CHAPTER 1

INTRODUCTION

It has long been known that sulfur is an essential element for plant growth; however, it has received little attention compared to the three main elements, nitrogen, phosphorus and potassium. Sulfur is often referred to as the fourth major plant nutrient, after these three. There is increasing interest in studies of the S cycle in different cropping systems in order to increase the efficiency of S fertiliser utilization (Till and May, 1970, 1971; Blair, 1986; Fox and Hue, 1986).

Sulfur is a constituent of some amino acids (cysteine, cystine and methionine), proteins, fats and other compounds in plants (Blair, 1979). Deficiency of this element not only reduces crop growth, but also reduces product quality. Sulfur and nitrogen are both required for protein synthesis in plants, and the plant requirement for S is similar to that of phosphorus (Duke and Reisenauer, 1986).

Scott *et al.* (1984) reported increased yields following sulfur fertilisation of a range of crops including barley, oilseed, rape and grasses. An increasing number of countries are reporting sulfur deficiencies (Mahler and Maples, 1987; Ismunadji *et al.*, 1983; Buttrey *et al.*, 1987; Blair, 1979, 1983, 1987b; Russell and Chapman, 1988; Tisdale *et al.*, 1986). These include many rice-growing areas in Asia (Blair, 1979; 1984). For instance, Blair *et al.* (1979) found that 18 out of 28 sites tested in South Sulawesi, Indonesia, responded to S application.

It has been recognized that the major reasons for the increase in S deficiencies are the reductions in sulfur inputs and the increase in sulfur offtake. The input of sulfur has declined because of the increasing use of low-S-containing high-analysis fertilisers, greater control of industrial emission of sulfur, the decreased use of high-sulfur fuels, decreased use of sulfur in pesticides and increased utilization of crop residues for feed and fuels (Blair, 1979; Morris, 1986, 1987). The offtake of sulfur has increased with the expansion of multiple cropping and the increased use of higher-yielding crops (Blair, 1979; Morris, 1987).

Changes in farming practices which have resulted in higher erosion and / or leaching losses, particularly in areas with high rainfall and soils of low sulfate adsorption capacity, may have also contributed to the increase in the incidence of S deficiency (Blair, 1979; Korentajer *et al.*, 1984; Morris, 1987).

There are many commercially available S fertilisers and most of them contain either sulfate or elemental S. Blair (1979) listed 40 S-containing products that are available, most of which have been used in agricultural areas. The effectiveness of these fertilisers depends on their capability to supply S to crops. Different forms of fertiliser S may be required to maximize the benefit of fertiliser application under particular cropping systems and different soil conditions.

Because of the commitment to fertilisers such as urea, TSP and DAP and the decline in the manufacture of AS and SSP, co-granulation or coating are the most likely ways in which S will be added to these fertilisers.

There has been an increase in the use of elemental S as a fertiliser. This source has the potential to profitably correct S deficiency because of the high concentration of S and the slow release of sulfate compared to sulfate fertilisers. Blair *et al.* (1979) reported similar grain yields of flooded rice resulting from surface application of elemental S and gypsum at transplanting in South Sulawesi, Indonesia. Since plants only taken up S in the sulfate form, the oxidation rate of elemental S by microorganisms is an important factor to be considered. The oxidation rate can be accelerated by reducing the particle size (Fox *et al.*, 1964; Li and Caldwell, 1966; Shedley, 1982; Janzen and Bettany, 1986).

Bloomfield (1967) reported that the oxidation of elemental S was increased when it was combined with diammonium phosphate and triple superphosphate. A greater oxidation was also reported when elemental S was combined with phosphate rock (Lee *et al.*, 1987). Elemental S has also been incorporated into urea, however this has been aimed at increasing N efficiency due to the reduction of N losses through leaching, volatilization and denitrification (Sanchez *et al.*, 1973; Wells and Shockley, 1975). There are problems associated with the handling and application of very fine particle size of elemental S. This can be overcome by combining it with different high-analysis fertilisers or by making it into a more convenient straight S fertiliser by combining it with bentonite clay (Boswell *et al.*, 1988a,b) or other binding agents.

There are few reports on the effectiveness of S from different sources under non-flooded and flooded conditions and few physical tests of granulated fertilisers. In addition, there is little information on the effect of the adhesive materials used to bind elemental S to high-analysis fertilisers on the release of S from coated or cogranulated products.

