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SULFUR NUTRITION OF WETLAND RICE

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SULFUR NUTRITION OF WETLAND RICE[1/]

ABSTRACT

The incidence of sulfur deficiency in rice is increasing as a result of increasing yields and the use of fertilizers that contain little or no sulfur. The cycling of sulfur through the rice plant and soil has not been studied intensively, but the general outline of the cycle is discussed from the viewpoint of soil transformations and plant requirements.

Published data suggest that soil testing to determine the sulfur status of rice soils is of little or no value for prediction and diagnosis. Plant analysis of whole tops sampled between tillering and panicle initiation, and perhaps grain sulfur content, correlate well with sulfur responsiveness and can be used for diagnostic purposes with some degree of confidence. A tentative system of diagnosis based on nitrogen and sulfur contents is presented.

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SULFUR NUTRITION OF WETLAND RICE

Among the thousands of rice fertilizer experiments throughout the world, few have evaluated the sulfur needs of rice. On the basis of the small amount of evidence available, the incidence of sulfur deficiency is increasing in this crop. Of the 17 papers on the response of rice to sulfur fertilization, published since 1938, 11 have appeared since 1970 (Table 1). Field trials were conducted in only 5 of the 17 studies, and in the experiments of Wang et al (1976a) 20 of 38 soils analyzed for sulfur content had crops growing on them that exhibited sulfur deficiency symptoms. In the field experiments of Mamaril et al (1977), in Indonesia, yield responses to sulfur ranged from 12 to 42% in 5 of 8 trials.

Table 1. Published reports on responses of rice to sulfur fertilization.

Location	Type of experiment	Author
Burma	field	Sen (1938)
Burma	field	Aiyar (1945)
Japan	pot	Araki (1955)
Bangladesh	pot	Karim and Majlish (1958)
USA	pot	Nearpass and Clark (1960)
Sri Lanka	pot	Subbiah and Venkateswarlu (1965)
Indonesia	pot	Yoshida and Chaudhry (1972)
Philippines	pot	Yoshida and Chaudhry (1972)
Indonesia	pot	Leijder and Aldjabri (1972)
Bangladesh	pot	Alam and Karim (1972)
Philippines	pot	Lockard et al (1972)
Indonesia	pot	Ismunadji et al (1975)
Nigeria	pot	Osiname and Kang (1975)
India	pot	Acharya (1973)
Brazil	pot and field	Wang et al (1976a,b)
Indonesia	field	Mamaril et al (1977)

Sulfur responses have been recorded in many crops, and, the incidence is increasing in rice. The most important reasons for the increase were listed by Blair (1971):

- the increasing use of high-analysis, low-sulfur fertilizers,
- the increase in yields obtained as a result of other technological advances,
- the decreasing use of sulfur-containing pesticides and fungicides,
- environmental control of sulfur dioxide emissions in industrial areas, and
- a greater number of experiments conducted where sulfur is studied as a nutrient in its own right. In many experiments, responses to fertilizers such as ammonium sulfate, potassium sulfate, zinc sulfate, and superphosphate were attributed to the nitrogen, potassium, zinc, or phosphorus content and the potential response to sulfur was ignored.

Plant sulfur varies considerably, but is generally equal to or less than plant phosphorus. Average contents for rice are given in Table 2. Sulfur deficiencies affect not only the yield of plants but also protein quality, through its effect on the synthesis of cystine, cysteine, and methionine. Sulfur and nitrogen are both constituents of plant protein and the protein N-protein S ratio has been shown to be relatively constant at 15:1 in plant tops (Leggett et al 1966).

The increasing awareness of the role of sulfur in rice fertilization and the fragmented nature of the literature on the subject prompted this review.

Table 2. Average content of macronutrients in whole-plant tops of rice.

Nutrient	Concentration (%) in dry matter	Relative abundance on atom basis
N	1.5	22.2
K	1.0	5.5
Ca	0.5	2.7
Mg	0.25	2.2
P	0.25	1.7
S	0.15	1.0

THE SULFUR CYCLE IN WETLAND RICE

There are many similarities in the dynamics of nitrogen and sulfur in wetland and dryland soils, particularly regarding mineralization and reduction. Like nitrogen, the major portion of soil sulfur is in organic forms, which must undergo mineralization before becoming available to plants.

Sulfur, like other plant nutrients, is cycled through the plant and soil phases of a cropping system. A simplified diagram of this cycle is in Figure 1. The maintenance of the sulfur cycle depends on both the size of the various sulfur pools or sources and the flow rates between them. As outlined in Figure 1, the sulfate supply to the rice plant is dependent on the balance between inputs and outputs and the rate of transformation of soil sulfur to sulfate.

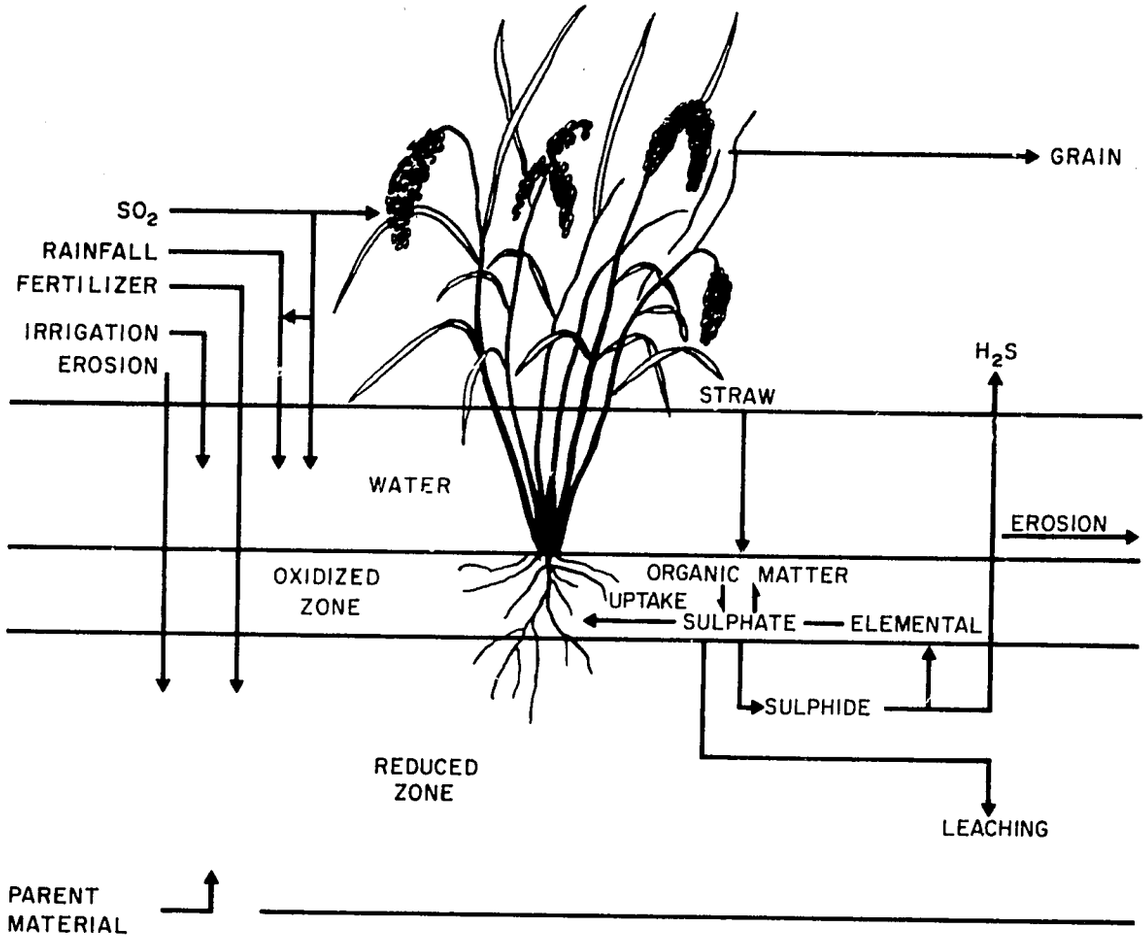

Fig. 1. Sulfur inputs, outputs, and transformations in wetland rice culture.

