philippines	Rice	P	Lockard et al. (1972)
Sri Lanka	Rice	P	Subbiah & Venkateswarlu (1965)
Sri Lanka	Coconut	F	Santhirasegarum (1967)
Taiwan	Pineapple	F	Su & Li (1962)
Thailand	Rice	F	IRRI (1977)
OCEANIA			
Australia (tropics)	Pasture	F	Probert (1974)
British Solomon	Cocoa	F	Leach et al. (1975)
Fiji	Pasture	F	Partridge (1973)
Papua & New Guinea	Coconut	F	Sumbak (1972)

listing does not imply that deficiencies are limited to those countries but rather reflects the availability of published information.

There are insufficient data available to permit an estimate of the actual area that may be sulfur deficient in the tropics or of the expected magnitude of S response. The small amount of published data, however, suggests that the problem is widespread and severe. A summary of these data is presented below.

Kenya--133 pot trials; 71% showed yield depressions of >20% without S (Mehlich, 1970).

East Africa--202 field trials; 18% showed yield depressions of >30% without S (Baud, 1970).

Brazil--21 pot trials; 81% showed yield depressions of >25% without S (McClung *et al.*, 1959).

Nigeria--45 pot trials; 17% showed yield depressions of >20% without S (Enwezor, 1976).

Senegal--29 field experiments showed an average S response in peanut yield of 71 kg/ha in a total fertilizer response of 522 kg/ha (Brockelee-Morvan and Martin, 1966).

Indonesia--26 field trials with rice; yield responses >20% at 77% of sites (Blair *et al.*, 1978a).

If these sites are representative of the soils in these regions, upwards of 50% of the area is responsive to S with yield increases of >20% expected as a result of S fertilization.

There are many reasons why a soil may be, or may become, deficient in sulfur but these can be grouped broadly into three areas: (1) inherently low initial S status; (2) low availability of S-containing soil organic matter; and (3) sulfur deficiency developed as the result of agricultural practices.

Inherent S Status

As indicated in table 2, soils of the tropics generally have low total S contents because of low S-containing parent materials and/or extreme weathering and leaching losses.

Few data are available on the S status of virgin tropical soils. McClung et al. (1959) found that all five soils collected from under virgin hardwood forests were responsive to S and that this deficiency became more severe after cropping. In contrast, Enwezor (1976) found that two soils collected from virgin lowland rain forests in southeastern Nigeria were nonresponsive to S.

Low Availability of S-Containing Soil Organic Matter

Sulfur deficiencies frequently occur in soils derived from volcanic parent materials. Such soils are common in Central America (Fitts, 1970). In these soils the organic matter is closely associated with allophane and the mineralization of the allophane-bound organic matter, i.e., the rate of release of SO_4^{-2} - S, is very slow. Plants growing on these soils are often S deficient despite the fact that the soil is high in organic sulfur.

Sulfur Deficiency Resulting from Agricultural Practice

Sulfur deficiencies often develop in the tropics following a period of agricultural exploitation. The major factors that contribute to the onset of a sulfur deficiency in these areas are: crop removal, organic matter losses, leaching and erosion losses, and fertilizer use and management.

Crop Removal--In figure 3 the crop S requirement is shown as a variable. The actual crop requirement depends on the productivity of the environment (e.g., moisture supply) and three other important factor : cropping intensity, crop type, and crop management.

Cropping intensity affects the amount of a product or products removed in a cropping system (e.g., single or multiple cropping, monoculture, or intercropping); the more intensive the cropping system, the greater the product removal and sulfur demand.

The type of crop grown (annual or perennial) and its total S requirement will govern the total amount of soil S utilized. The net requirement is governed by the amount of S removed in the product and the fate of the plant residue. Because of nutrient recycling and the generally low growth rate of native vegetation, the S requirement of these systems is generally low. When this vegetation is replaced by an agricultural crop, the demand increases considerably (figure 3).

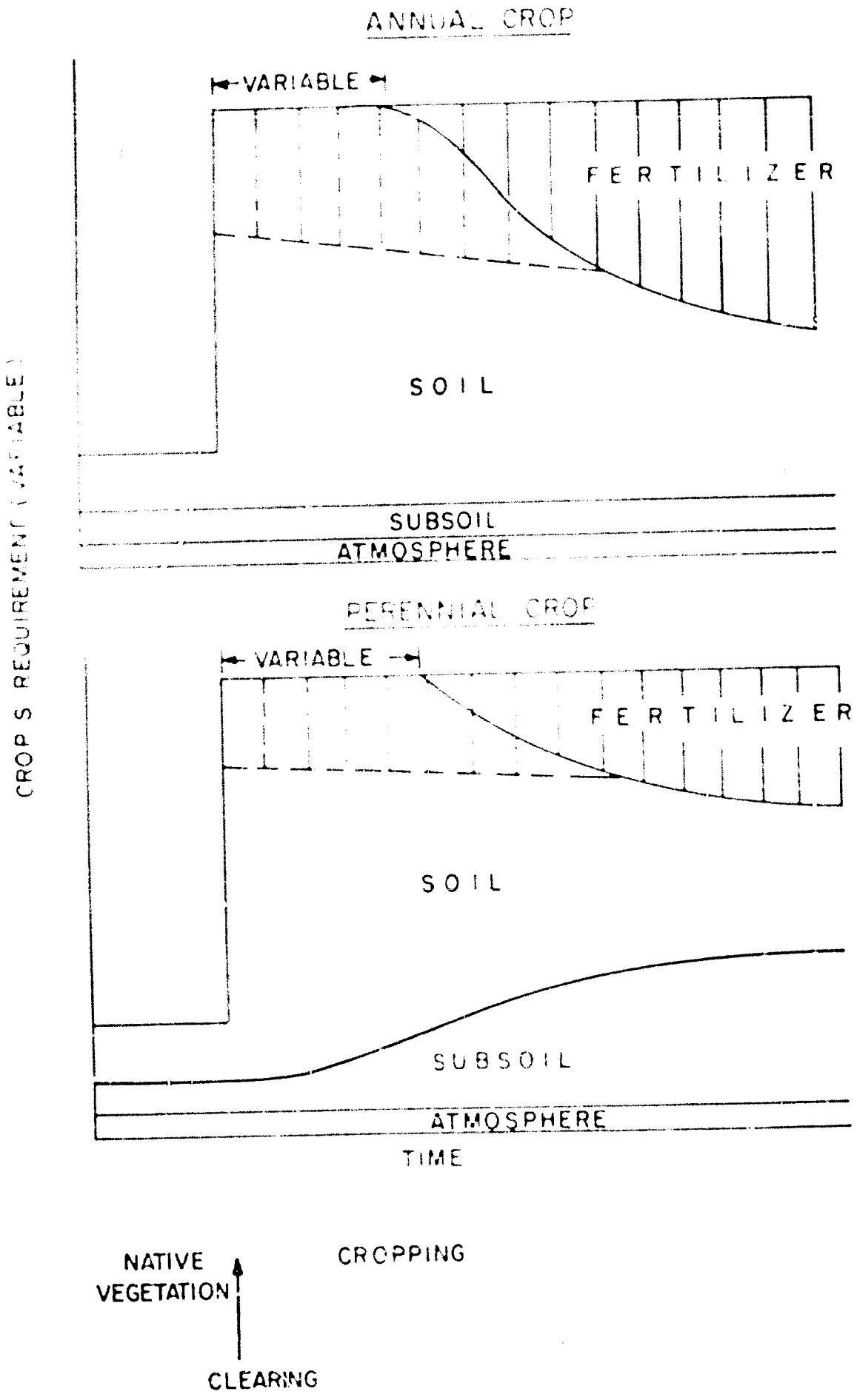

Figure 3. Diagrammatic [illegible] the soil supply and plant demand for S in [illegible] and annual crops.

The increased sulfur demand puts stress on the soil supply and the soil may or may not be able to meet this demand. If it can meet the demand, the time period before S deficiencies are experienced varies depending on the soil reserves, turnover rates, and the inputs from external sources. Soils unable to meet the increased demand which will always require S fertilization are shown with dotted lines in figure 3.

Since sulfur removal by the product is dependent on both the sulfur content of the product (table 4) and its yield, the data presented in figure 4 should be used only as a guide. For example, published grain sulfur contents for rice vary from 0.034% under deficiency conditions up to 0.16% S in a nonresponsive situation, and rice grain yields may vary from 0.75 tons up to 8 tons. This gives a sulfur demand ranging from 0.26 to 12.8 kg/ha.

A further factor that must be taken into account when considering the effect of crop removal on S demand is the zone of removal within the soil. Shown in figure 3 is the basic difference between the perennial and annual crop in the amount of S recovered from the subsoil. The generally deeper pattern of rooting of perennial crops means that they are able to utilize S that has been leached into lower soil zones. This is particularly true on soils with a clay or oxide layer at a depth within the rooting zone.

Crop Management--The values given in figure 4 represent the material actually exported from the field and includes residue that may or may not be returned to the field. The removal of this residue contributes significantly to losses in some situations (e.g., sorghum, millet).

Incorporation of crop residues back into the soil may, in some instances, decrease plant-available S. Stewart et al. (1966) found that there was a net immobilization of soil S when wheat straw with less than 0.15% S was added to the soil. In a review of published literature, Blair [illegible] (1978a) found only two cases where the S content of rice straw was above this level. This aspect of straw management requires further study.

The recycling of S in crop residues is important in livestock systems where the residue material is used as an animal feed or bedding. Decau (1972) gives a range of returns from various straw management systems (table 5) and shows the significance of S returns through the animal.

Table 4. The Sulfur Content of a Selected List of Foods (Edible Portions Only) (Masters and McCance, 1939)

Food	Sulfur Milligrams per 100 Grams
Fruits:	
Apples, Empire, eating	3.7
Avocado pears	19.4
Bananas	13.0
Figs, green	12.9
Strawberries	13.4
Nuts:	
Almonds	145.0
Brazils	293.0
Coconuts	44.0
Peanuts	377.0
Walnuts	104.0
Vegetables:	
Beans, baked	50.7
Beetroot, boiled	22.1
Cabbage, winter, boiled	23.4
Carrots, old, boiled	5.0
Onions, raw	50.7
Potatoes, old, boiled	22.2
Spinach, boiled	86.5
Cereals and Starch Products:	
Bread, white	54.5
Flour, white	108.5
Macaroni	95.0
Oatmeal	155.0
Rice	78.5
Dairy Products:	
Butter	9.1
Cheese, Cheddar	230.0
Egg yolk	164.5
Ice cream	30.6
Milk, fresh, whole	29.2
Beverages:	
Cocoa	160.0
Coffee	110.0
Tea	177.0

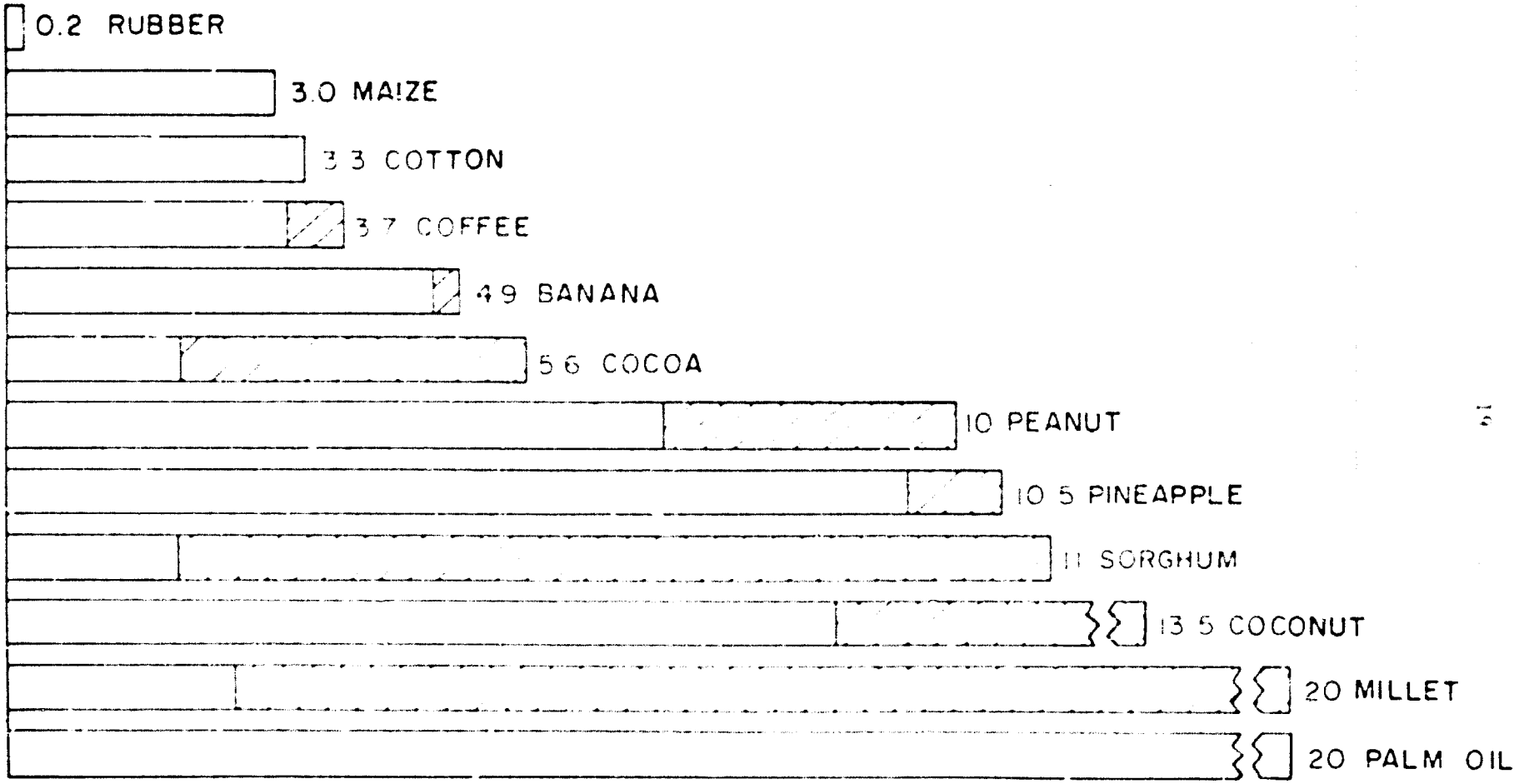

Figure 4. Sulfur uptake by crops. Hatched areas represent product that may or may not be returned to the field (Martin-Prevel, 1970).