Lefroy (1989) listed advantages and disadvantages of S and P fertiliser combinations and indicated that there are five advantages of elemental S coated TSP (minimal capital investment, simple manufacturing, manipulation of P : S ratio, S could be added locally, P and S applied at sowing or transplanting). The only disadvantage of this was need to grind elemental S. Furthermore, he emphasized that S and P combinations were likely to be more appropriate than any other combination.

The broad objectives of this study were to investigate a range of commercially available S-containing fertilisers and some developmental TSP-S products which were made at the University of New England. The products were evaluated for their initial and residual effects on growth and nutrient uptake of flooded and non-flooded rice and pastures, and for the physical strength and S-release characteristics of S-coated products.

The review of literature in Chapter 2 describes the global and agricultural S cycles, as well as the adsorption and desorption of S in soil which influences the availability of S to crops. Factors affecting the oxidation of elemental S are also discussed in this chapter. The results of these experiments are presented separately in Chapters 3, 4 and 5. The experiment reported in Chapter 3 investigated the initial and residual effects of S from different sources for rice under flooded and non-flooded conditions. The experiment in Chapter 4 examined the effectiveness of various S and P sources for pastures. In this experiment the amount of S loss through leaching was also investigated. The physical strength and S release from S-coated products, as well as development of S model to predict S oxidation are reported in Chapter 5. In this chapter, the amount of elemental S loss through leaching and the physical strength of S-coated products against frictional force were investigated. Cross-sections of the granules were scanned using the electron microscope and microprobe. The S demand of pasture and effects of temperature, moisture and particle size on S oxidation at different climatic conditions are also discussed. In this study the model developed by McCaskill and Blair (1989) was used to predict S release from elemental S as affected by particle sizes and time of application. This model was also used to compare predicted and observed elemental S oxidation under flooded and non-flooded rice and pasture conditions. Chapter 6 contains an integrating discussion of the experimental work, a discussion on the matching of elemental S release to plant demand and proposes some areas for further studies.

CHAPTER 2

REVIEW OF LITERATURE

2.1 INTRODUCTION

Plants mostly obtain sulfur (S) from the soil, with a small part of their requirement derived from the atmosphere (Trudinger, 1986). S is mainly absorbed by plant root as the sulfate (SO_4^{2-}) ion and a small amount is absorbed by plant leaves as SO_2 from the atmosphere (Tisdale and Nelson, 1975). The S supply from organic matter, soil minerals and atmospheric S varies markedly from one area to another (Blair, 1979).

In general, plants do not require as much S as they do N or K; however, S plays an important role and is classified as one of the essential nutrients (Tisdale and Nelson, 1975 and Blair, 1979). It is recognized that inadequate amounts of S result in limited plant growth and inferior quality (Tisdale and Nelson, 1975 and Rendig, 1986). Although sulfur is known as one of the essential plant nutrients, less attention has been focussed on this element compared to N, P or K (Blair, 1979).

In the past, S-containing products such as ammonium sulfate and superphosphate, as well as S-containing pesticides, were the main sources of S in agriculture. These sources probably masked S deficiency in crop production in many areas (Blair, 1979). Increasing use of high analysis fertilisers such as urea or triple superphosphate, which contains little or no S, has been reported as one of several factors which has led to the increased incidence of S deficiency (Blair, 1979; Lefroy, 1989). Because of the complexity of the S cycle, a better understanding of S transformation in soil and plant systems is required to support better S management strategies in cropping systems.

In this review, global and agricultural S cycles, roles and requirements of S in plant nutrition, as well as form and transformation of organic and inorganic S in the soil are discussed. Reduced forms, particularly elemental S, are discussed in more detail because this form is evaluated and compared to the other S-containing fertilisers during the course of the experiments.

2.2 GLOBAL SULFUR CYCLE

The great development of human civilization has influenced the S balance. This has been recognized and scientists have attempted to predict the earth's total resources of S and the changes in the sizes of the man-made and natural pools (Bolin *et al.*, 1983; Trudinger, 1986). The distribution of the world's S has been described by Freney *et al.* (1983), who estimated that the major S pools are contained in the lithosphere (24.3×10^9 Tg S) and hydrosphere (1.3×10^9 Tg S), with moderate amounts occurring in the pedosphere, including S in soil, soil organic matter and land plants (2.7×10^5 Tg S) and small amounts (4.8 Tg S) in the atmosphere.