The sulfur pool

Estimates of some of the sulfur pool sizes have been made in a range of production systems throughout the world.

Sulfur dioxide

The average concentration of sulfur dioxide in the air is 0.05 ppm, and in the atmosphere the gas can be absorbed directly by plants or brought to the earth surface in rainfall. Metcalfe (1953) reported damage to plants at sulfur dioxide concentrations above 0.5 ppm. Alway et al (1937) measured sulfur inputs to the soil from sulfur dioxide throughout Minnesota, USA, and found annual rates ranging from 2 to 384 kg/ha. The highest values were near industrial centers where the sulfur dioxide concentration was high enough to retard plant growth at some periods of the year.

Rainfall

The amount of sulfur introduced into the sulfur cycle by rainwater varies greatly among places and seasons, but it is generally higher near industrial centers, volcanoes, swamps, and the seas. Ensminger (1958) estimated that industrialization in Alabama, USA, increased average accretion of sulfur in rainwater from 5.6 to 11.2 kg/ha per year. Hutton and Leslie (1958) found that the sulfur input from rainwater decreased from 7.8 kg/ha per year on the coast to 2.2 kg/ha per year about 16 km inland in Victoria, Australia. In tropical areas where winds are light and rainfall is heavy, the area influenced by the sea may not be extensive; thus sulfur deficiencies are found in the field within 2 km of the sea in South Sulawesi.

Fertilizer

Fertilizer sulfur inputs vary greatly and are discussed in detail in the section Fertilizer sulfur.

Irrigation water

In a pot experiment where rice was grown under dryland and wetland conditions, Yoshida and Chaudhry (1972) found that 68-70% of the sulfur in the plant came from the tap water used as irrigation source. From these experiments, they calculated that irrigation water with a sulfur content of 2.7 ppm would supply the needs of a rice crop, assuming 50% sulfur recovery from irrigation water.

Irrigation waters vary markedly in sulfur content, with extremes of 0.9 ppm in Ngale, Indonesia (Yoshida and Chaudhry 1972) and 4.7 ppm in Japan (Kobayashi 1958).

Erosion

Where soil is transported from sulfur-rich areas to areas of low initial-sulfur status there is a net sulfur gain, both in the soil particles that are transported and in the water, which would be expected to have a higher sulfur content. Where the transported material comes from low-sulfur areas, there may be a lowering of the overall sulfur status. No estimates of inputs or outputs of sulfur in the form of erosion have been made to date.

Product removal

Published measurements of the sulfur content of rice grain vary from 0.034% to 0.16%. In straw the variation is from 0.035% to 0.16%. This gives a range of sulfur removal of 0.34 to 1.6 kg/t in grain and 0.35 to 1.6 kg/t in straw. In cultivation systems where the straw is cut close to the ground and burned in heaps after threshing, the loss of sulfur is higher than in the traditional system where only the panicles are removed and the straw is reincorporated.

SOIL SULFUR

Soil submergence brings about a variety of chemical, biological, and electrochemical changes due to a decrease in oxygen supply and the consequent changes in reduction-oxidation (redox) potential, pH, ionic strength, and mineral equilibria. The oxidized forms of iron (Fe^{3+}), manganese (Mn^{4+}), nitrogen (NO_3^-), and sulfur (SO_4^{2-}) undergo transformation to their reduced forms Fe^{2+}, Mn^{2+}, NH_4^+, and S^{2-}, with drastic effects on mineral equilibria and concentrations in the soil solution. In addition, unstable organic substances produced during the decomposition of organic matter lead eventually to the production of methane and carbon dioxide. It is important to note that these changes are not uniform throughout a submerged soil because varying degrees of aerobism are maintained in some zones, such as at the point of soil-water contact, the area adjacent to roots, and within soil aggregates.

Brinkman (1970) described a *ferrolysis* process that is associated with the alternate oxidation and reduction that occur in flooded soil. During the reduction phase ferric ions (Fe^{3+}) are reduced to (Fe^{2+}) ions at a higher redox potential than sulfate to sulfide. The cations displaced from the exchange site by Fe^{2+} migrate to the reduced zone and are lost. Associated with these cations are the anions, particularly SO_4^{2-} and Cl^-, which are still present at this redox potential, and, to a limited extent, $H_2PO^-_4$.

When the soil is drained, the reduced iron is reoxidized and reprecipitated leaving an excess of H^+ ions, which then occupy the exchange sites. This leads to a loss of cations and anions, particularly SO_4^{2-}, which results in a gradual reduction in base saturation of the soil.

pH changes

The equilibria of hydroxide, carbonate, sulfide, phosphate, and silicate ions in submerged soil are influenced greatly by pH. Such equilibria regulate the concentration of ions in solution through precipitation, and the absorption of ions such as Al^{3+}, Fe^{2+}, H_2S, and H_2CO_3, and undissociated organic acids.

Redox potential changes

Microorganisms that respire aerobically produce oxygen as the end product, which combines with hydrogen and four electrons to form water. In the absence of oxygen a number of other substances can accept electrons, which causes them to be reduced. For example:

$$SO_4^{2-} + 10H^+ + 8e^- = H_2S + 4H_2O$$

The reduction of various compounds in the soil solution occurs at different redox potentials, depending on the ease of acceptance of electrons. At pH 7, ferric is reduced to ferrous at -180mV and sulfate to sulfide at -220mV (Russell 1973). Although the reduction of a submerged soil proceeds in a stepwise manner, in a thermodynamic sequence it is not possible to specify a potential at which one system predominates. It appears that there is some overlap between the various systems, and that while ferric ions are being reduced to ferrous ions, sulfate ions can begin to be reduced to sulfide.

It is essential to distinguish between the surface-oxidized layer of flooded soils and the more reduced subsurface zones.

After a stable situation is reached in the reduced layer the redox potential lies somewhere between +200 and -300mV. In contrast the redox potential of the oxidized surface layer and the zone adjacent to the root is in excess of +200mV. This means that in the oxidized layer the reduction of ferric and sulfate ions does not occur to any appreciable extent. These same conditions occur adjacent to the root surface where oxygen diffuses from the growing root and maintains positive redox potentials.

Both the surface-oxidized layer and the oxidized root zone are critical for the sulfur nutrition of rice plants because in these zones the sulfur is retained in the sulfate form and, as such, is available to plants.

Sulfur transformations in flooded soils

The flooding of soil during rice cultivation can be expected to lead to a lower availability of sulfate to the plant. Nearpass and Clark (1960) found that rice plants grown in a flooded soil had a lower sulfur content than those grown on the same soil without flooding. That was because the plant could use only the SO_4^{2-} ion as its source of sulfur, and this ion was reduced in the anaerobic soil. The transformation of sulfur in a flooded soil is shown in Figure 2.