Organic Matter Losses--One of the major consequences of cropping a tropical soil is the loss of organic matter that occurs. The effect of cropping on the soil organic matter levels can be seen from the data of Enwezor (1976) who studied this issue in a brown sandy ferruginous soil derived from acid crystalline metamorphic rock from the lowland rain forest area of southeastern Nigeria. In the virgin state, the 0- to 15-cm zone of this soil contained 1.35% total C while a sample from a cropped area contained only 0.97% C.

Since organic matter acts as a reserve of S in soils, these losses have serious implications for their S-supplying power. Data showing a decline in organic S resulting from cropping are presented in table 6. Such declines may eventually lead to a sulfur deficiency.

In many parts of the tropics, the burning of plant matter is an integral part of farming, and this can be an avenue for sulfur loss. When carbon is burned off by combustion, there is a concentration of S in the ash. Bromfield (1974) has shown that the S content of ash can be from 2 to 10 times higher than that in dried plant material. The actual values depend on the ignition conditions and plant species. In his sulfur studies in northern Nigeria, Bromfield (1974) found inputs from ash ranging from 0.05 to 0.25 kg/ha during the dry season. In areas of prevailing winds, the amount of S lost may be high; however, in regions of variable winds, the gains may equal the losses. One additional consequence of burning is that organic forms of S are converted to inorganic forms which, at the beginning of the rainy season when fields are bare, are susceptible to leaching losses. No data are available on this form of loss.

Leaching and/or Erosion--Sulfate which is contained in readily soluble fertilizers and which is produced by the mineralization of organic matter enters the soil solution where, if not taken up or adsorbed, it is subject to leaching. Field observations of sulfate movements in soil were made by Bromfield (1972) in his Nigerian studies (figure 5). The sulfate that was mineralized from the organic matter moved down the profile and accumulated at depth. The zone of accumulation was at approximately 30 cm in this soil, but in another series of trials conducted on a sandy soil, the sulfate S leached to about 40 cm.

Data on losses of S due to erosion are not readily available. Since a large proportion of the S present in the soil is in the organic matter and this is often accumulated on the soil surface, losses from wind and water erosion may be high in some circumstances.

Table 5. The Recycling of S from Crop Residues and Forages (Decau, 1972)

Crop Type	Utilization	Average % Returned
Cereals	Grain sold and straw manuring	50
	Grain consumed on the farm and manure returned to field	60
Forages	Consumed on farm and manure returned	70

Table 6. The Effect of Cropping on the Total S Levels in Soils from Brazil (McClung et al., 1959) and Nigeria (Bromfield, 1972)

Soil Description	Previous History	Organic S (ppm)
Brazil		
Red-Yellow Podzolic 1 (Bouru soil group)	Virgin	36
	Cropped	24
2	Virgin	61
	Cropped	32
3	Virgin	116
	Cropped	52
4	Virgin	247
	Cropped	60
Nigeria		
Brown to R.B. terruginous clay loam	Uncleared	54
	Cleared & uncropped	38
	Cleared cropped-fertilizers	38
	Cleared cropped+fertilizers	50

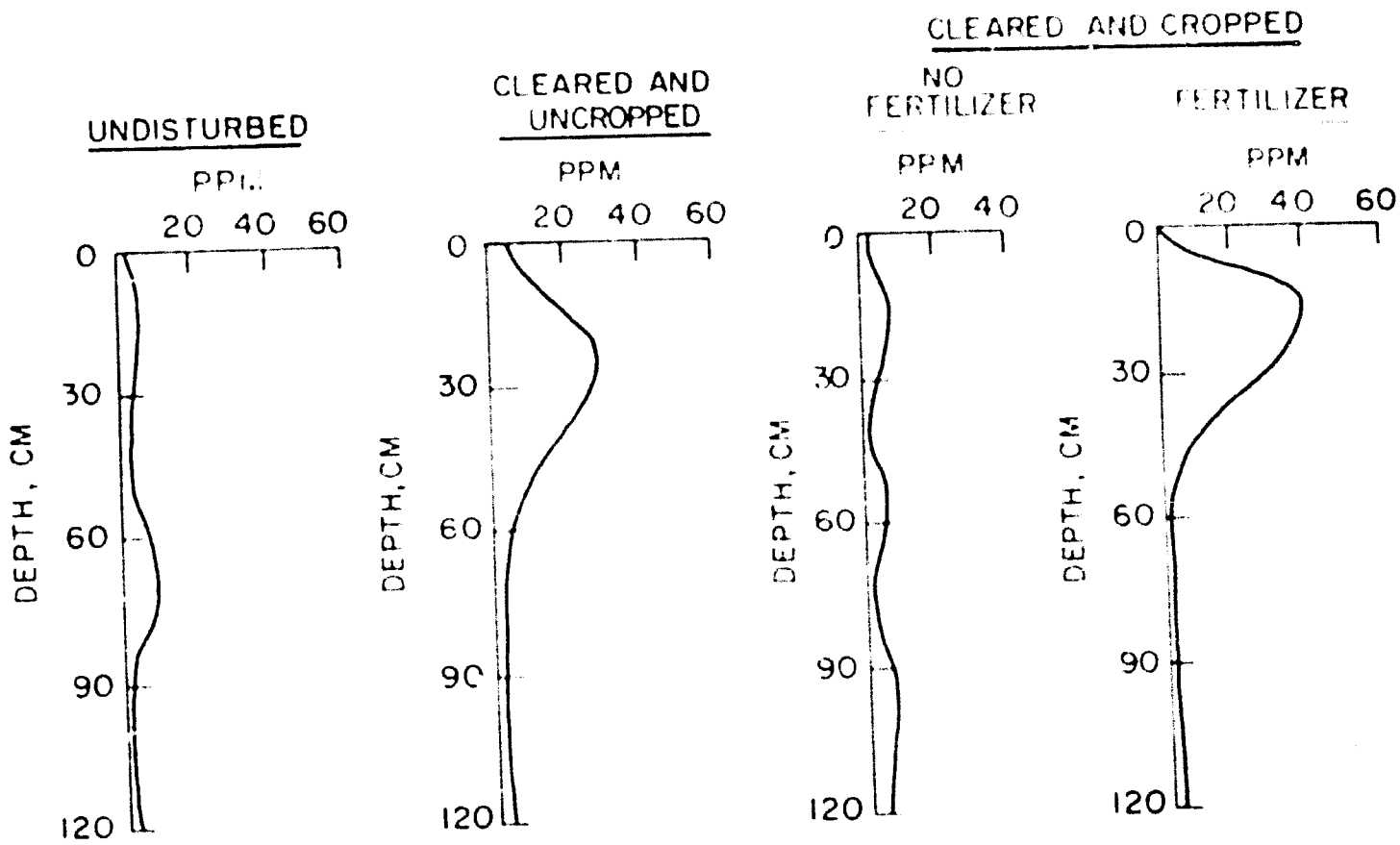

Figure 3. The effect of clearing, cropping, and fertilization on sulfate sulfur concentrations in a sandy clay to clay loam soil in northern Nigeria (Bartfield, 1972).

Fertilizer Use and Management--Direct inputs from sulfur-containing fertilizers are major sources of S to agriculture and major factors determining the length of time required for a soil to become responsive to such fertilizers. Fertilizer S additions are generally made as a secondary component of ammonium sulfate, single superphosphate, potassium sulfate, or compound NPK fertilizers, but there are some locations in the world where sulfur applications are made as a primary fertilizer. Use of these conventional sulfur-containing fertilizers is declining, however, and this is a major concern of the tropics (see section on "Sulfur Usage Trends and Sulfatic Fertilizers of the Future").

Since adsorbed sulfur is a major source of plant nutrients in weathered tropical soils, the use of non S-containing phosphatic fertilizers may aggravate the S problem by its replacement with phosphate. In this regard there are two aspects of sulfate adsorption that are important.

First, phosphate ions will replace sulfate ions on charged surfaces. This effect is shown in the work of Barrow (1969) (figure 6). In the soil used in this experiment, there was an almost linear decline in sulfate absorption with added phosphate.

This means that, where phosphatic fertilizers are added to a soil, the phosphate ions would be expected to remove sulfate ions from the clay, oxide, or organic surfaces. The displaced ions are then free in the soil solution and can be leached into the profile and either lost in percolating water or readsorbed at a lower depth. This appeared to be the case in the experiments of Bromfield (1972) where the sulfate level in the 0- to 7.5-cm layer declined from 10 ppm, where ammonium sulfate had been applied, down to 4 ppm where a combination of ammonium sulfate and single superphosphate had been applied. This occurred despite the addition of an extra 277 kg/ha of S in superphosphate over the 19-year period of the experiment. In this work most of the applied S was retained in the top 180 cm of the profile, but the zone of major accumulation was below 20 cm.

The second major effect of other fertilizers on sulfur nutrition is that brought about by pH changes. The adsorption of sulfate is concentration- and pH-dependent (Kamprath et al., 1956) (figure 7). This means that the application of fertilizer materials (rock phosphate) or soil amendments (lime) which increase soil pH may decrease sulfate retention.