The global S cycle is a very complex system involving the addition of S to the biosphere from the atmosphere and, vice versa (Figure 2.1). The S transformations that take place on the earth's surface are essentially biological (Freney and Swaby, 1975). Some S that is lost to the atmosphere through the activity of organisms is recycled and redistributed to the earth's surface. Various factors can influence the transformation of S over the globe. Natural drainage, water, wind and various weather conditions can serve both to lower the concentration of S in areas of high concentration and increase the S content of regions of low concentration. In this respect, the addition of sulfate to the atmosphere from sea-spray is particularly important in transferring S from the ocean to the land (Bolin *et al.*, 1983; Trudinger, 1986).

Anthropogenic emissions contribute significant amounts of S into the global biogeochemical S cycle through combustion of fossil and non-fossil fuels, metal smelting, input in fertilisers and emission from chemical industries (Bolin *et al.*, 1983).

The component pool sizes and flux rates of the S cycle shown in Figure 2.1 describe the general S cycle in the world as a whole. Some of the component processes can be very localized, e.g. the anthropogenic emissions of SO_2 into the atmosphere from point sources concentrated in the major industrial centres of the world or the emission of S from volcanoes; these may markedly affect localized areas.

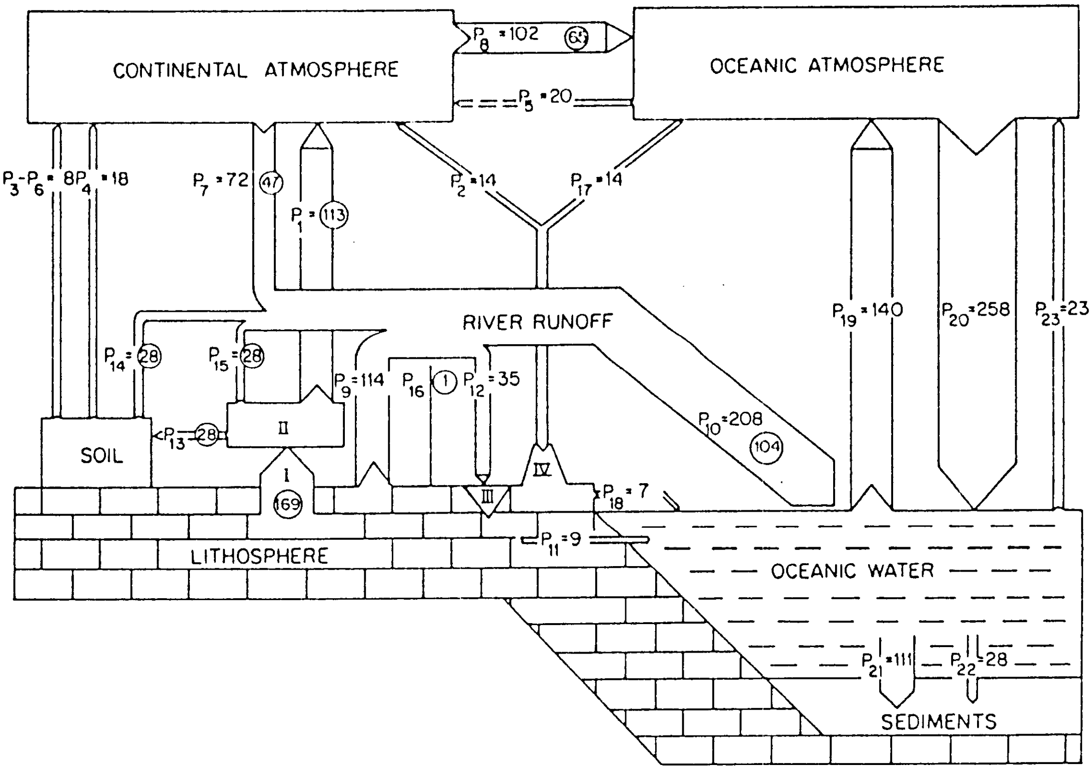


Figure 2.1 The major natural (uncircled) and anthropogenic (circled) pool sizes and fluxes of the global biogeochemical S cycle (Tg yr^{-1}) (Source : Freney *et al.*, 1983).

Roman figures denote :
I-output of S-containing minerals;
II-industrial treatment of the S-containing raw material;
III-inland water bodies;
IV-volcanoes.