Sulfate production

Because sulfur is absorbed by the roots almost exclusively as the sulfate ion (Fig. 1) an adequate supply of this ion to the root surface is necessary for optimum plant growth. Sulfur is found in soils as a variable mixture of the following:

- *Primary minerals.* The original source of most soil sulfate is the metal sulfides of plutonic rocks, which undergo oxidation during weathering. The earth's crust contains about 0.06% sulfur (Tisdale and Nelson 1975) but the distribution is variable, ranging in field soils from zero (Ensminger 1954) to above 500 ppm (Starkey 1950).

- *Sulfate ions in solution.* Although the level of soluble sulfate in the soil is generally below 10 ppm, considerable fluctuations may occur. These changes are the net result of mineralization from organic sources, leaching of soluble sulfate, uptake by plants

(Williams 1968), sulfate additions from rainfall and irrigation water, and fertilizer additions. Such fluctuations make soil testing for sulfur content difficult.

- *Sulfate adsorbed to clay.* Sulfate ions are readily adsorbed on clay surfaces; the process is reversible and concentration dependent (Chao et al 1962). Harward et al (1962) proposed that sulfate is adsorbed to the surface of clays coated with hydrated iron and aluminum. The sulfate adsorption capacity of soil varies widely and is dependent on a number of soil properties, the most important of which are clay content (Ensminger 1954), clay type, and pH. Harward et al (1962) ranked clays in decreasing order of adsorption capacity as kaolinite> illite>montmorillonite. Aylmore et al (1967) showed that sulfate adsorbed to iron and aluminum oxides is held more firmly than that adsorbed to kaolinites. Sulfate adsorption is generally negligible above pH 6.5 and increases with decreasing pH (Kamprath et al 1956). This may be a reflection of the higher reactive iron and aluminum content of soils of low pH (Blair and Nicholson 1975).

- *Organically bound ester sulfates.* Organically bound sulfate that is reducible by hydriodic acid is referred to as ester sulfate and may constitute from 30% to 70% of the total organic sulfur in a soil (Williams 1975). Ester sulfate is easily split from organic matter on drying, which yields plant-available sulfate (Barrow 1961).

- *Organic sulfur compounds.* Little is known of the chemical nature of soil organic sulfur compounds, but the sulfur-containing amino acids cystine, cysteine, and methionine have been isolated and may constitute up to 30% of the total organic sulfur in soils (Freney et al 1972). There is a close correlation between carbon, nitrogen, and sulfur contents of organic matter, and studies from many parts of the world report a carbon-nitrogen-sulfur ratio of about 108 : 8 : 1 in surface soils. A major fraction of organic sulfur present in soils is that which is bonded directly to carbon and which must undergo mineralization to sulfate before becoming available to plants. Many factors are known to affect the rate of mineralization of organic sulfur compounds, a complete account was published by Freney and Swaby (1975). Because the mineralization process is primarily microbial, factors that influence the growth of the microorganisms will influence the rate of conversion of organic sulfur compounds to plant-available sulfate.

The major factors affecting mineralization of organic sulfur are:

1. *Temperature.* Optimum about 40°C (Williams 1967)

2. *Soil moisture.* Optimum about 60% of field capacity (Chaudhry and Cornfield 1967).

3. *Presence of plants.* Mineralization of sulfur is higher in the presence of plants than in bare soil (Freney and Spencer 1960), presumably because of the greater number of microorganisms present in the rhizosphere.

4. *Sulfur content of organic matter.* Stewart et al (1966) showed that sulfur mineralization occurred only when the sulfur content of the straw was above 0.15%. The few data available that report sulfur contents of rice straw suggest that the level of 0.15% is rarely exceeded (Aiyar 1945, Osiname and Kang 1975).

Sulfide production

The reduction of sulfate to sulfide can occur by both chemical and microbial processes. The implications for rice culture are a decrease in available sulfate, immobilization of zinc and copper and possible H_2S toxicity.

The soil solution concentration of nitrate and sulfate may be high at the start of the wet season because of the mineralization of organic matter and the splitting of organically bonded ions caused by soil wetting and drying. High concentrations of nitrate in the soil can inhibit the reduction of sulfate to sulfide by maintaining a positive redox potential.

When sulfate is added to a soil with a high organic matter content, the organic matter acts as a H^+ donor, which chemically reduces the SO_4^{2-} to S^{2-}. The alkali produced by this reaction (NaOH) combines with carbon dioxide and the resulting carbonate and bicarbonate leads to an increase in pH and ferrous (Fe^{2+}) ion concentration. Such a reaction may be common in paddy soils where organic matter is incorporated prior to flooding, or large applications of sulfate-containing fertilizers are made, *e.g.* ammonium sulfate.

In addition to chemical reduction, microbial reduction of sulfate to sulfide can be brought about by two genera of sulfate-reducing bacteria, *Desulfovibrio* and *Desulfomaculum* (Fig. 2). These bacteria develop the pH range 5.5 to 9.0 but grow best at a near-neutral pH. They are tolerant of high salt concentrations and can derive their nitrogen from ammonium salts; some fix molecular nitrogen. Anaerobic decomposition products of cellulose and carbohydrate, such as malate and lactate, serve as hydrogen donors for these organisms. Molecular hydrogen can serve as an energy source for some sulfate-reducing bacteria, but these require organic compounds to meet their carbon requirements (Starkey 1966).

Sulfide losses

When sulfide (S^{2-}) is produced in the reduced zone of a paddy soil it can undergo any one of four major reactions:

- *Chemical or microbial oxidation to elemental sulfur,* which may or may not oxidize further to sulfate. Microbial oxidation of sulfide is brought about by two genera of bacteria: *Thiobacillus* (Starkey 1966) and *Beggotia* (Hollis et al 1975). *Thiobacillus* thrives in acid conditions and some species can tolerate pH as low as 2.0. *Beggotia* is a filamentous bacterium that is common in the root zone of rice plants and removes hydrogen sulfide from the root surface by oxidizing it to elemental sulfur.

- *Production of hydrogen sulfide,* which is lost from the water surface. Hydrogen sulfide is extremely toxic to roots and a concentration of

10^{-6}M affects the functioning or growth of many plants (Russell 1973). Hydrogen sulfide evolution has also been shown to occur on soils that contain a high concentration of iron (Hollis et al 1975). On such soils the ferrous ion does not precipitate sulfide because of the formation of iron chelates with certain fractions of the organic matter. Hydrogen-sulfide-induced physiological diseases of rice growing on iron-poor soils are reviewed by Tanaka and Yoshida (1970). Two factors known to regulate the accumulation of hydrogen sulfide in submerged rice soils are pH and oxidizable carbon (Allam et al 1972). Joshi et al (1975) indicate a wide range of tolerance of rice varieties for hydrogen sulfide. Varieties tolerant of high hydrogen sulfide levels are those with high root oxygen release rates and low rates of nutrient absorption compared to susceptible varieties. The oxygen release rate from rice seedlings was reduced by hydrogen sulfide concentrations as low as 0.63×10^{-6}M (Joshi et al 1975).