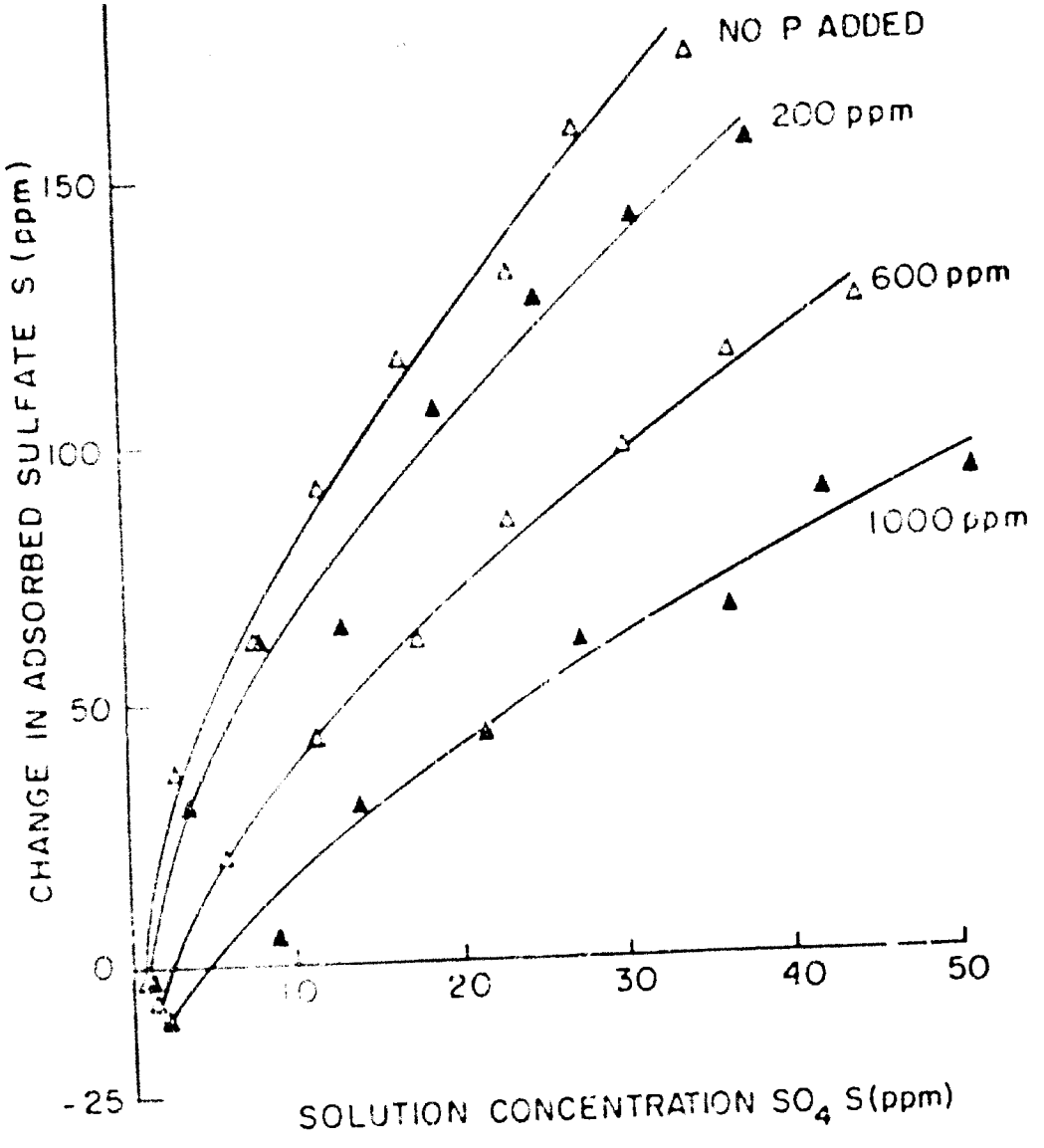

Figure 6. Effect of adding [illegible] phosphate to a soil on the [illegible] sulfate. The phosphate was added in solution to the soil and kept moist at 25°C for 2 weeks before samples were equilibrated with sulfate solutions in [illegible] M [illegible] chloride (Barrow, 1969).

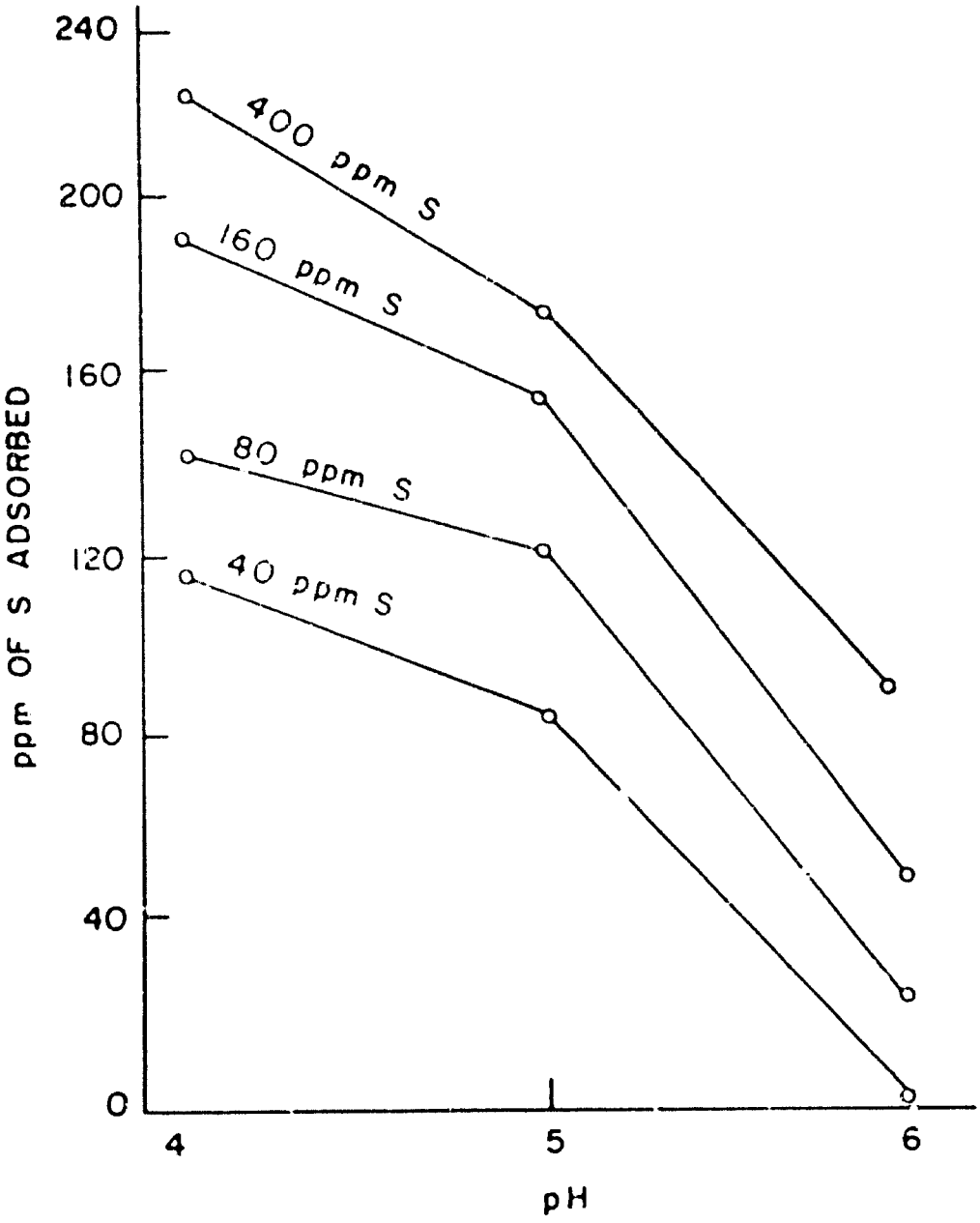

Figure 7. Effect of pH on the adsorption of sulfate by a Cecil soil at various solution concentrations of sulfate (Kamprath, et al., 1956).

Indonesia--A New Area of Sulfur Deficiency

To illustrate the effects of changing technology on fertilizer needs, a case study is presented from the province of South Sulawesi, Indonesia. In this part of Indonesia, rice production methods have changed from using traditional varieties without chemical fertilizer to the growing of high-yielding varieties fertilized with TSP and urea. Initially, yields were reported to be satisfactory, but after a number of years yields began to decline. Plant deficiency symptoms similar to those of sulfur deficiency were observed in many fields. Experiments were conducted to study this problem, and these included sulfur treatments.

Nutrient responses to N, P, and S were determined at six sites, and the results highlighted the need for all three nutrients (table 7). The fertilizer practice in common use in the region was equivalent to the NP treatment (urea and TSP).

In a wider survey of rice soils, 20 out of 26 field sites had grain responses exceeding 20%. The magnitude of the S responses ranged from 20% to 278% in grain yield. The average return on capital spent on sulfur fertilizer was 550%. In these experiments responses to elemental S were equal to those of ammonium sulfate and gypsum under flooded paddy conditions.

Results of studies with pasture on upland areas of South Sulawasi have also shown these soils to be deficient in S. Responses to elemental S were equal to those responses to gypsum (table 8). These experiments indicate that some 60%-70% of the agricultural area of the province is deficient in S and that elemental S is as useful as sulfate sources under both flooded and upland conditions.

Summary

The limited data which are available indicate widespread sulfur deficiencies in the tropics and areas in which there is a major deficiency of sulfur.

While some tropical soils may be deficient in their native state, many of the deficiencies develop as a result of agricultural exploitation. Technological advances that bring about yield increases and changes in stubble management result in

Table 7. The Response to N, P, and S (Average of Six Sites) in Grain Yield of Rice in S. Sulawesi, Indonesia (Mamaril, Personal Communication)

Treatment	Grain Yield (kg/ha)
Control	2,178
N	3,092
P	3,025
S	3,084
NP	3,509
NS	3,866
PS	3,707
NPS	4,113

Table 8. Responses in Centrosema Pubescence to Sulfur Surface Broadcast 4 Months Earlier, S. Sulawesi, Indonesia (Blair et al., 1978b)

Treatment	Yield (kg Green/ha)
Control	4,086
10 kg P) as single	
13 kg S) superphosphate	10,491
10 kg P as TSP	5,054
13 kg S as elemental	9,993

increased S removal, as do the organic matter losses that result from exploitative cropping.

The use of phosphatic fertilizers and soil amendments can, in some instances, aggravate the sulfur problem by reducing the amount of S retained in the adsorbed form against leaching.

The trend to nonsulfur-containing, so-called high-analysis, fertilizers is a major factor determining the incidence of S deficiency in the tropics, and this has been illustrated with a case study in South Sulawesi, Indonesia.

THE DIAGNOSIS OF AREAS DEFICIENT IN S USING DIFFERENT TECHNIQUES

In attempting to identify areas that may be sulfur deficient or to indicate areas where the problem may arise, it would be extremely useful if an association could be found between sulfur status and some factor in the environment. Alternatively, the analysis of soil or plant samples may be useful. If such relationships could be found, this could reduce the necessity of conducting costly field experiments and lead to an earlier recognition of problem areas.

Environmental Factors and Sulfur Status

Rainfall

Hasan *et al.* (1970) suggested that sulfur accumulations and distribution in soil profiles are related to rainfall in three ways:

1. The capacity of soils to stabilize organic matter which contains S is a function of reactive products of weathering which, in turn, are related to rainfall.

2. The capacity of soils to adsorb sulfate is related to weathering products.

3. Rainfall can be a major source of sulfate.

In a study of soils from northern New South Wales, Australia, McArthur and Spencer (1970) found that sulfur responses were least on soils from the highest rainfall areas. Soils from these areas also had the greatest sulfur adsorption capacity and were able to retain sulfate against leaching. Although rainfall and sulfate adsorption capacity have been related, the relationship varied between soil types (Barrow, 1970), and no direct relationship has been found to exist between adsorption capacity and the sulfur status of soils.

The relationship between adsorption capacity and rainfall can be complicated by other factors. Negative correlations between rainfall and pH and rainfall and sulfur response and a positve correlation between rainfall and sulfate adsorption were found on the Dorrigo soils used by McArthur and Spencer (1970). This may not indicate a cause and effect relationship between sulfur responsiveness and the measured parameter. Sulfate adsorption occurs by reaction with surface aluminum and iron. In some soils the amount of reactive aluminum has been closely related to the pH and both of these to rainfall (Barrow, 1970).

Rainfall is a major source of S in industrialized temperate areas, and in these areas the annual accessions are often in excess of 20 kg/ha/yr of S (Coleman, 1966). In such areas S deficiencies are unlikely. Few data are available on the amount of S in rainfall in tropical areas, but indications are that input from this source is low. Bromfield (1974b) estimated that the mean annual S input in rainfall was only 1.14 kg/ha in Nigeria.

Sulfur inputs from rainfall are generally higher near the sea than inland. Fox et al. (1965) recorded 5 ppm S in rainwater 0.5 km from the sea on the island of Kauai, Hawaii, but only 0.8 ppm 8 km inland. Probert (1976) measured inputs of 6.0 kg/ha/yr 9 km away from the sea near Townsville, Australia, and 3.2 kg/ha/yr 40 km inland. The level of input from the sea in Indonesia is unknown but Blair et al. (1978a) recorded S responses in crops within 50 m of the sea in South Sulawesi.

Sufficient data are not available to establish a direct relationship between rainfall and S status, and the data available suggest that it may be dangerous to generalize, as is often done in temperate areas, that areas near the sea in the tropics may be free of sulfur deficiency.

Irrigation Water

Irrigation water is a source of S for crops. Yoshida and Chaudhry (1972) suggested that irrigation water with a sulfur

content of 2.7 ppm would be able to supply the entire needs of a rice crop. On the other hand, Wang (1976) suggests this value should be 6 ppm. Severe sulfur deficiencies have been recorded in rice in South Sulawesi, Indonesia, in paddies supplied with water containing 2.8 ppm S. This suggests that the S contribution from irrigation water needs some reassessment. To generalize that areas supplied with irrigation water of >2.7 ppm S would not be responsive to S is not valid.

Soil Factors

Little work has been done in the tropics to relate S deficiencies to soil factors, but experience from subtropical and temperate areas would suggest little likelihood of finding worthwhile associations. A survey of information from Australia was made by Blair and Nicholson (1975), and much of the discussion that follows comes from that source.

Many factors contribute to the poor relationships established to date. An early attempt to relate sulfur responses to various measurable factors was carried out on 32 virgin soils collected from eastern temperate Australia (McLachlan, 1955). No relationship was found between responses and climatic and soil factors apart from pH. In an examination of 40 Northern Tableland soils from New South Wales (Spencer and Barrow, 1963), no relationship was found between pH and sulfur response. The pH range of these soils was narrower than that of those tested in the previous survey, and the pH relationship noted earlier may have been unduly influenced by a small number of soils of high pH (>8.0).