Fluxes :
P_1-fuel combustion and metal smelting; P_2 and P_{17}-volcanic emission; P_3-aeolin dust; P_4-biogenic emission from land; P_5-sea air-land air transport; P_6-deposition of large dust particles; P_7-wash-out and dry deposition; P_8-land air-sea air transport ; P_9-weathering; P_{10}-river runoff to oceans; P_{11}-transport to ocean in underground water; P_{12}-runoff to inland water bodies; P_{13}-input in fertilisers; P_{14}-leaching of fertilisers; P_{15}-efflux from chemical industries; P_{16}- efflux of acid mine water; P_{18}-abrasion of shores; P_{19}-sea spray; P_{20}-wash-out and dry deposition; P_{21}-sedimentation of reduced S; P_{22}-sedimentation of sulfate; P_{23}-biogenic emission from oceans.

2.3 THE AGRICULTURAL SULFUR CYCLE

In agricultural systems, human activities play an important part in the S cycle. For instance, the transformation of forest into agricultural land, the addition of fertiliser and pesticide as well as water management are most likely to influence the natural cycle of S. Kamprath and Till (1983) noted that the S cycle in agricultural systems included the S inputs (addition of S from the atmosphere and fertiliser) and S removal (animal products, plant products, erosion and leaching). The S cycle in agricultural soil, including flooded and non-flooded components has been presented by Blair and Lefroy (1987).

A range of agricultural S-cycling models has been developed and these vary widely in complexity (Till and May, 1970; Kamprath and Till, 1983; Blair, 1986; McCaskill and Blair, 1988). An example of a simplified agricultural S cycle is presented in Figure 2.2 (Kamprath and Till, 1983), whilst a more complex one is presented in Figure 2.3 (McCaskill and Blair, 1988).

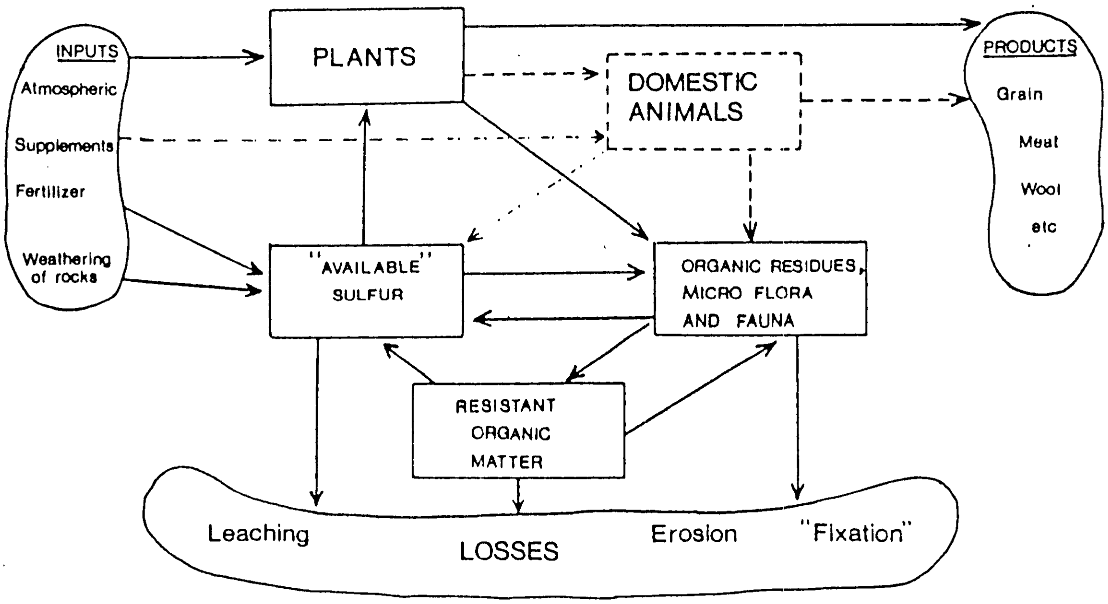


Figure 2.2 S utilization in crop and animal production. The irregular-shaped compartments show S inputs to and outputs from the production system(s). The rectangular boxes represent pools of S-containing materials which have been grouped together for simplicity. All the materials in these pools can take part in the recycling of S. The arrows show flows of S between the components. The system in broken lines shows the additional complexity when considering domestic animals as part of the production scheme.