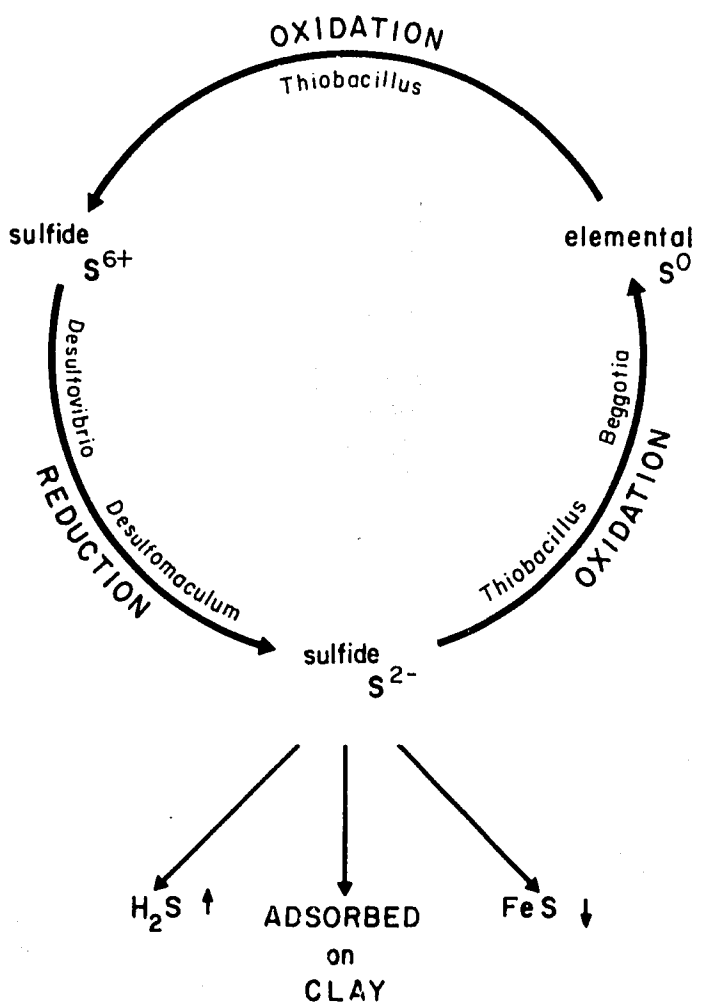

Fig. 2. Sulfur transformations in flooded soil.

- *Adsorption of hydrogen sulfide onto clays.* Hollis (1967) showed that hydrogen sulfide can be readily adsorbed on clays. Allam et al (1972) showed in laboratory studies that montmorillonite clays sorb hydrogen sulfide whereas kaolinitic clays do not. Adsorption of hydrogen sulfide by clays can act as a detoxifying mechanism. These observations support the field information that physiological diseases related to hydrogen sulfide occur mainly on sandy soils with predominantly 1:1 kaolinite, and illite clays rather than 2:1 montmorillonite clays.

- *Precipitation as ferrous sulfide.* The redox potential at which sulfate is reduced (-220mV) is below that at which ferric ions are reduced to ferrous (-180mV). When the sulfide reduction takes place in the presence of ferrous ions, a precipitate of ferrous sulfide (FeS) is formed. This removes the sulfide from solution and prevents the formation of hydrogen sulfide. Starkey (1966) characterizes this reaction as follows:

$$Na_2SO_4 + Fe(OH)_3 + 9H \rightarrow FeS + 2NaOH + 5H_2O$$

This reaction is not uniform throughout a flooded soil since different degrees of anaerobism exist within small distances.

Wakao and Furusaka (1976) have demonstrated the presence of micro aggregates of sulfate-reducing bacteria in paddy soils, and Furusaka (1968) has demonstrated that ^{35}S-sulfide produced from $^{35}SO_4$ is scattered in micro-deposits throughout the soil. In such microsites the sulfate-reducing bacteria multiply in the presence of organic matter and ferrous ions and the ferrous sulfide produced forms a precipitate at the periphery of the micro-colony which encloses the cells, the clay particles, and organic debris and prevents further reduction.

Bloomfield (1969) observed that sulfide was not precipitated as FeS, but rather evolved as H_2S in some anaerobic cultures that contained appreciable quantities of ferrous ion. He found that at a constant pH and ferrous (Fe^{2+}) concentration different FeS-H_2S ratios were produced when leaves of rice or lucerne were incorporated into the soil. It may be that the organic compounds that result from the decomposition of some plant material act as chelating agents that effectively remove ferrous (Fe^{2+}) ions from solution and allow the formation of hydrogen sulfide.

Ferrous sulfide may also be produced by the action of hydrogen sulfide on ferrous phosphate (Sperber 1953) and on crystalline ferric (Fe^{3+}) oxides (Berner 1964).

SOIL TESTING FOR SULFUR STATUS

The predication of soils responsive to sulfur has proved to be a difficult task, owing to the dynamic nature of sulfur and the ease with which it can be transferred from available to unavailable pools over short periods of time. Response prediction is further complicated by the variety of sources of sulfur available to plants (Fig. 1). Varying proportions of the total requirements may be obtained from the soil, atmospheric sulfur dioxide, sulfate in rain and

irrigation water, fertilizers, soil amendments, and pesticides. Despite these difficulties a great deal of effort has gone into the determination of soil sulfur status and response prediction under upland conditions. Little work has been done, however, on flooded soils.

Many procedures have been used to evaluate the sulfur status of soils, including chemical extractants, sulfate release on incubation, microbial growth, and plant uptake. The subject has recently been reviewed by Reisenauer et al (1973). Reisenauer (1975) groups the chemical extractants used into three types:

- Those that remove readily soluble sulfate, e.g. water.
- Those that remove readily soluble plus a portion of the adsorbed sulfate, e.g. calcium dihydrogen phosphate.
- Those that remove readily soluble and adsorbed sulfate plus a portion of the organic S, e.g. 0.03M $NaH_2PO_4.2H_2O$ in 2M acetic acid.

All testing procedures used have been shown to correlate with plant response under some conditions. The major problem so far encountered in such studies is the variability of the results. Some of the factors contributing to this variability follow:

1. Depth of sampling

In soils with a sandy surface horizon and a clay layer at depth, the sulfate content of the sandy layer may be low but the plants may be able to reach the source of sulfur in the clay layer that is below the sampling depth. This problem was encountered by Neller (1959) in this study of soils from Florida, USA. He found a positive linear relationship between sulfate extractable with ammonium acetate and clay content. An illustration of the problem of sampling depth is given in Table 3.

Table 3. The infuence of sampling depth on extractable sulfate (from Meller 1959).

Sampling depth (cm)	Sulfate S (ppm)	Clay content (%)
0 - 7.5	0.5	3.6
7.5 - 17.5	3.5	5.5
91 - 122	97.0	31.0

2. Sample preparation

Sample preparation must be standardized if meaningful estimates of sulfur status are to be made. The major problem is one of drying the sample before analysis. Williams (1967) found a tenfold increase in extractable sulfur in some soils dried at 100°C. Air-drying at 20°C has been found to cause least change in sulfate content and is the recommended procedure.

3. Variation in relationship between test and response

The normal procedure for assessing the efficacy of a soil test is to correlate the test with some parameter of plant response, e.g. sulfur uptake, % maximum yield. Many such studies have been reported for sulfur tests, and two problems are evident in this literature. The first is that, in the main, the experiments have been conducted in the greenhouse where the supply of sulfur from sources other than the soil is controlled. While this gives good information under the conditions of the experiment, often it is of little value in the field. The second problem is the lack of publication of negative results. It is possible to select evidence from the literature to support or condemn sulfur soil testing based on correlation studies.