The color of basaltic sedentary soils in northern New South Wales was found to be significantly correlated with sulfur status (r = 0.92), the reddest soils being most deficient (Spencer, 1966). There was no relationship between soil pH or redox potential. The red soils were probably high in exposed iron oxide, reflecting better aeration and drainage and greater sulfur leaching. Because of the comparative nature of such an assessment, it appears to be of limited value in delineating sulfur-responsive areas.

This past lack of success in establishing a meaningful relationship between the occurrence of sulfur deficiency and some predictable factor in the soil or climatic environment means that we must either conduct more studies of associations in various areas or revert to agronomic response data or soil and/or plant tissue testing to delineate areas of sulfur deficiency.

Soil Testing for Sulfur Status

Little information is available on the usefulness of sulfur soil tests under tropical conditions while, on the other hand, a great deal of effort has gone into correlation studies of available sulfate and plant response under temperate conditions. Studies in this field fall into two categories: (1) those where an attempt is made to find a correlation between degree of deficiency and soil test and (2) those where an attempt is made to find a soil test value below which a response is certain or likely.

The major problem encountered in studies of soil sulfur in temperate areas is the variability in the size of the soil sulfur pools over short periods of time. This is brought about by the nature of the sulfur sources present. Since such a large proportion of the S is in an organic form or associated with organic matter (ester S), it can undergo rapid mineralization and/or splitting to plant-available forms. This is a major problem in areas with marked short-term fluctuations in moisture and large seasonal temperature differences. In tropical areas where short-term temperature and soil moisture fluctuations are not as great, it may be that soil testing would be of more use. This should be investigated further.

The major problems encountered in sulfur studies are those associated with analytical methods and sample preparation. Errors in these stages of estimation lead to great variability in results. To minimize such variations precautions must be taken in each of the following steps: sampling, sample preparation, S extraction, analysis, and interpretation.

Sampling

There are three aspects of sampling that must be taken into consideration: pattern and intensity, depth, and timing.

Pattern and Intensity--No hard-and-fast rule can be made on these two factors, but care must be taken to obtain a representative sample of the area under test. This can best be checked by taking several separate bulk samples (made of at least 20 cores each) from the test area and comparing the results from each. Variation among samples should be less than 10%. If there are different soil types, drainage areas, etc., within the test area, separate samples should be taken from each area.

Core samples, generally of 2.5-cm diameter, should be taken either from a zig-zag of the whole area or as a pattern sample from random areas within the test area. In both cases, a minimum of 20 cores should be used as a bulk sample for testing.

Sampling Depth--A common depth of soil sampling is 7.5 cm. While this depth may be acceptable for an immobile nutrient, such as phosphorus, it may be inadequate for a mobile nutrient, such as sulfur, which accumulates at variable depths in the profile. This problem was experienced by Cooper (1968) in her study of New Zealand soils. This also may be a major problem on tropical soils where sulfates have been leached into the profile and the deeper-placed S source is still accessible to plants. Any experiments where sulfur soil testing is evaluated should include a study of vertical distribution of S at least at the start of the experiment.

Timing--Because of the dynamic nature of S in soils, the time of the year when the soil sample is taken must also be carefully considered. Generally, the sampling should be taken as long as possible after the previous fertilizer application and as close as practicable to the planting of the crop.

Sample Preparation

The labile nature of ester sulfate compounds means that samples must be carefully prepared before chemical extraction. Freney et al. (1962) state that many failures to find correlations between extractable sulfate and responce may be due to the method of sample drying. Williams and Steinbergs (1964) found variable increases in extractable S between soils and extractants when soils were air-dried at 17°-19°C. These increases ranged from 0 to 12.1 ppm in KH_2PO_4 extractable S. Peverill et al. (1974) studied this problem and found that the addition of activated charcoal to the calcium phosphate extracting solution reduced to an insignificant level the variation resulting from storage and drying.

There is a need to study the effect of drying and the usefulness of the activated charcoal method in tropical soils.

S Extraction

The methods used can be grouped into four basic categories: soluble sulfates, soluble and adsorbed sulfate, total and organic S, and microbiological methods.

The first three methods involve the removal of S by one of several chemical extractants. Not all extractants perform equally well on all soils. Those that remove soluble-plus portions of adsorbed sulfate tend to be better correlated with S status than those removing only readily soluble sulfate. Adsorbed sulfate is removed by neutral and slightly alkaline extracts and by extractants containing a strong replacing ion such as phosphate. Excellent prediction of response in field trials has been reported in isolated areas of the temperate zone for extractants that remove soluble, adsorbed, and portions of the organic S. Included are the acetic acid-phosphate solutions employed by Cooper (1968) and Hoeft et al. (1973) and the pH 8.5 sodium bicarbonate solution used by Bardsley and Kilmer (1963) which is commonly used as an extractant for "available P." Because of the neutralizing effect, acidic solutions should never be used with calcareous soils (Reisenauer, 1975).

Solutions containing phosphate are most commonly used as sulfate extractants since the phosphate effectively replaces sulfate on the adsorption complex. Of the phosphate extractants calcium phosphate is generally the most acceptable because the divalent calcium does not cause the clay and organic matter to disperse as may occur when potassium or sodium is used. For these reasons, calcium phosphate (500 ppm P) should be one of the extractants considered in any proposed testing program.

Relationships between total S or organic S and plant response have generally been found to be poor or nonexistent in soils from the temperate areas. However, one study of tropical soils, where the S released on incubation (organic S) was related to plant response, should be noted. In a study of 45 soils from Nigeria, Enwezor (1976) found that soils mineralizing <6 ppm of S (extracted by sodium acetate) gave responses to S in a pot trial with maize. In this experiment the maize was grown for only 45 days, and more field work using this method needs to be done with the condition that the crop is grown to maturity. Perhaps in areas with marked wet/dry seasons this method, applied to samples taken towards the end of the dry season, would be useful.

Microbiological methods have never really gained much acceptance, allegedly because they are impractical and time consuming. Perhaps this is a bias on the part of soil chemists rather than a true indication of the worth of these tests. In one study of soils from Kenya, Mehlich (1970) compared the response by greenhouse tomatoes with the growth of Cunninghamella on 28 topsoils and found good agreement between the growth of Cunninghamella and tomatoes. This method requires minimal equipment and is worthy of further investigation in the tropics.

Analysis

The lack of an accurate, rapid, and uncomplicated method for sulfate analysis is a major factor contributing to the lack of interest in this nutrient.

The most accurate and sensitive method for determining sulfate is that of Johnson and Nishita (1952) which involves its reduction to H_2S and its adsorption in zinc-sodium acetate. This method, while accurate, is time consuming and costly. The equipment required is specialized, and the availability of chemicals and nitrogen gas limits its use in less-developed tropical areas.

Once the sulfate has been extracted from the soil and all the sulfur in the plant sample has been oxidized to sulfate, the S content of the sample must then be determined. There are many methods available for this. Beaton et al. (1965) list some 107 methods of extraction and analysis of soil S and 66 combinations of ashing and analytical methods for plant material. For laboratories with limited equipment, the barium sulfate turbidimetric method of Chesnin and Yien (1951) is the most practical. The major problem of instability in the $BaSO_4$ precipitate experienced in this method has been overcome by the use of stabilizers, such as Tween 80 (Quin and Woods, 1976), poly-vinyl-alcohol (Rocks et al., 1972), etc.

The extraction of soil with $NaHCO_3$ and digestion of plant material with $Mg(NO_3)_2$ + $HClO_3$ allow the simultaneous determination of P and S in soil and plant material and, for this reason, these methods should be evaluated further under tropical conditions.

Interpretation

All of the published sulfur methods have, in some way, been correlated with plant response. As mentioned previously, the two general methods of calibration are: (1) a relationship between percent of maximum yield [(yield without sulfur ÷ yield with sulfur) x 100] and soil test and (2) the selection of a value above which little or no response is likely. The basic difference between these two methods is that, in the former, an attempt is made to define the degree of deficiency while, in the latter, a simple presence/absence statement is made.

Correlations are generally better from pot experiment data than from field data because rooting density is high and there is minimal influence of other factors (other nutrients, climate,

etc.) on the plant growth. These studies are often of limited value because they are generally short-term exhaustion studies rather than a measure of the soil's ability to supply S throughout the entire growth of the crop.

In general, researchers have listed the "critical values" proposed for soil S by various extractants (Ensminger and Freney, 1966; Reisenauer 1975), and their findings, along with other published data from tropical soils, are presented in table 9. These data come from a wide variety of crops and soil types and indicate great variability in critical levels found among studies. This does not agree with Reisenauer (1976) who concluded from his summary of the data that "the values agree surprisingly well and indicate a high level of dependability in these tests."

This variability between results obtained in different studies does not render the soil test procedure useless; instead, it serves to emphasize the need for correlation studies to be conducted in limited areas with specific crops, soil extractants, and methods.

Tissue Testing for Sulfur Status

In surveying the literature on sulfur tissue testing, the problem of method of determination is immediately evident. This is highlighted by the following excerpt from Kang and Osiname (1976:336) who, in their own study, used the sodium carbonate fusion/HCl method:

> From the relationship between grain yield and total S content in the ear leaf, the critical S level in the ear leaf is estimated at about 0.14% S. This value is lower than the 0.24% S in sweet corn ear leaf as suggested by Daigger and Fox (1973). Part of this discrepancy in values might also be due to differences in the method of digestion of the plant material. (Daigger and Fox used nitric-perchloric acid procedure.) Sansum and Robinson (1974) reported that S recovery depends on the method of digestion of plant material; they demonstrated that dry combustion methods give lower S values [see table 10].

A tabulation of data showing critical levels without a specification of the method of digestion and determination, such as that made by Eaton (1966), is, therefore, of little value for setting levels of adequacy.

Table 9. Levels of Soil S Extracted by Various Means Below Which a Response to S is Likely (Critical Level)

Method of Determination and Crop	Sampling Depth cm	Critical Level ppm	Country	Reference
Readily Soluble Sulfate				
Water (legume-grass)		3	Canada	Walker & Doornenbal (1972)
0.1 M $CaCl_2$ (legume-grass)		3	Canada	Walker & Doornenbal (1972)
0.01 M $CaCl_2$ (pastures)		6	Canada	Beaton & Fox (1971)
LiCl (*Brassica*)	0-20	Variable	West Indies	Haque (1971)
$MgCl_2$ (*Brassica*)		Variable	West Indies	Haque (1971)
Readily Soluble Plus Portions of Adsorbed Sulfate				
KH_2PO_4-500 ppm P				
Pasture	0-7.5	8	New Zealand	Cooper (1963)
Pasture		4	Australia	Spencer *et al.* (1969)
Maize	0-15	4	Nigeria	Kang & Osiname (1976)
Brassica		Variable	West Indies	Haque (1971)
$Ca(H_2PO_4)_2$-500 ppm				
Alfalfa	n.a.	10		Fox *et al.* (1964)
Maize	n.a.	8		Fox *et al.* (1964)
Various crops and pastures	(0-15)	13	Australia	Andrew (1975)
Pasture	n.a.	5-4	Australia	Andrew (1975)
Brassica	n.a.	Variable	West Indies	Haque (1971)
Maize	(0-15)	4	Nigeria	Kang & Osiname (1976)
NaOAc-HOAc				
Alfalfa		12	USA	Harward *et al.* (1962)
Maize	(0-15)	6[a]	Nigeria	Enwezor (1976)

Table 9. Levels of Soil Extracted by Various Means Below Which a Response to S is Likely (Critical Level) (Continued)

Method of Determination and Crop	Sampling Depth cm	Critical Level ppm	Country	Reference
NH_4OAc				
Brassica	(0-20)	Variable	West Indies	Haque (1971)
Maize	(0-15)	4	Nigeria	Kang & Osiname (1976)
Pearl millet	(0-20)	6-7	Brazil	McClung *et al.* (1959)
0.5 $NaHCO_3$				
Cotton		10	USA	Kilmer & Nearpass (1960)
Readily Soluble, Adsorbed, and Portions of Organic Sulfate:				
$Ca(H_2PO_4)_2$-2M HOAc				
Alfalfa		10		Hoeft *et al.* (1973)
NaH_2PO_4-2M HOAc				
Pasture	0-7.5	10		Cooper (1968)
0.01M HCl				
Pasture	n.a.	200		Andrew (1976)
Total S				
Various crops		Variable		Andrew (1976)
'A' Value				
Cotton		15		Nearpass *et al.* (1961)
Alfalfa		10		Harward *et al.* (1962)
Pearl millet		70		McClung *et al.* (1959)

a. After incubation at 30°C for 2 weeks.
n.a. Not available.