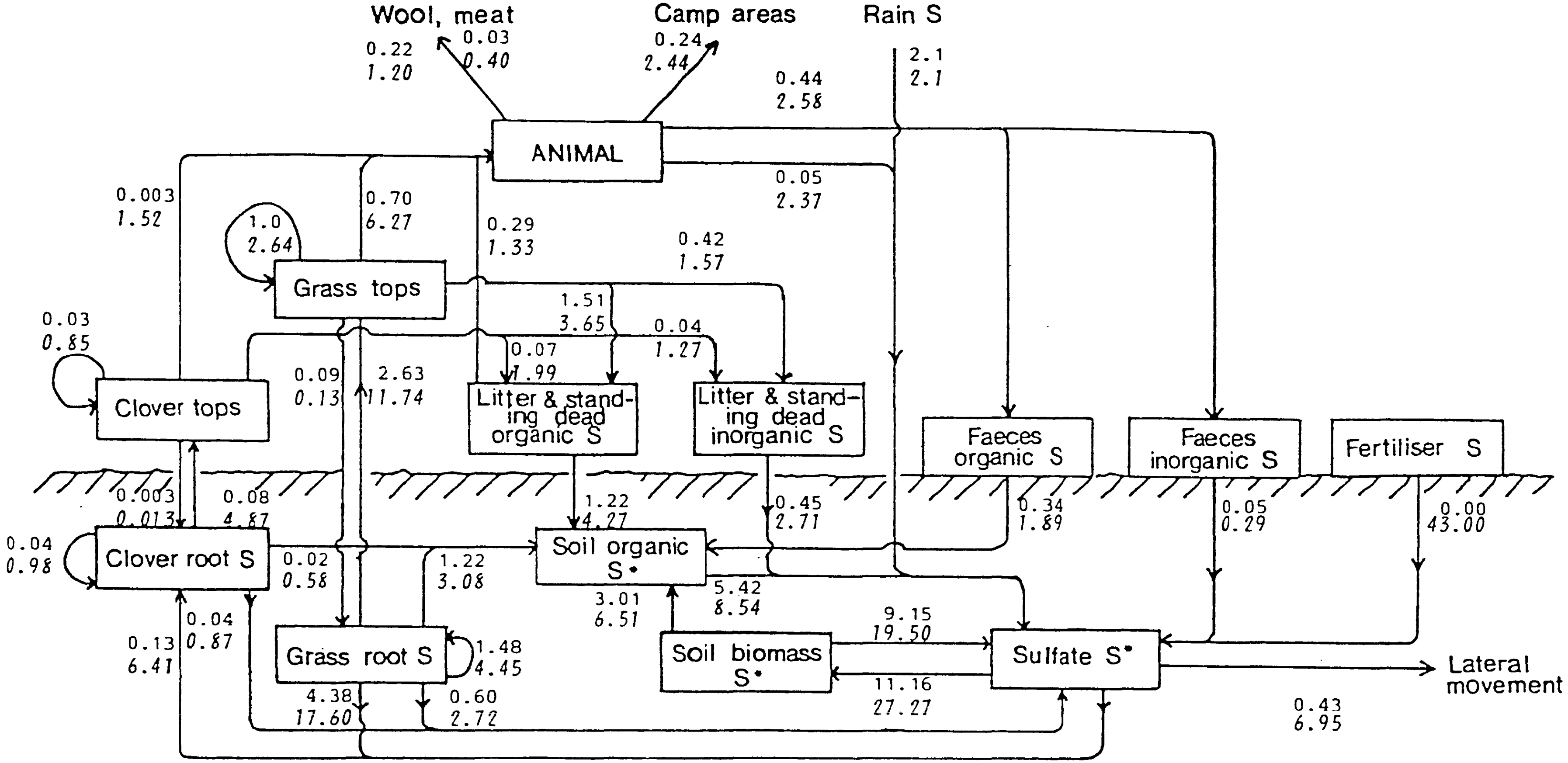


Figure 2.3 S pools and fluxes simulated by a computer model and calculated annual S fluxes (kg S ha^{-1} yr^{-1}) over a 10-year period for a pasture system to which no S is added (Roman type), and one receiving 43 kg S ha^{-1} yr^{-1} (italics). Pools marked '*' are simulated at various depths.