Too few studies have been conducted on flooded soils to allow any conclusions of the value of soil testing for sulfur at this stage, but one published study suggests that the chance of success is probably less than in upland conditions. Lockard et al (1972) found that rice plants grown in a soil with an ammonium acetate extractable sulfur level of 11 ppm before flooding had a higher plant sulfur content and were nonresponsive to sulfur compared with plants grown on a soil with 51 ppm, which responded to sulfur. They suggested that the lack of relationship between soil levels and plant response may have been due to differences in organic matter content, which may have affected the degree of reduction in the paddy. This conclusion is not supported by their data from a third soil, which contained the same amount of organic matter as the 11 ppm soil and which was tested at 30 ppm sulfur. This soil showed maximum response to applied sulfur.

Soil samples collected by Wang et al (1976a) from lowland rice areas showing sulfur deficiency symptoms in the crop ranged in sulfate sulfur content from 1 to 3 ppm, and those from areas without deficiency symptoms, from 2 to 50 ppm. Only 3 of the 18 soils from the nondeficient areas had soil sulfate values above 3 ppm.

Because the sulfate status of a flooded soil depends not only on the sulfur content but also on the degree of reduction of that soil, it is doubtful if testing for sulfate status prior to flooding will be of any value. In addition, since it is not feasible to sample the oxidized surface layer of the mud or the oxidized layer adjacent to the roots, the opportunity to determine sulfate levels in constantly flooded soils does not exist. Because of the multiplicity of factors that influence the balance between sulfide and sulfate in flooded soils a determination of sulfide concentration would again be of little or no value.

PLANT SULFUR

Uptake

There are no published studies of sulfur uptake by flooded rice, but in other species sulfur is absorbed by roots almost exclusively as the sulfate (SO_4^{2-}) ion. Since the major portion of a flooded soil is under reduced conditions, the supply of sulfate to the root surface is dependent on an oxidized zone adjacent to the root where sulfate can exist or sulfide can be oxidized to sulfate prior to uptake. Oxygen release from rice roots is a well-known phenomenon as is the proliferation of roots in the surface-oxidized soil layer. Both these mechanisms are adaptations that allow the uptake of oxidized forms of nutrients such as sulfate. In addition the oxidized zone acts as a detoxifier of hydrogen sulfide (Joshi et al 1975).

Sulfate enters the apparent free space of the root by both diffusion and mass flow, and uptake into the root appears to occur on specific binding sites (Leggett and Epstein 1956). Selenate competes with sulfate during uptake on about equal terms, whereas nitrate, phosphate, and chloride offer little competition.

Yoshida and Chaudhry (1972) showed that the rate of sulfur uptake by rice plants is low in the first 3 weeks of growth and declines again at flowering. Wang et al (1976b) demonstrated that for maximum benefit, sulfur must be applied as early in the growth cycle as possible and at least before the active tillering stage.

Transport

Although organic sulfur compounds can be synthesized in the roots, most sulfur is transported to the tops as sulfate (Lauchli 1972). Sulfur which is mobile within the plant structural compounds does not move under conditions of deficiency (Bouma 1967). This means that a sulfur deficiency exhibits symptoms in the most recently formed tissue.

Function

The amino acids cystine, cysteine, and methionine all contain sulfur and are important in protein formation, structure, and function. Sulfur also plays an important role in the functioning of many plant enzymes, enzyme activators, and oxidation-reduction reactions. Although sulfur is not a part of the chlorophyll molecule, Nanawati et al (1973) showed that the content of chlorophyll, water-soluble protein, and peroxidase in rice were significantly reduced under conditions of sulfur deficiency (Table 4). These results are similar to those of Thomas et al (1950) who found 40% less chlorophyll in the leaves of sulfur-deficient *Medicago sativa* plants than in nondeficient plants.

The reduction in water-soluble protein is the result of a lower synthesis of the sulfur-containing amino acids cystine, cysteine, and methionine (Mertz et al 1952), which form an integral part of structural and functional protein. Ismunadji (1978) found a lower methionine content in rice grain from sulfur-deficient areas than from areas adequately supplied with sulfur. This could have important implications for human nutrition as methionine is one of the essential amino acids for humans.

In addition to the above changes in chemical composition, Needham and Hauge (1952) reported that sulfur-deficient plants of *Medicago sativa* had a lower content of the vitamins biotin, folic acid, pantothenic acid, pyridoxine, riboflavin, and thiamine. It is suggested that sulfur is involved directly or indirectly in many plant processes and that sulfur deficiency can result in many changes in plant chemical composition.

Sulfur deficiency symptoms

Sulfur deficiency first shows in a rice plant as the yellowing of the youngest leaves (Yoshida and Chaudhry 1972), which is the result of the lower chlorophyll production and nonmobility of the nutrient. This contrasts with nitrogen deficiency, which is first seen on the older leaves. The yellowing from sulfur deficiency gradually extends to all the leaves, so that in the advanced stages the plant appears uniformly yellow.

As with nitrogen, sulfur deficiency results in reduced plant height and tiller number, and thin straw. Maturity may be delayed and there may be many unfilled grains.

Plant analysis for diagnosing sulfur status

There are many reports on sulfur content in the tissue of legumes, but few experiments have reported sulfur content in cereals. Three problems are evident when an attempt to set levels of adequacy by plant analysis is made. The first is the stage of growth of the plant. In cereals there is a general decline in the sulfur content of the tops with age. Yoshida and Chaudhry (1972) reported that the sulfur content of IR8 rice declined from 0.26% total sulfur 2 weeks after planting to 0.11% at flowering (Fig. 3).

The second difficulty arises from the variety of analytical methods that have been used. Some of the older methods using barium sulfate precipitation are known to give variable results. This makes comparisons between experiments extremely difficult.

The third problem that besets the setting of criteria is the definition of adequacy. The most commonly used term to establish adequacy is *critical level*. This has been defined in various ways. Yoshida and Chaudhry (1972) used two criteria, namely DC 50 and DC 100, the sulfur content required in plant tissue for 50% and 100% of maximum yield, respectively. Spencer (1975) used the criterion of the minimum amount of sulfur per unit of dry weight associated with maximum growth by the plant. The definition that is more generally accepted is the nutrient content to produce 95% of maximum yield.

There are three criteria that have been used with varying degrees of success to define the sulfur status of plants: sulfate sulfur, total sulfur, and nitrogen-sulfur ratio. Some workers (Table 5) used one of these criteria alone, while others used a combination of two or three parameters. The argument advanced by Blair and Crofts (1970) for the use of more than one criterion was that under conditions of a secondary deficiency, e.g. molybdenum the sulfur content may appear adequate, but because of the interference in nitrate reduction and protein synthesis there may be an accumulation of

Table 4. The influence of sulfur on the chlorophyll and water-soluble protein content and peroxidase enzyme activity in fresh leaves of 21-day-old rice seedlings (Nanawati et al 1973).