Of the methods available to oxidize organic sulfur to sulfate, wet ashing, using nitric/perchloric acid plus dichromate and metavanadate and ≥ 1-hour digestion beyond color change, appears the most acceptable (Sansum and Robinson, 1974). A second method worthy of investigation is the magnesium nitrate/perchloric acid method proposed by Quin and Woods (1976). Both of these methods require a minimum of equipment and, with trained personnel, are rapid and reproducible.

Often "critical levels" are established on shaky evidence. The example in figure 8 is taken from De Freitas et al. (1972) who conclude from these data that "about 200 ppm SO_4^{-2} - S in coffee leaves indicates adequate S nutrition." However, on examination of the correlation data, it is found that 10 samples had a relative yield of >90% with an S content below 200 ppm, and 27 samples a relative yield >90% with an S content above 200 ppm. This spread of data indicates this criterion to be too insensitive for use as a diagnostic tool.

Many researchers have suggested that the N:S ratio can be used as a diagnostic tool. Dijkshoorn and Van Wijk (1976) made a comprehensive study of the literature regarding N:S ratios in the protein of leaf material of growing plants. A ratio of about 15 parts N for every 1 part S was applicable for a wide variety of field crops. The ratio differed slightly with species, ranging from about 14:1 for gramineous plants to about 17:1 for legumes.

Variations in the amounts of N and S fertilizers added do not appreciably change the N:S ratios of the protein. The composition of a given protein is constant, being controlled by the genetics of the plant species. However, environmental factors do influence the relative proportions of various cytoplasmic proteins. Data reviewed by Dijksnoorn and Van Wijk (1967) indicate that these changes in distribution were not great enough to change materially the N:S ratio of 15:1.

The consistency of the protein N:protein S ratio is shown in the data of Leggett et al. (1966) on sugar beets (figure 9b). Stewart (1969) suggests that these data, when plotted as in figure 9a, can be used for diagnosis with those points falling to the left of the line being deficient in S. This is an unsatisfactory criterion on its own as it does not distinguish between S deficiency and N excess. The data in figure 9a suggest that the use of total S alone for the diagnostic purposes is as beneficial as N:S ratio.

Lott et al. (1960) concluded that sulfate-S was more sensitive than total S as an index of deficiency for coffee. This criterion is not satisfactory on its own as sulfates may

Table 10. A Comparison of Ashing Methods for Plant Material on Sulfur Determinations (Adapted from Sanson and Robinson, 1974: 367)

Method	% S
Dry ashing	0.156
$HNO_3/HClO_4$	0.207
$HNO_3/HClO_4$ + 1-hour digestion after clearing	0.335

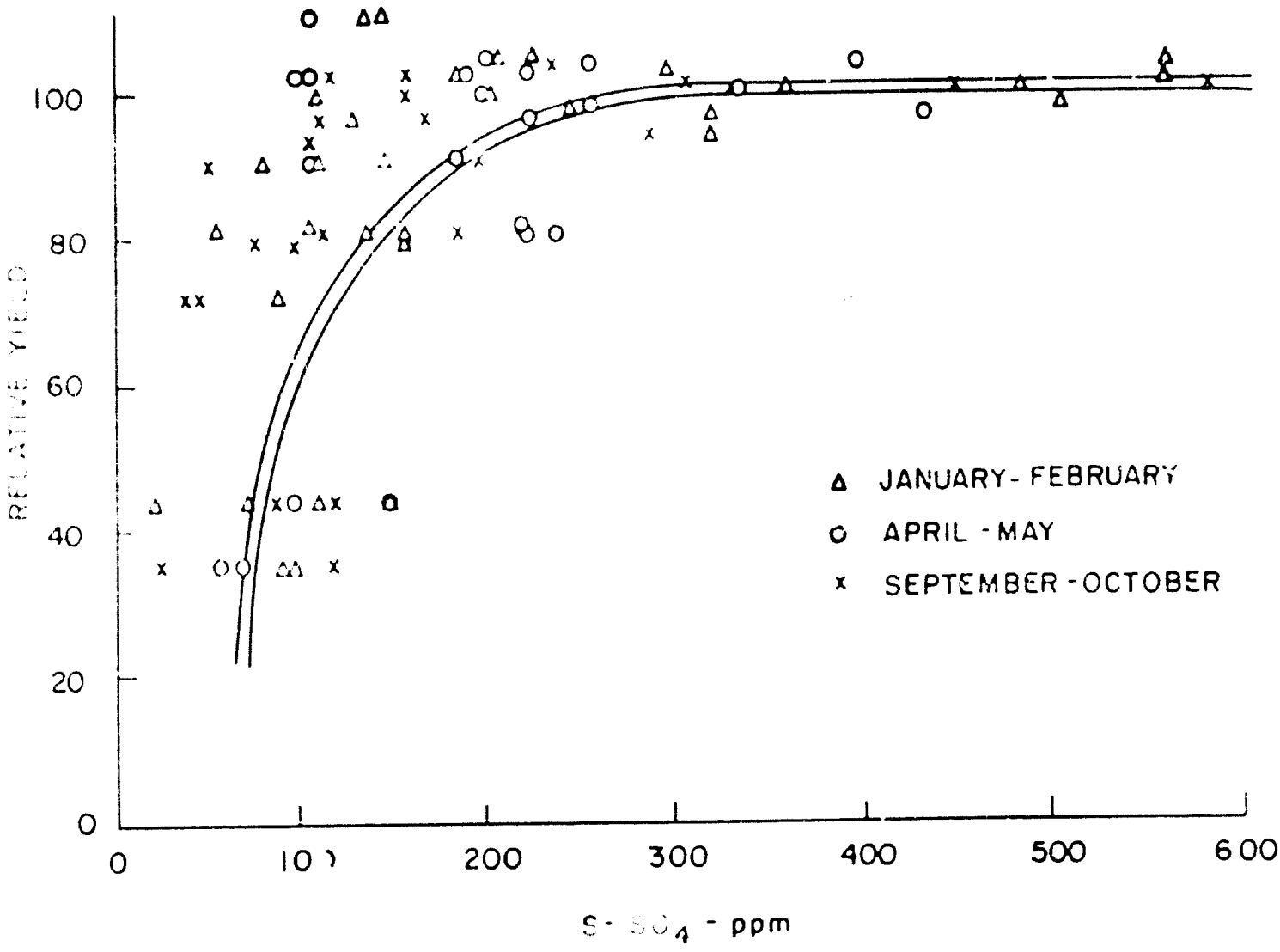

Figure 5. Relative yields [illegible] as a function of the concentration of sulfate-sulfur in leaf samples at various seasons of the year (De Freitas, et al., 1972).

accumulate under conditions of molybdenum deficiency even in circumstances where S is deficient (Anderson and Spencer, 1950).

Fox et al. (1977) have shown that the "critical level" of S in cowpeas (Vigna unguiculata [L.] Walp) varies between cultivars. In their solution culture experiment, the critical value varied between 0.032% total S in cultivar Sitao Pole and 0.064% in TVU76-2E. This cultivar-specific variation makes the setting of critical levels even more difficult.

The use of multiple criteria of N:S ratio, SO_4^{-2} - S, and total S in cereals has been suggested by Blair and Crotts (1970) to overcome the deficiencies inherent in the single factor classification system. This approach has been extended to published rice data (Blair et al., 1978a). The criteria used are given in table 11, and it is suggested that any attempt at setting critical levels should consider the use of multiple criteria.

Ensminger and Freney (1966) list the effect of age on S contents in several species. Since it is desirable to select a plant part that is relatively insensitive to maturity, an examination should be made of the effect of maturity on the S content of the plant part(s) to determine the sensitivity to sampling time.

Summary

In the published data available, no relationship could be found between the incidence of sulfur deficiency and some measurable parameter of the climate or soil environment. For this reason, soil and tissue testing must be used to delineate problem areas.

Soil testing for sulfur has not been shown to be very successful in temperate areas but, because of important environmental differences, its role should be reassessed in the tropics. In doing so, care should be taken in sampling, analysis, and interpretation to evaluate properly the tests.

Plant analysis for sulfur appears to offer more promise, but problems with analytical procedures must be overcome before useful data can be obtained. More correlation data are required.

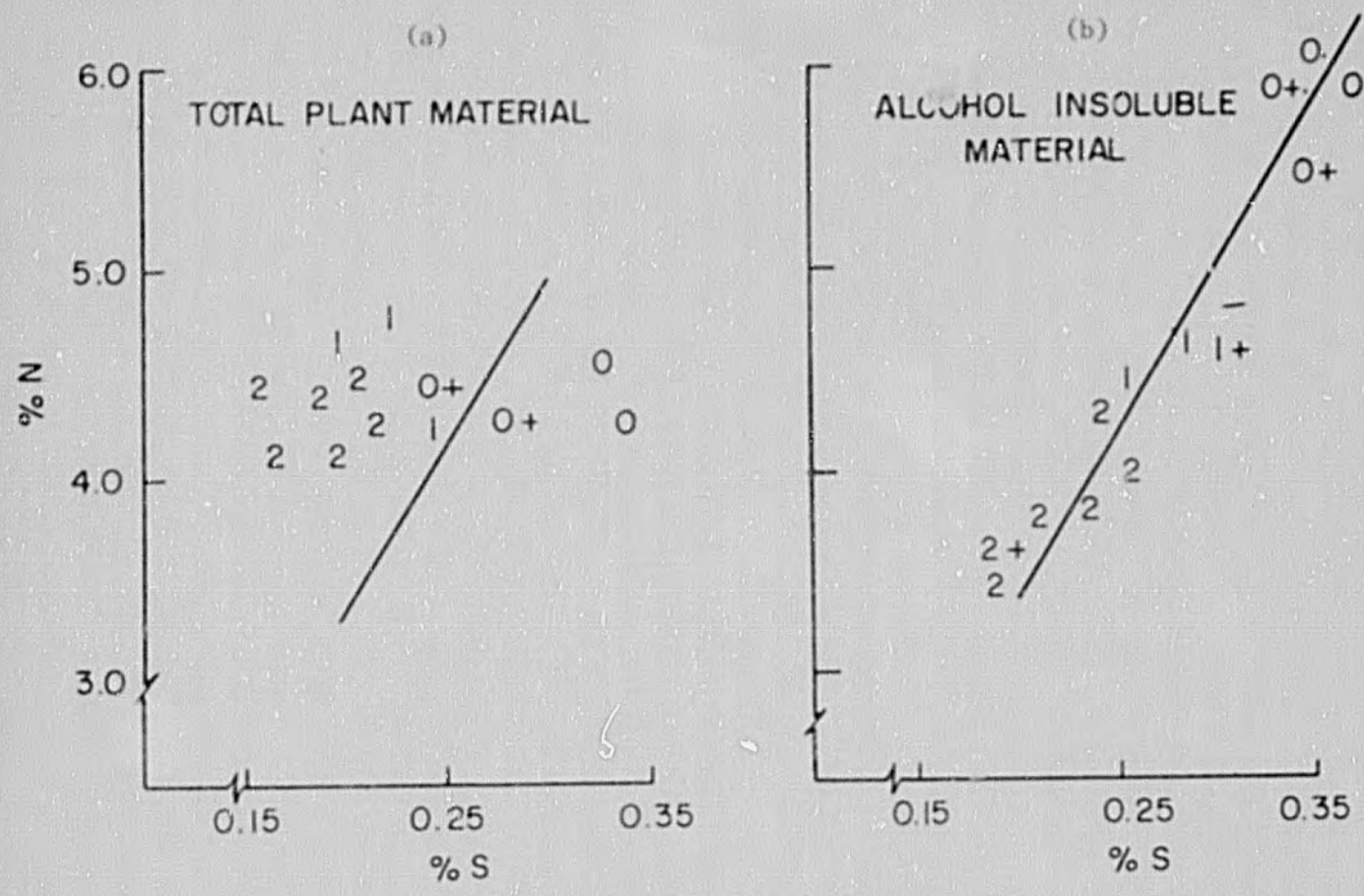

Figure 9. The percent N and S in the total plant material (figure a) and alcohol-insoluble residue of plant material (figure b) of sugarbeet leaf blades from plants having various degrees of S deficiency (0--no S deficiency symptoms; 1--chlorotic; 2--severely chlorotic) (Stewart, 1969).

Table 11. Preliminary Classification of N and S Status of Whole Rice Tops Sampled from Tillering to Flowering Stages of Growth (Blair et al., 1978a)

Category	N (%)	S (%)	N/S Ratio	Status N	Status S
I	> 1.6	< 0.10	> 15	adequate	deficient
II	> 1.6	0.10-0.15	> 10	adequate	marginal
III	> 1.6	> 0.15	< 10	adequate	adequate
IV	< 1.6	> 0.15	< 10	deficient	adequate
V	< 1.6	< 0.10	variable	deficient	deficient

SULFUR USAGE TRENDS AND SULFUR FERTILIZERS OF THE FUTURE

Sulfur Fertilizers Available

As mentioned previously, the major fertilizer sources of sulfur used to date have been single superphosphate and sulfate of ammonia. These have generally been used as primary N and P sources with S applied incidentally.