2.3.1 Atmospheric Sulfur

Fox and Hue (1986) reported that atmospheric S comes from a variety of sources. Anthropogenic S may be the most important source in a particular local area and includes emissions of SO_2 during industrial, agricultural and domestic burning of fossil fuels, burning of plant residues and smelting of ores. The amount of S which is contributed by this source has been estimated to be less than from natural sources (Figure 2.1). The S derived from natural sources includes volatilization of hydrogen sulfide and dimethyl sulfide during biological organic matter decomposition, reduction of sulfate in waterlogged soils and swamps, sea-spray and volcanic emission. The amount of S added to the atmosphere as a result of volcanic emission varies enormously between volcanoes. On a global scale, the geothermal areas and volcanic sources are considered to be of little consequence, although locally they are capable of contributing significant amounts of S which may affect agricultural management (Trudinger, 1986). Logan *et al.* (1979) cited by Trudinger (1986) estimated geothermal and volcanic emissions contributed 28 Tg S yr^{-1} to the atmosphere in the form of SO_2 and H_2S.

Presently, a significant amount of the atmospheric SO_2 is emitted from the burning of fossil fuels and smelting of ores which together contribute about 113 Tg S yr^{-1} (Trudinger, 1986). This is slightly less than the supply of S to the atmosphere of about 142 Tg S yr^{-1} from natural sources (Robinson and Robins, 1968 cited by Evans, 1975).

Microbial activity has been reported to be accountable for the production of several atmospheric gases including H_2S, CS_2, COS, $(CH_3)_2S$ and these gases are constituents of biogenic S in the atmosphere (Trudinger, 1986); and returned to the land by rain as sulfate (Fox *et al.*, 1983). Deposition of sulfur to the soil which is derived from the atmosphere may be taken up by plants or microorganisms or can be lost by erosion or leaching. A smaller amount of S may be returned to the atmosphere (Figure 2.1).

2.3.2 Hydrospheric Sulfur

The hydrosphere plays an important role in the S cycle. The oceans and the seas are the major storage of hydrospheric S, mainly in the form of SO_4^{2-}. Trudinger (1986) reported that the biggest S input to the hydrosphere was derived from rivers (approximately 208 Tg S yr^{-1}) and small proportions derived from shore erosion (approximately 7 Tg S yr^{-1}) and groundwater (9 Tg S yr^{-1}).

Bolin *et al.* (1983) stated that the sources of S in rivers are precipitation, erosion, entrainment from flood plains, chemical weathering, slope run-off and leaching. S contributed by this sources is generally in the sulfate form. River water contains an average of approximately 1 to 4 mg S L^{-1}, largely as SO_4^{2-} (Ivanov *et al.*, 1983). However, even at this level, irrigation water can be a major source of S for flooded rice in some areas (Blair *et al.*, 1979).

Rain water is reported to contain considerable amounts of S and this varies from one area to another (Fox *et al.*, 1983). Higher S contents were found in areas close to the sea or industrial regions (Lefroy *et al.*, 1989). Tisdale and Nelson (1975) stated that in the United States, approximately 1 kg S ha^{-1} yr^{-1} was deposited in rainfall in rural areas and this was considerably lower than in the industrial areas, where up to 112 kg S ha^{-1} yr^{-1} could be deposited. Increasing concerns about air pollution may lead to a decline in S accession from the atmosphere in industrial areas (Blair, 1979).

2.4 ROLES AND REQUIREMENT OF SULFUR IN PLANT NUTRITION

2.4.1 Roles of Sulfur in Plant Nutrition

Sulfur has been recognized for over 100 years as one of the essential elements required for the growth of plants (Evans, 1975). Knowledge of the functions of S-containing compounds in plant physiology and biochemistry is required to understand the role of S in plant nutrition. Plant metabolism depends on S and a deficiency will cause basic metabolic impairment which will result in reductions in crop yields and quality (Duke and Reisenauer, 1986). Increasing evidence of sulfur deficiency from many parts of the world has led to an increasing interest in detailed studies of the role of S in agriculture (Blair, 1979).

Sulfur plays many important roles in plant nutrition (Tisdale and Nelson, 1975; Blair, 1979 and Morris, 1987) including :

(a) synthesis of protein and the essential S containing amino acids, methionine, cystine and cysteine
(b) synthesis of coenzyme A as well as biotin, thiamine and glutathion
(c) synthesis of chlorophyll
(d) synthesis of the volatile oils found in members of the families Cruciferae and Liliaceae
(e) as a requirement for nitrogen fixation by leguminous plants.

2.4.2 Sulfur Requirements of Plants

Spencer (1975) stated that "the sulfur requirement has been considered as the amount of sulfur necessary for the plant to absorb over some given period of time. This infers that when the requirement is just being met, sulfur compounds will occur inside the plant at a particular concentration". He also stated that in a given situation requirement can also be considered in terms of amount of S needed to achieve optimum plant growth.