S content of nutrient solution (mg/liter)	Chlorophyll (mg/g fresh wt) a	b	Total	Water-soluble protein (%)	Peroxidase activity (units/g fresh wt)
3.1	1.17	0.80	1.97	4.86	1.80
15.5	1.38	0.85	2.23	5.63	1.87
124.0	1.48	0.97	2.45	5.92	2.45

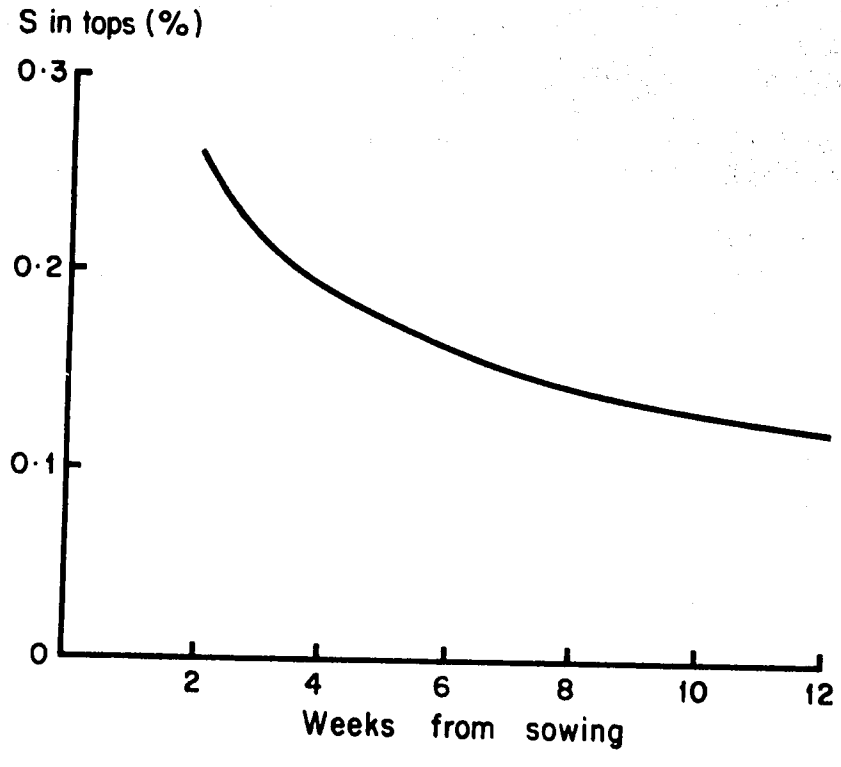

Fig. 3. Decline in rice plant sulfur content with age (Yoshida and Chaudhry 1972).

sulfur sulfate. In addition, the inclusion of the N-S ratio allows the separation of data indicating sulfur deficiency, nitrogen deficiency, or both.

Table 5. Criteria for determining the sulfur status of cereals.

Plant	Plant part	Sampling time	Critical level[a] % total S	% S as $SO_4^=$	N-S ratio	Reference
Oats	Whole tops	Tillering-flowering	0.15	0.05	20	Blair and Crofts (1970)
Rice	Leaf blades	Tillering	0.135			Yoshida and Chaudhry (1972)
Rice	Leaf blades	Flowering	0.15			Osiname and Kang (1975)
Rice	Leaf blades	21 days from emergence	0.16			Osiname and Kang (1975)
Rice	Leaf blades	42 days from emergence	0.13			Osiname and Kang (1975)
Rice	Leaf blades	63 days from emergence	0.11			Osiname and Kang (1975)
Rice	Grain		0.12			Osiname and Kang (1975)
Rice	Straw		0.10			Osiname and Kang (1975)
Rice	Whole tops	About 60 days	0.034[b] 0.04			Sen (1938)

[a]Note various criteria used by various authors. [b]Plants showing sulfur deficiency symptoms. Nondeficient plants, 0.065% to 0.125% sulfur.

A compilation of the published data on sulfur levels in rice at various stages of growth is presented in Figures 4 to 7. It is possible to separate the data of Figure 4 into at least three distinct zones labeled I, III, and V. These numbers refer to the categories shown in Table 6.

The importance of considering the nitrogen, sulfur, and N-S ratio together is highlighted by those plants that fell in category V (Fig. 4). These plants

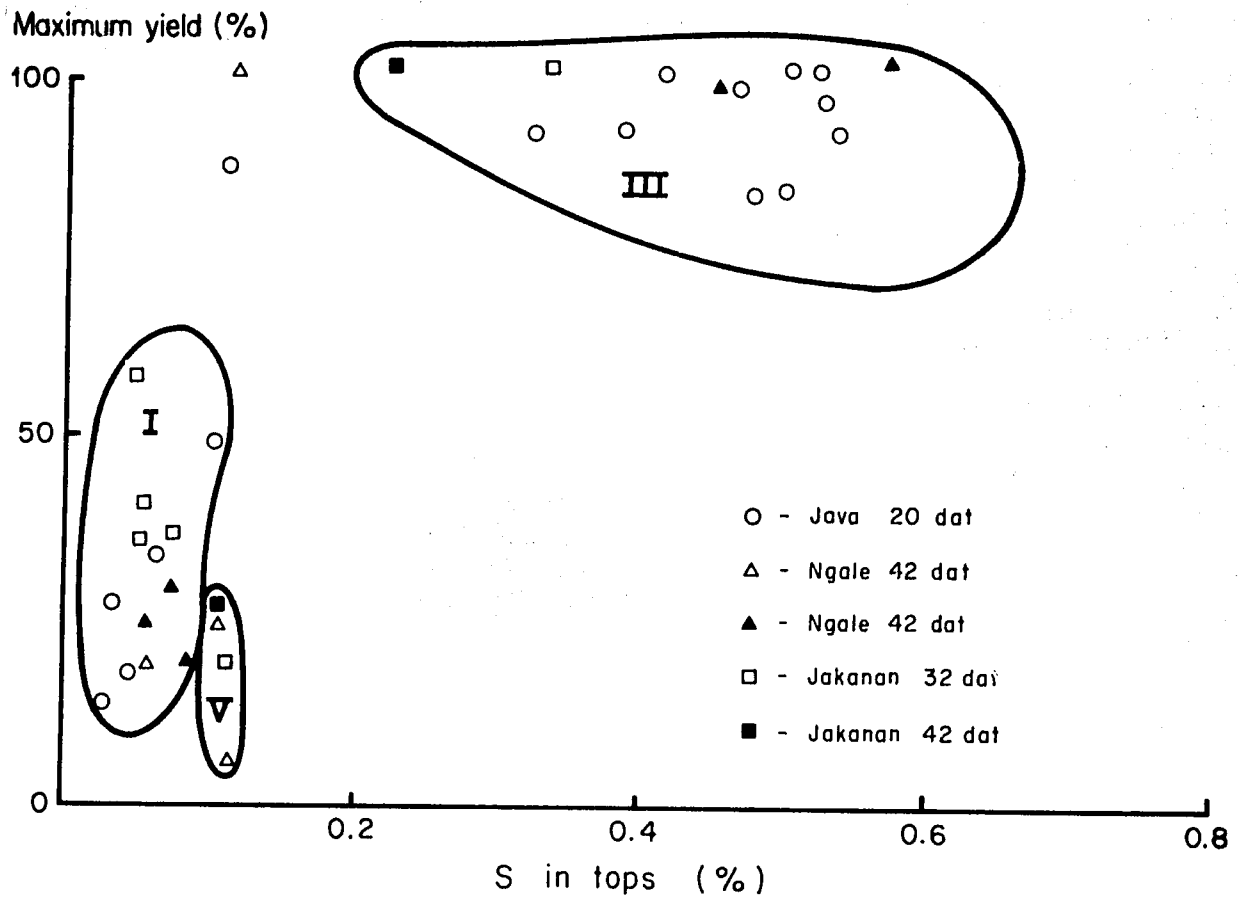

Fig. 4. Relationship between total sulfur content (%S) of whole tops and % maximum yield of rice plants from the experiments of Ismunadji et al (1976). Percent maximum yield calculated as yield in -S treatment ÷ yield in +S treatment x 100.

Table 6. Preliminary classification of nitrogen and sulfur status of whole rice tops, sampled from tillering to flowering stages.