Where S deficiencies have been recognized and fertilizers used to correct the deficiencies, elemental S and gypsum ($CaSO_4.2H_2O$) have been two of the major sources used. The sulfur content of fertilizers varies greatly, and the form varies between sulfate, elemental S, and organic S (table 12). The sulfur content of compound NPK fertilizers is not given because their composition varies according to the formulation. The method of manufacture of sulfatic fertilizers is given in Beaton and Fox (1971).

Sulfate sources that are soluble are immediately available to plants, but elemental S must first be oxidized to sulfate by Thiobacillus organisms. Organic forms must also be mineralized to sulfate, before becoming available.

Consumption Patterns

The proportion of world fertilizer production that is made up of sulfur-containing fertilizers is declining. Ammonium sulfate consumption has fallen from 19.1% of total N usage in 1961-66 to 8.4% in 1973-74 and is projected to fall to 6.2% by 1980. At the same time, urea is increasing in importance throughout the world. The British Sulphur Corporation (1974) projects an increase in world demand for urea of 9.1 million tons N between 1973-74 and 1980-81. At the same time, ammonium sulfate production is forecast to increase by only 0.53 million tons N. The N:S ratio of the projected increases is 41:1, while the crop demand is in a ratio of approximately 15:1. In addition, single superphosphate production has declined from 63% down to 22% of the world consumption (figure 10) of phosphatic fertilizers in the period 1961-72.

Table 12. The Sulfur Content of Fertilizer S Sources Presently Available

Source	% S
Sulfate Containing	
Ammonium sulfate	24
Potassium sulfate	16-22
Calcium sulfate (gypsum)	18
Superphosphate, single	12
Superphosphate, double	5
Superphosphate, triple	1
Diammonium phosphate	1-3
Rock phosphate	0-1
Ammonium nitrate-sulfate	5-11
Ammonium phosphate-sulfate	14-20
Ammonium sulfate-nitrate	15
Ammoniated superphosphate	11-13
Diammonium phosphate-sulfate	10-15
Magnesium sulfate (Kiserite)	23
Potassium-magnesium sulfate	22
Ammonium phosphate-sulfate-gypsum	8
Ammonium phosphate-sulfate-urea	6
Urea-ammonium sulfate	4-13
Elemental Sulfur Containing	
Diammonium phosphate-sulfur	12-15
Elemental sulfur	100
Diammonium polyphosphate sulfur	15
Diammonium phosphate-urea phosphate-S	5-20
Urea-sulfur	10
KCl-Urea-S	Varies
Sulfur-coated urea	Varies
Rock P-S	7-16
Sulfur-bentonite	90
Sulfur fortified superphosphate	27
Ammonia-sulfur solution	10
Other Inorganic Forms	
Ammonium thiosulfate solution	26
Sulfur dioxide	50
Ammonium bisulfite	8-17
Ammonium bisulfite polyphosphate	3-5
Ammonium polysulfide	40-45
NH_4-P_2S_5	31
Polyamides	29-32
Pyrite and pyrhotite	40-80
Organic S Containing (partial listing)	
Sewage sludge	0.4
Bone meal	0.2
Peanut meal	0.1
Animal manure (cattle)	0.2

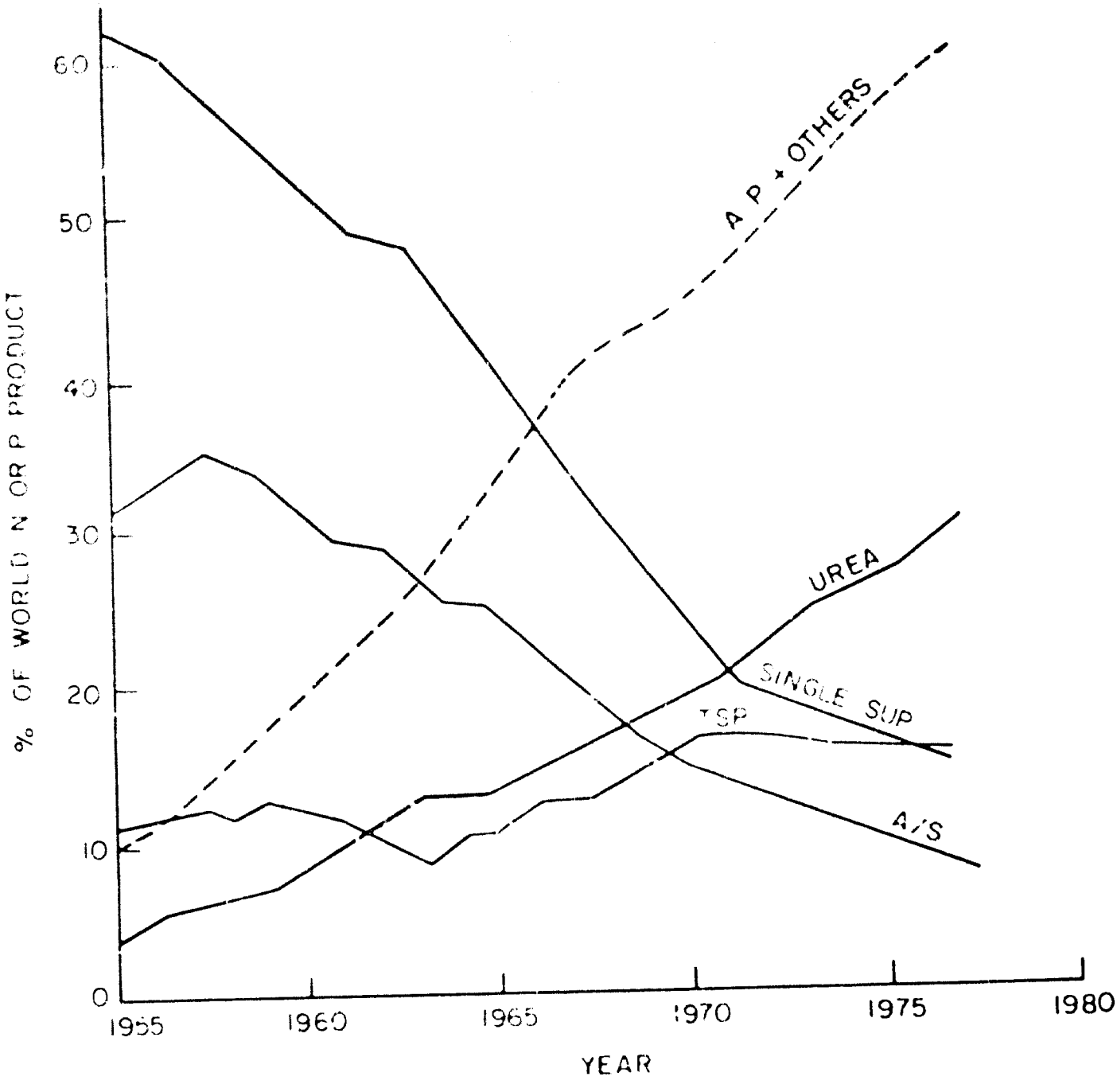

Figure 10. World fertilizer consumption trend (Blynett, 1970, 1974).

Table 13. Changes in Consumption of N, P, K, and S Over Time in Six Countries of the Developing World (FAO, 1975)

Country	Years	N	P	K	S from N	S from P	S from K	Total
		consumption (metric tons)						
Brazil	1961-66	57,757	37,581	66,406	39,352	34,997	957	74,349
	1972-73	411,642	301,518	378,764	170,539	103,494	2,468	276,033
Change		+353,885	+263,937	+312,358				+201,684
Chile	1966-67	36,432	33,590	16,098	0	1,935	1,824	3,759
	1973-74	59,324	50,448	11,534	0	4,227	2,704	6,921
Change		+22,892	+16,858	-4,564				+3,162
Korea	1966-67	239,691	54,523	48,801	40,189	17	700	40,906
	1973-74	411,236	85,659	124,361	0	0	19,670	19,670
Change		+171,545	+30,936	+75,560				-21,236
Indonesia	1970-71	201,742	12,495	5,373	13,251	0	221	13,472
	1972-73	347,404	28,791	24,890	32,265	0	1,056	33,321
Change		+145,662	+16,296	+19,517				+19,849
Egypt	1961-66	232,120	20,382	960	80,588	27,128	200	107,916
	1972-73	360,923	24,315	1,760	57,681	32,885	606	91,172
Change		+128,803	+3,933	+800				-16,744
Senegal	1966-67	5,355	2,170	4,802	6,120	0	0	6,120
	1973-74	7,360	3,417	6,558	43	0	0	43
Change		+2,005	+1,247	+1,756				-6,077

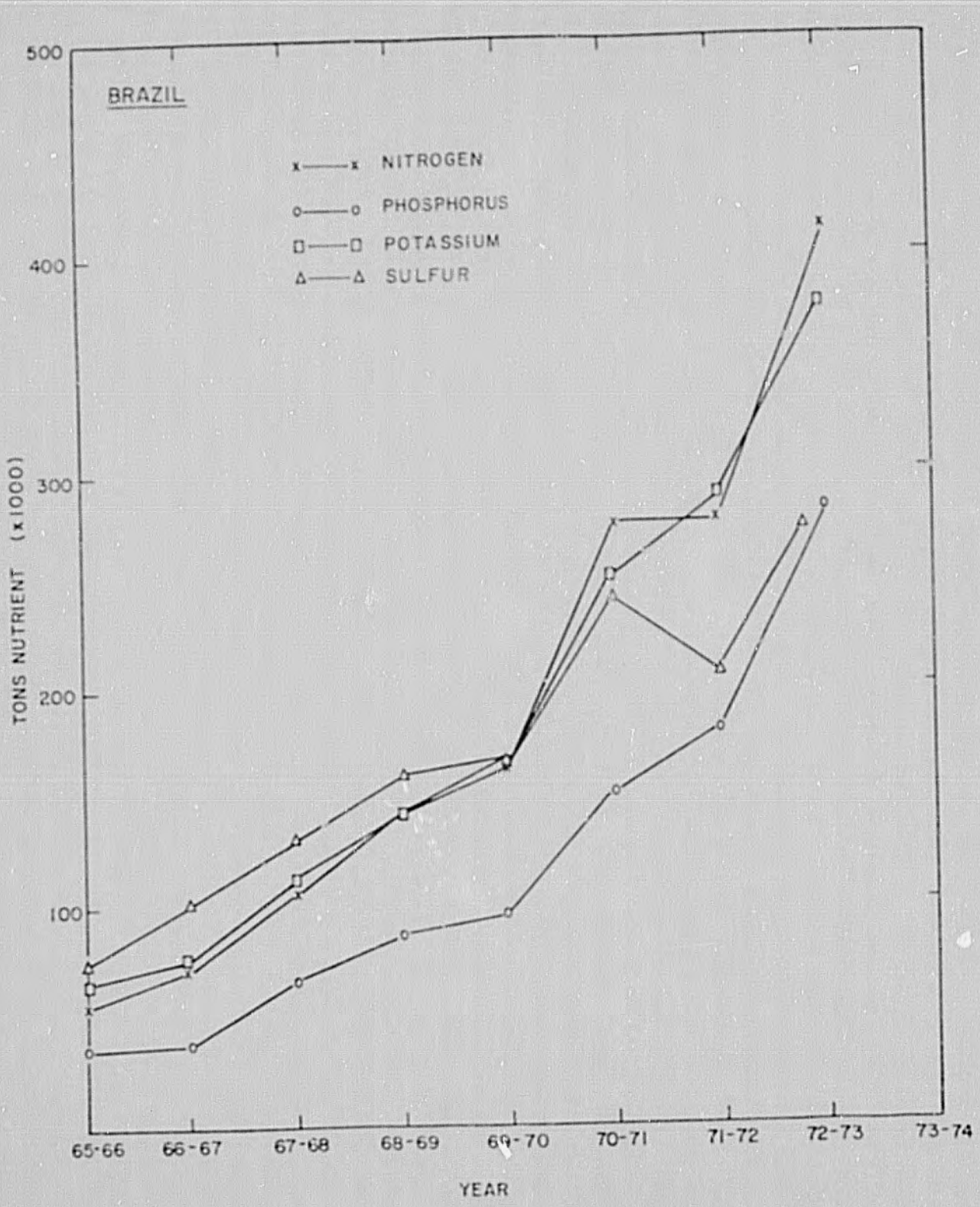

Figure 11. Consumption of N, P, K, and S (metric tons) in Brazil over the years 1965/66-1973/74 (FAO, 1975).