According to the S requirement, Spencer (1975) classified crops into three groups : crops with high S requirement (rapeseed, lucerne and cruciferous forages), moderate S requirement (coconut, sugarcane, clover and grasses, coffee and cotton) and low S requirement (sugar beet, cereal forages, cereal grains and peanut). The crop requirements need to be considered when developing fertiliser recommendations.

The S content of crops (Table 2.1) has also been reported to vary among species, among cultivars within species, with stage of development of the crop (Duke and Reisenauer, 1986) and in parts of plants (Blair, 1979). Within a cultivar, tissue S concentration can vary over wide ranges depending on the amounts supplied and in some cases, on the cation composition of soils (Blair, 1979).

Table 2.1 Sulfur content of selected crops at harvest (Duke and Reisenauer, 1986).

Crop	Component	Yield (t ha^{-1})	S content (kg ha^{-1})
Alfalfa	Hay	18.0	45.0
Barley	Grain	6.0	12.0
Cabbage	Head	80.0	73.0
Maize	Grain	9.0	17.0
Cotton	Lint	1.5	7.5
Mixed grasses	Hay	15.0	52.0
Onion	Bulbs	70.0	44.0
Peanut	Nuts	4.5	11.0
Rice	Grain	8.0	6.0
Sorghum	Grain	8.0	22.0
Soybean	Grain	4.0	14.0
Sugar-beet	Roots	70.0	12.0
Sugar-cane	Tops	452.0	40.0
Tomato	Fruit	70.0	24.0
Wheat	Grain	4.0	9.0
Tobacco	Leaves	3.5	14.0

2.5 FORMS AND TRANSFORMATION OF ORGANIC AND INORGANIC SULFUR IN SOIL

2.5.1 Forms of Organic Sulfur in Soil

During the formation of soil, the sulfides of primary minerals are converted to sulfates which are in turn transformed to various organic compounds by microorganisms, plants and animals. Some of the S reappears as sulfate when the plant and animal residues are incorporated into the soils and decomposed by microorganisms, but part remains in the soil humus (Alexander, 1961).

There is a close relationship between organic C, total N and the total S in surface soils (Freney, 1986) and thus it can be concluded that most of the S in the surface horizons is in the organic form.

A wide variation can occur in the C : N : S ratios of soils, but the mean ratios for groups of related soils from different parts of the world are similar (Freney, 1986). Sulfur fractions and carbon, nitrogen and sulfur relationships in grassland, forest and associated transitional soils were investigated by Bettany *et al.* (1973). In their study they found that in the Ap horizon, C, N and S ratios ranged from 58:6.4:1 in the arid Chernozemic Brown soils to 129:10.6:1 in the leached Grey Wooded soils. Bailey (1985) reported that the N : S ratio of eastern Canadian prairie soils declined down the profile with value of 8.3 : 1 (0-15 cm), 7.2 : 1 (15-30 cm) and 6.5 : 1 (30-60 cm) and concluded that soils with N:S ratios of 6.0 : 1 (0-15 cm), 5.2 : 1 (15-30 cm) and 4.7 : 1 (30-60 cm) could have a high potential to supply sulfate S to plants and were unlikely to be deficient in S. Blair (1979) stated that a great variety of S compounds exist in plants but most of the S (approximately 90 %) is bound in proteins in the amino acids, cysteine, cystine and methionine. Freney *et al.* (1972) found that the majority of the amino acid S in soil is bound to the mineral and humus fractions and that amino acid S ranged from 21 to 30 % of the total organic S in two Australian Podzolic soils.

Barrow (1961) stated that ester sulfate, which is believed to be largely organically bound, may constitute from 30 to 70 %, with an average of 50 % of the total organic S in the soil. Ester sulfate is easily split from organic matter on drying, producing plant-available sulfate (Barrow, 1961).

Bettany *et al.* (1979) separated the organic-S in four soils by reaction with 0.1 M NaOH, 0.1 M $Na_4P_2O_7$ at pH 13 under N_2, and dispersion, acidification and centrifugation. This method extracted 63 to 72 % of the total S, and the S was distributed as follows : fulvic acid A (36 %), fulvic acid B (3 %), humic acid A (13 %), humic acid B (21 %), humin > 2 µm (15 %) and humin < 2 µm (11 %).