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

came from control treatments of the Ngale soil used by Ismunadji et al (1975) at 42 days and flowering, and had nitrogen contents of less than 1% and sulfur contents between 0.10 and 0.15%, which indicates a deficiency of nitrogen and a possible sulfur deficiency. Plants on soil with a gross nitrogen deficiency may appear to have adequate sulfur levels but show a response to sulfur when nitrogen is applied. In these cases growth was markedly depressed by the nitrogen deficiency and the sulfur deficiency has been masked.

The ratio of nitrogen to sulfur is sometimes expressed as the S:N on an atom basis. This was first proposed by Dijkshoorn et al (1960) who suggested a S:N of 0.0258 when expressed as a decimal. This is equivalent to a N:S of 17.1. Walliham and Sharpless (1974) found the maximum yield of rice in solution culture experiments at a S:N value of 0.0258, which is the approximate ratio of nitrogen to sulfur in plant protein.

When considering the relationship of final grain yield to total sulfur in whole tops collected from active tillering to flowering, the critical value approximates 0.15%, as seen from the data of Osiname and Kang (1975) and Acharya (1973) in Figure 5. Ishizuka and Tanaka (1959) reported that in their experiments the critical total sulfur content in straw appeared to be 0.068%.

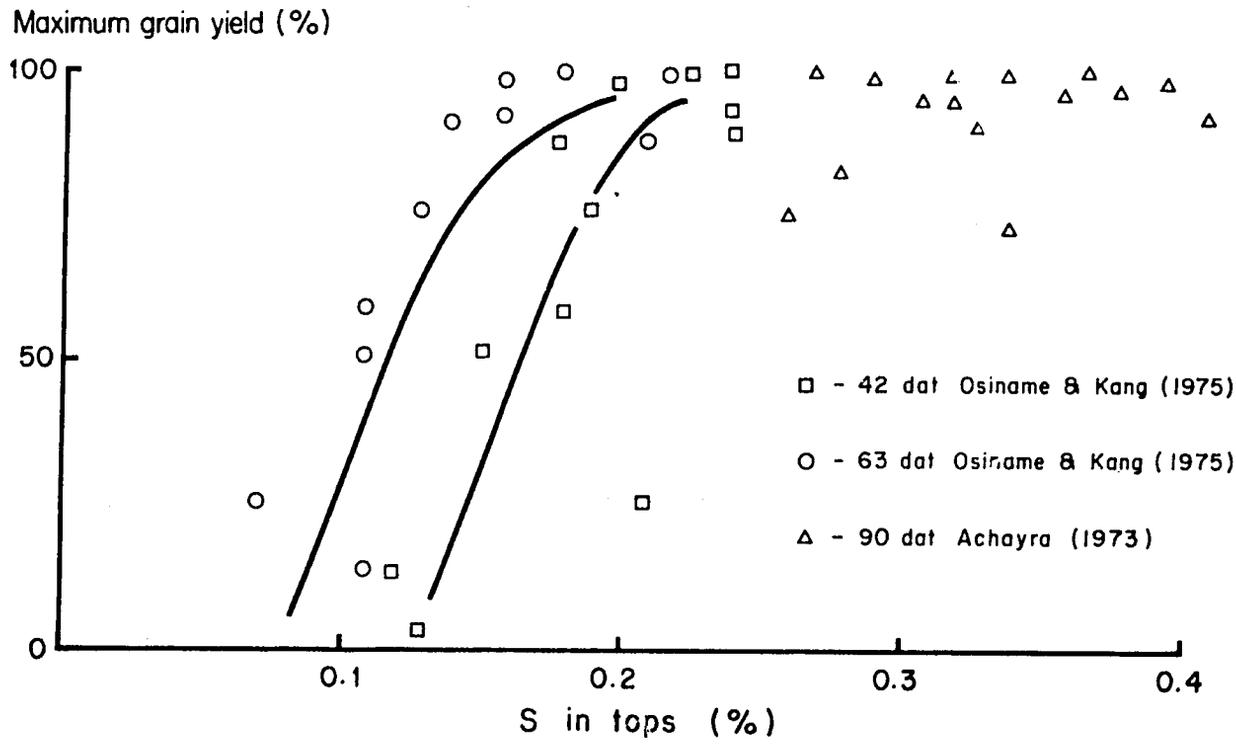

Fig. 5. Relationship between total sulfur content (%S) of whole tops sampled at various times in the vegetative phase and final grain yield.

The data presented in Figure 6 suggest that the relationship between straw sulfur levels and yield is too variable to be of value in prediction. A better relationship (critical value of about 0.1%) exists between grain sulfur content and yield response (Fig. 7). It may be that grain methionine levels will prove a better indicator of sulfur status than will total sulfur content.

It must be remembered that any classification system can only be used as a guide to nutrient status because the growth of the plant may be affected by many factors in addition to those analyzed, e.g. climate, pests, other nutrients. Even with these limitations the prospects for successfully diagnosing sulfur status of rice by tissue analysis are infinitely greater than those by soil analysis. More data need to be collected to establish these relationships more firmly.

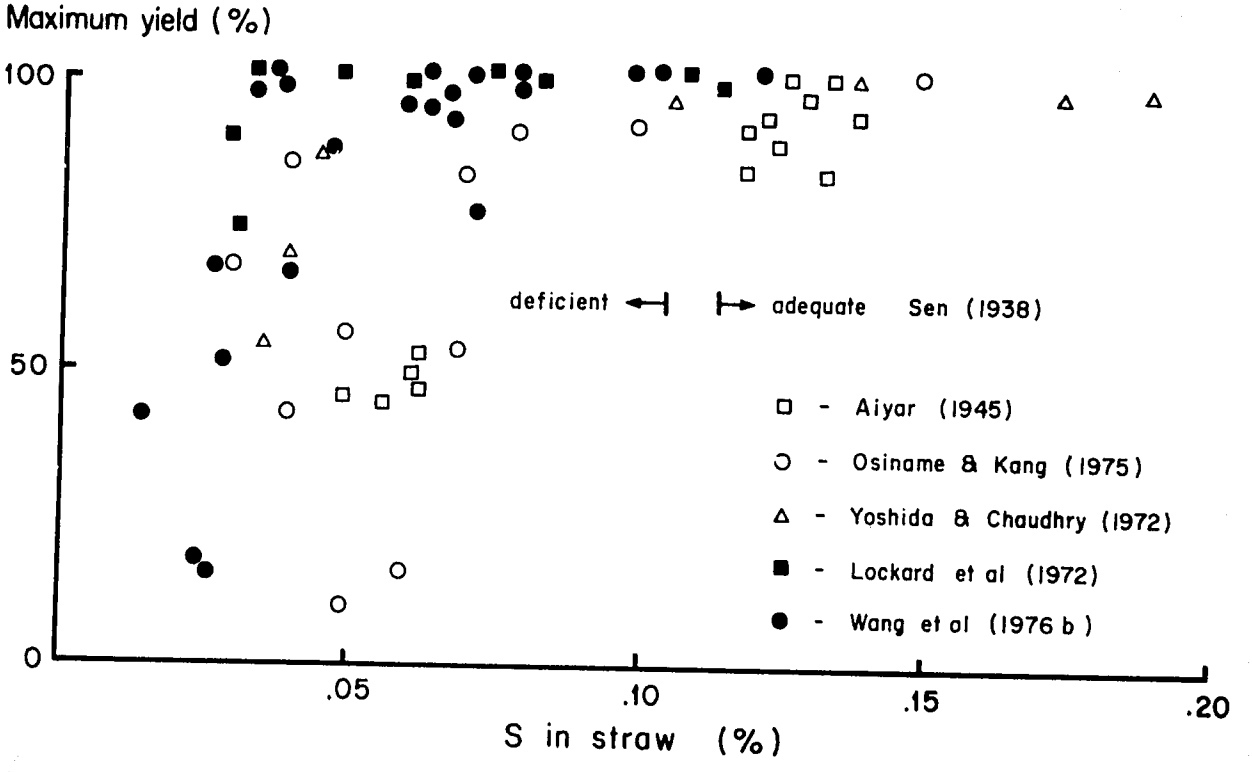

Fig. 6. Relationship between total sulfur content of straw (%S) and % maximum yield.