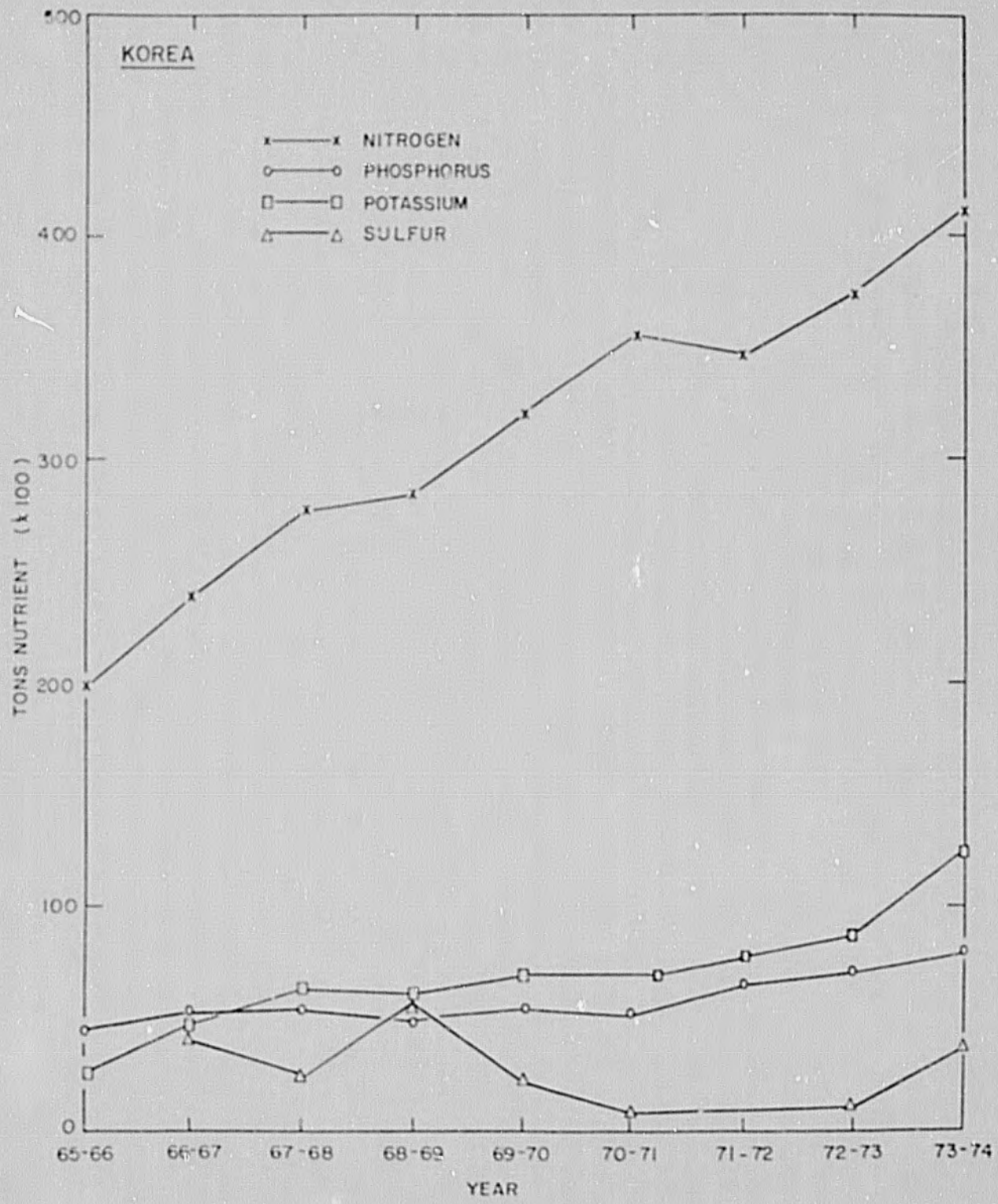

Figure 12. Consumption of N, P, K, and S (metric tons) in Korea over the years 1965/66-1973/74 (FAO, 1975).

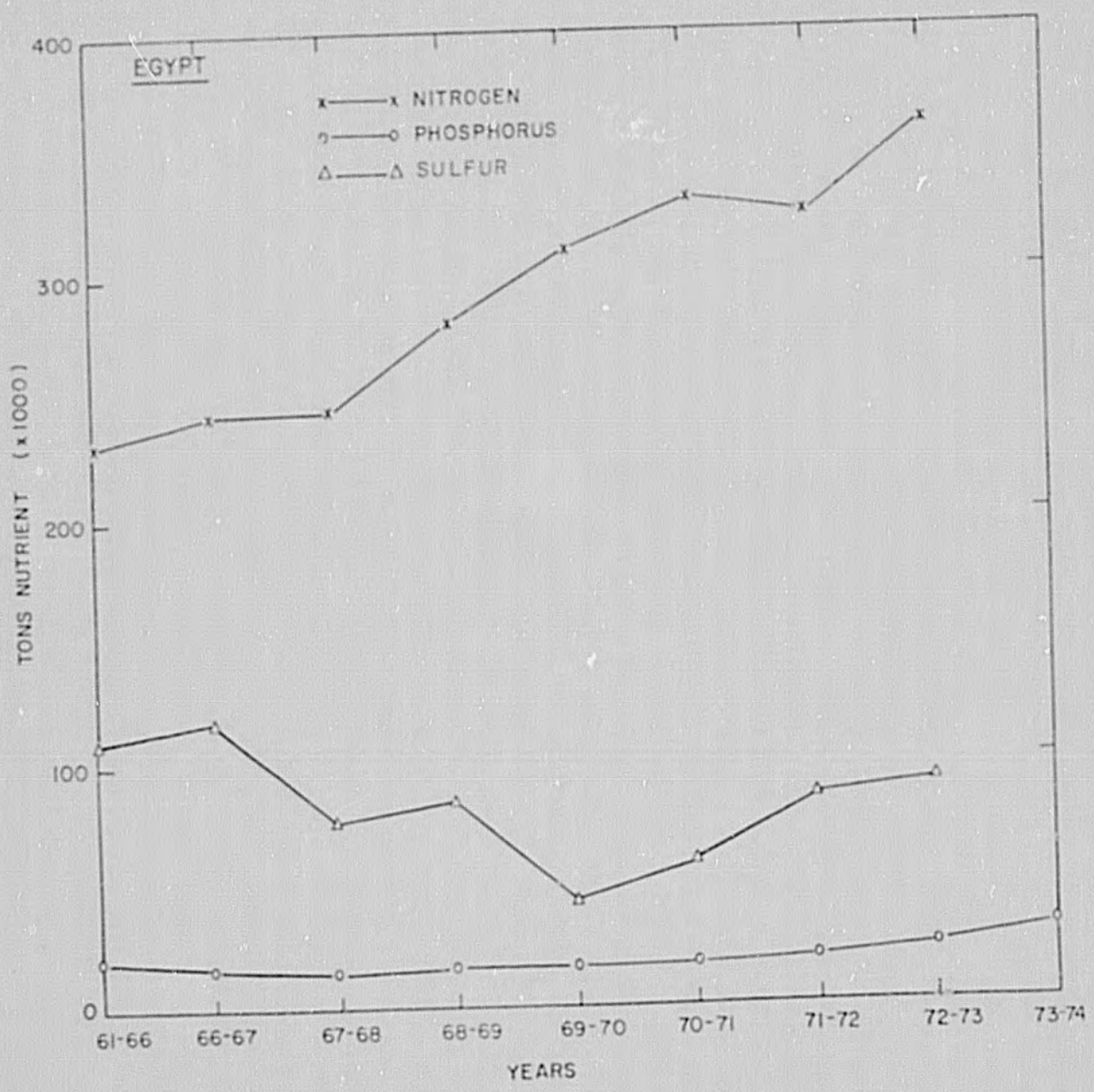

Figure 13. Consumption of N, P, K, and S (metric tons) in Egypt over the years 1965/66-1973/74 (FAO, 1975).

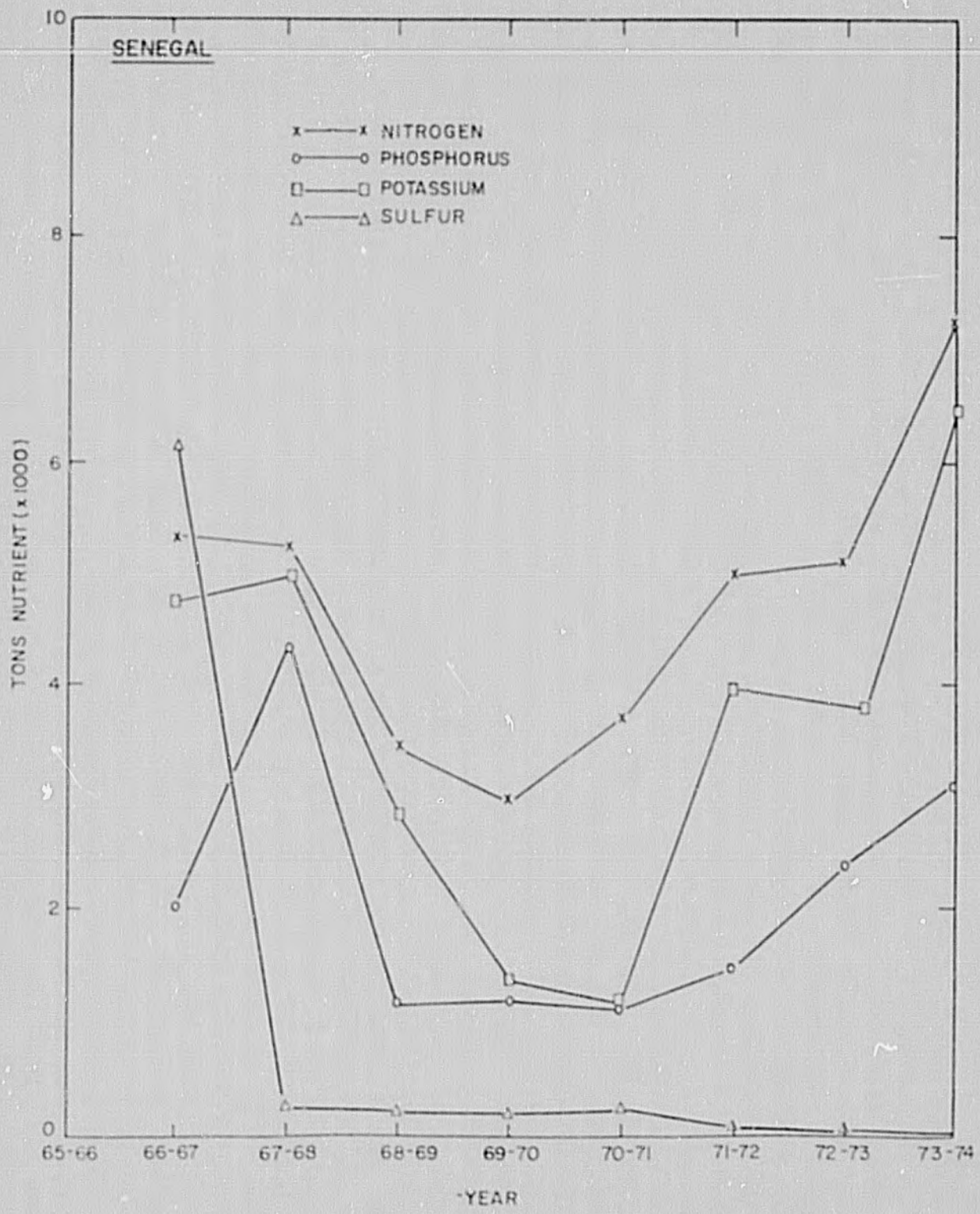

Figure 14. Consumption of N, P, K, and S (metric tons) in Senegal over the years 1965/66-1973/74 (FAO, 1975).

As mentioned previously, data on fertilizer consumption are not available for all countries. Six countries from the developing world for which data are available are used to illustrate trends (table 13, figures 11, 12, 13, and 14). Clearly these countries fall into three categories:

1. Those where there has been no shift away from S-containing fertilizers, e.g., Brazil (figure 11).

2. Those where there has been a partial shift from production of sulfur-containing fertilizers, e.g., Indonesia (table 13).

3. Those where the use of S-containing fertilizers has not been maintained, e.g., Korea (figure 12), Egypt (figure 13), and Senegal (figure 14).

Based on data (table 14) on new fertilizer production facilities (FAO, 1975), the trend away from sulfur-containing P forms of fertilizer is likely to continue at least until 1980. These data show that P production will increase by 1.19 million tons P, while S usage in these forms will increase by only 30,650 tons S. These changes in consumption are a major contributing factor to the increased incidence of sulfur deficiency.

Raw Material Supply Situation

Supply

S consumption in 1974 in the western world was distributed among the various forms approximately as follows (million tons S) (Bixby, 1976):

Brimstone	23.4
Smelter S	5.5
Pyrites	5.0
Other	5.5
Total	39.4

As estimated by Merwin (1975), the total consumption of 39.4 million tons is well below the industry supply capacity of 55.0 million tons, and world consumption will increase at an annual growth rate of 3.5% between 1973 and 2000. Assuming a

linear growth rate, consumption would be expected to be 63.1 million tons in 1980 which is again below the expected production capacity.

There is little or no concern for the adequacy of world sulfur reserves. These are estimated at present (table 15) to be approximately 2,000 million tons that are recoverable at present price levels using current technology. In addition to these reserves, Bodenlos (1972) estimates that at least an additional 1,830 million tons S is available from anhydrite, H_2S, petroleum, pyrite, and elemental S which at present is subeconomic.

Geographical Distribution

Sulfur in its different forms is produced worldwide with no one country being a predominant producer or supplier to world markets. In 1974, world production of sulfur in terms of S content of the products amounted to 50.9 million tons. The United States was the leading producer, accounting for 22% of the output. Together, in descending order of production, U.S.S.R., Canada, Poland, Japan, Mexico, France, West Germany, Spain, and the People's Republic of China accounted for an additional 61% of the production. The remaining 17% of the output was distributed among 57 other countries.

Insufficient data are available to draw up a country-by-country inventory of S reserves. Information is available for South America (figure 15), and this shows the widespread occurrence of sulfur reserves in this part of the world.

Future Sulfur Fertilizers for the Tropics

In tropical areas of the world, capacity has been established to produce large quantities of urea, TSP, monoammonium phosphate, and diammonium phosphate which are devoid of or low in sulfur. For this reason it seems that future additions of sulfur in tropical agriculture will be primarily as admixtures of S to the above-mentioned products. Many such products have been developed to date (table 12) and these must be evaluated as multiple nutrient sources under tropical conditions.

Elemental S added to the soil as a fertilizer must undergo oxidation to form plant-available sulfate. This process results in increased acidity. With modified fertilizers that are

Table 14. N, P Fertilizer Production Facilities to Start up or Planned to Start Production Before 1978 in Tropical Areas of the World (FAO, 1975)

Region	Planned Production Capacity			
	Phosphoric Acid	TSP	Single Super	MAP + DAP
	tons P			
Africa	144,084	0	26,820	0
Central and South America	518,704	52,200	0	0
Asia	433,560	0	0	19,800
Total	1,096,348	52,200	26,820	19,800

Table 15. World Sulfur Production Capacity (in 1974 and 1980) and World Reserves (Merwin, 1975)

Region	Capacity		Reserves[a]
	1974	1980	1974
	million tons		
North America	23.70	25.20	735
South America	0.60	1.10	30
Europe	22.00	26.20	495
Africa	0.70	0.80	20
Asia	7.60	12.20	695
Oceania	0.40	0.50	25
Total	55.00	66.00	2,000

a. Recoverable at present price levels using current technology.

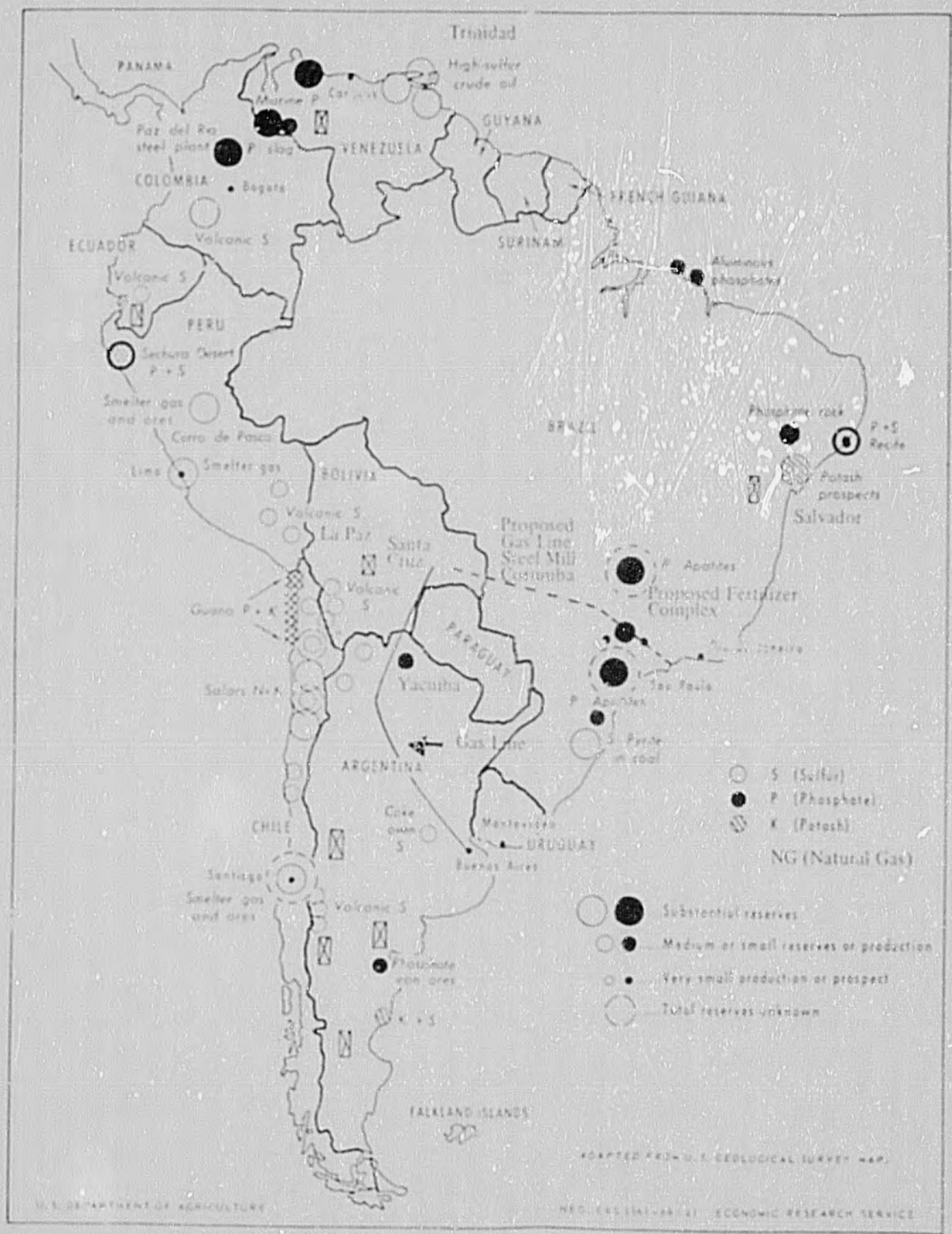

Figure 15. Principal known deposits and prospects of phosphate, potash, sulfur, and natural gas in South America (Economic Research Service, 1968).

developed, there is a need to study this aspect of sulfur fertilization to avoid or minimize long-term detrimental changes in soil pH.

The addition of elemental S to TSP and rock phosphate offers an attractive, low-cost way of adding S to existing fertilizer materials. Rock phosphate (RP) reactions are slow under field conditions, and it has been demonstrated (Swaby, 1975) that mixtures of RP and elemental S are successful in increasing the P release rate from RP under tropical conditions. Formulations of this material should be made with different rock sources and evaluated as P and S sources under tropical conditions.

The reactions of TSP with soil constituents are rapid, and often the applied P is "fixed" into less available or unavailable plant forms before an active plant root system has been developed. The release rate of P from TSP granules could be slowed by the use of elemental sulfur coating. This type of material would have the advantages of slowing down the initial release rates of P from the granule and, in addition, supplying S to the plants. This type of material should be developed and tested under tropical conditions.

Experiments in Indonesia (Blair et al., 1978c) have shown that elemental S is a satisfactory source of S for flooded rice. Not enough is known of the transformations of S in rice paddies in the presence of plants, and basic studies should be conducted to evaluate this source of S for rice and to evaluate its nutritional value in SCU.

Because of the wide and varied range of S-containing fertilizers available and the problems inherent in the use of TSP and RP in tropical soil, it may be anticipated that there will be no radical new developments in sulfur fertilizers but rather modifications to existing materials.

Whatever materials are developed, these must be evaluated under tropical conditions, in tropical soils, and with tropical plants. Classical incubation studies at 20°-25°C to study fertilizer reactions are of limited value in these situations because of the temperature sensitivity of biological S oxidation reactions (figure 16).

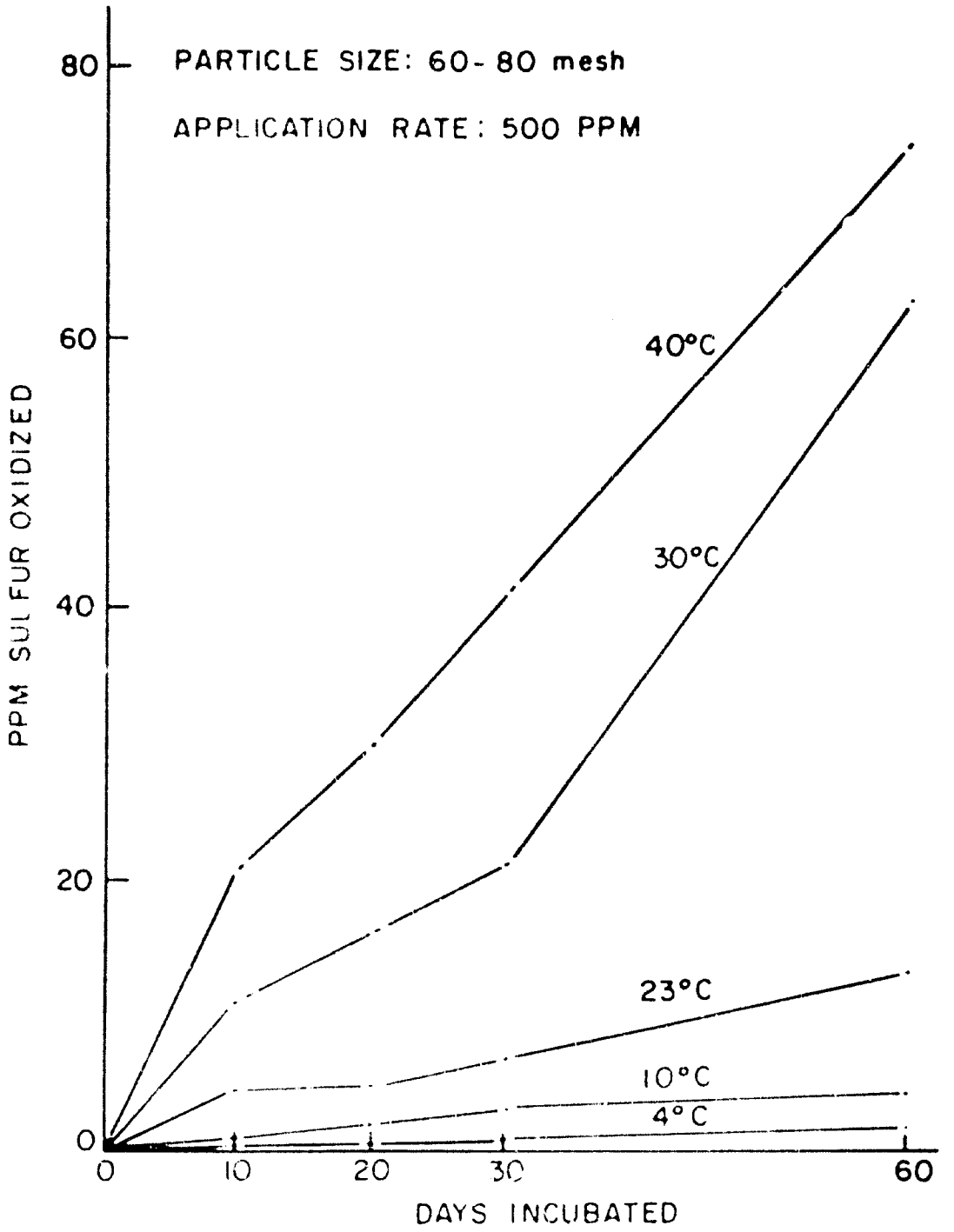

Figure 16. The relationship between S oxidation rate and temperature in an incubation experiment (Lu, 1965).

Summary

A wide range of sulfatic fertilizers has been developed but the worth of these plant nutrient sources has not been adequately assessed under tropical conditions. A pronounced trend away from sulfur-containing fertilizers is a major cause of the increasing incidence of sulfur deficiency. World reserves of S are adequate to meet anticipated demands well into the future. The problem seems to be insufficient use rather than too much use. No radical changes are expected in the sulfur fertilizers that will be used in the future. When fertilizer materials are assessed, account should be made of their total nutrient content to ensure proper comparison.

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