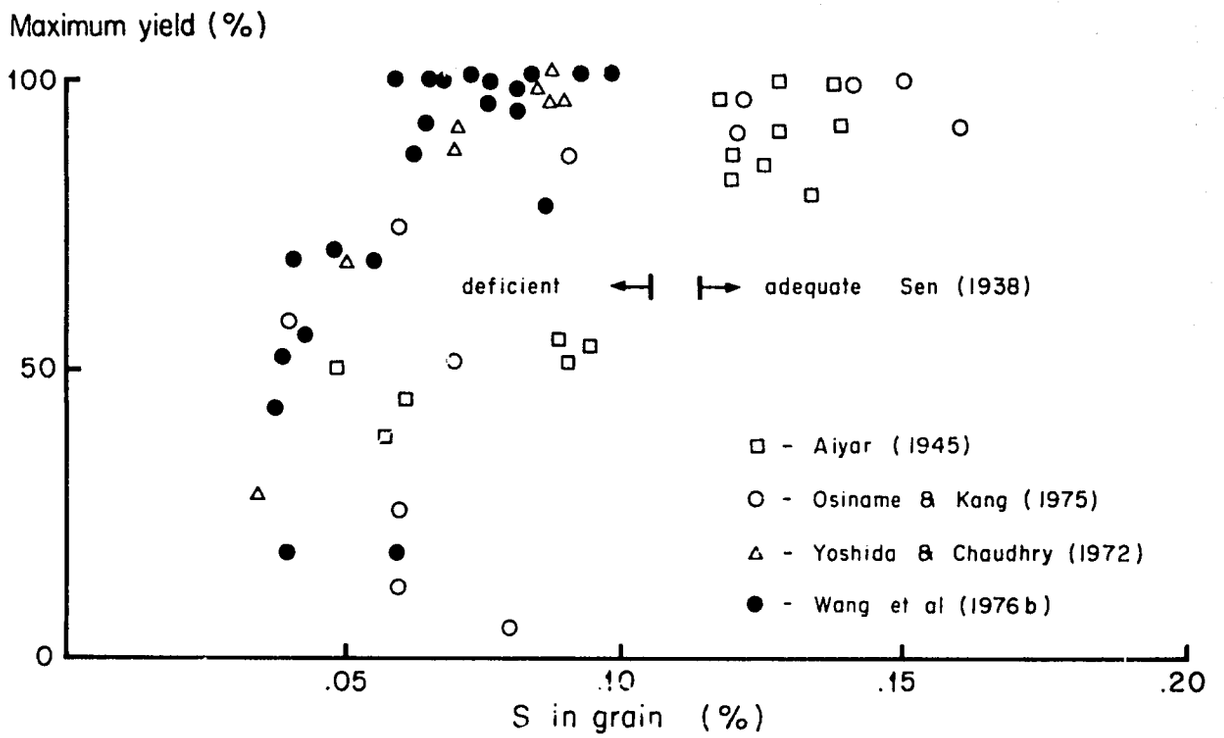

Fig. 7. Relationship between total sulfur content of grain (%S) and % maximum yield of grain.

FERTILIZER SULFUR

Fertilizer sources of sulfur may be divided into three categories:

1. sulfate-containing fertilizer,

2. inorganic sources that must undergo oxidation before becoming available to plants, and

3. organic sulfur sources.

Many fertilizer materials contain sulfur. Bixby and Kilmer (1975) list some 39 different sources. Many of the materials are available only in western Europe and the USA. In the major rice-producing areas of the tropics a limited range of products is available (Table 7).

There is almost a complete absence of data from field experiments to determine the rates of sulfur required by wetland rice, and there is an urgent need for such data.

Table 7. Nutrient content of fertilizer materials available in tropical rice-growing areas.

Fertilizer	Nutrient content (%)[a]			
	N	P	K	S
Sulfate-containing				
Sulfate of ammonia	21	0	0	24
Potassium sulfate	0	0	48	16
Calcium sulfate (gypsum)	0	0	0	18
Single superphosphate	0	9.5	0	12
Double superphosphate	0	17.5	0	5
Triple superphosphate	0	19.6	0	1
Diammonium phosphate	16	21	0	1
Nonsulfate				
Elemental sulfur	0	0	0	99
Sulfur fortified single super 1[b]	0	7.7	0	27 (9% as sulfate)
Sulfur fortified single super 2[b]	0	5.9	0	45 (8% as sulfate)
Organic forms				
Sewage sludge	6	0.9	0	0.4
Bone meal	3.5	9.0	0	0.2
Peanut meal	7.2	0.6	1	0.1
Fishpond mud[c]	–	–	–	0.43
Animal manure (cattle)	0.5	0.1	0.5	0.2

[a]Phosphorus and potassium contents are given in % element, not as P_2O_5 and K_2O. [b]Available in Australia and New Zealand. [c]Sampled from a fishpond at Barru, South Sulawesi, Indonesia.

Sulfur that is present as sulfate in fertilizer is readily available to plants. In areas of high leaching this may be a disadvantage because sulfate can readily move through the profile and be lost from the system.

The sulfur in organic and nonsulfate fertilizers must be converted to sulfate before it can be available to plants. Both the mineralization of organic forms, and the oxidation of sulfide and elemental sulfur to sulfate require aerobic conditions; thus, these forms may be of less value in permanently flooded rice soils.

Elemental sulfur is valuable because it is a high-analysis material and sources are often readily available in volcanic areas. Apart from temperature and moisture, which were mentioned earlier, the particle size of elemental sulfur is important. The oxidation rate of elemental sulfur to sulfate is increased as the particle size of the material decreases (Fox et al 1964), because finer particles have a much greater surface area on which microbial and chemical oxidation can take place. By adjusting the particle size of the material used it may be possible to change the rate of sulfate production in flooded soils. It is important that elemental forms of sulfur not be incorporated into the zone that will be reduced during crop growth. Oxidation will only occur in the aerobic surface layers or in areas adjacent to the roots.

Elemental sulfur can easily be added to phosphate fertilizers as a molten spray. This has been done successfully in Australia and New Zealand where molten sulfur is sprayed into the fertilizer granulator to produce materials containing either 25% or 45% finely divided sulfur. It is also possible to add elemental sulfur to triple superphosphate and produce a material containing 15.6% phosphorus and 20% sulfur. A product of this type may be useful in areas where both phosphorus and sulfur are deficient.

Sulfide-containing fertilizer sources (pyrrolite, pyrites) are available in some areas but their slow rate of oxidation would render them unsuitable in most rice-growing situations.

A wide range of organic materials can be used as a sulfur source, but organic sulfur must undergo mineralization to sulfate before it can be available to plants. Generally the sulfur content of such materials is low and large quantities must be applied to meet the crop requirements.

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