A study on soil organic matter fractions as sources of plant-available S was conducted by Freney *et al.* (1975). In that study they incubated two soils with $^{35}SO_4^{2-}$ for eight weeks and then grew plants in the soil to investigate the proportion of S released from the various organic matter fractions. During incubation, most labelled S (64.9 %) moved into the reducible fraction and a smaller proportion (35.1 %) moved into carbon-bonded S form. During plant growth, the percentage of indigenous S released and taken up from the two fractions was identical. However, there was a considerable decrease in the labelled HI-reducible S fraction and only a very small change in the labelled C-bonded S. Some of the labelled HI-reducible S was converted to C-bonded S fraction during plant growth.

A similar experiment was conducted by Shedley (1982) with the exception that plants were also grown during the period when labelled S was being incorporated into the soil organic matter. In both experiments added sulfate was rapidly changed into the C-bonded and reducible forms, and the reducible fraction released significant amounts of S compared to C-bonded S. Chemical equilibrium between soil sulfate and HI-reducible S only occurred for the labelled S. In contrast, an equilibrium of indigenous S was not established.

2.5.2 Distribution of Organic Sulfur in Soils

Generally, the total S content of tropical soils is lower than that of temperate soils due to low S-containing parent materials, extreme weathering, leaching losses and small organic matter reservoirs (Blair, 1979). In most temperate areas, soil organic matter constitutes the largest S pools in the soil-plant-animal cycle and the total S and organic matter contents are highly correlated (Kamprath and Till, 1983).

Under aerobic conditions plant residues are mineralized by microorganisms, releasing plant available sulfate into the soil solution. Till and Blair (1978) investigated the S cycling rate from residues of pasture and indicated that 15 % of S contained in surface applied plant top litter was re-incorporated into the growing pasture plants in 56 days and 30 % of S contained in roots or top litter which was mixed with the soil, was incorporated into the growing pasture plants in 70 days.

2.5.3 Transformation of Organic S in Soil

The mineralization of sulfate from soil organic S plays an important role in the S nutrition of plants. This is particularly so in parts of the world where atmospheric inputs of S to the soil are low. However, despite many studies of S mineralization and immobilization there is still considerable uncertainty regarding the biological turnover of soil S (Freney and Swaby, 1975).

Radioactive S (^{35}S) has been successfully used to examine certain aspects of the soil S cycle (e.g. Freney *et al.*, 1971; Goh and Tsuji, 1979; Saggar *et al.*, 1981). Freney (1986) stated that the two main reactions of organic S in soils which are important for agriculture are mineralization and release of volatiles to the atmosphere. Microorganisms play an important role in the mineralization process and they obtain their energy from the oxidation of carbon in the organic residues. During the decomposition of organic S (mineralization), the microorganisms incorporate some S into microbial protein and that not required by the microorganism is released as SO_4^{2-} which can be utilized by plants. Alexander (1961) stated that the addition of microbial inhibitors will impair mineralization. Thus any factors which affect microbial growth, should also affect S mineralization. It has been shown that temperature, moisture, pH and availability of nutrients affects mineralization (Williams, 1967; Chaudry and Cornfield, 1967 a, b). In addition to the factors described above, Maynard *et al.* (1985) showed that net mineralization was significantly greater in cropped soils compared with uncropped soils. They suspected that this difference was related to the plant demand for S which lowered the concentration of sulfate in the soil solution.

2.6 Inorganic Sulfur

Sulfate and compounds of lower oxidation state such as sulfide, polysulfide, sulphite, thiosulfate and elemental S are the major constituents of inorganic S in soils (Williams, 1975). Freney, (1961) stated that in well aerated, well drained soils the amounts of reduced-S compounds are generally less than 1 $\mu g\ g^{-1}$ soil. Sulfate may occur in soils as water-soluble salts, adsorbed to the soil colloids, or as insoluble forms (e.g. $CaSO_4$; Fe and Al-sulfates) (Bohn *et al.*, 1986).

Tabatabai and Bremner (1972) reported that analyses of the 37 surface soils (0 - 15 cm), representative of the major soil series in Iowa, showed that inorganic S represented only 1 - 5 % of the total S in these soils and occurred entirely as sulfate.

2.6.1 Adsorption and Desorption of Sulfate

Adsorption and desorption of sulfate in soils are important processes because of their effect on S availability to crops. There has been an increasing amount of research conducted on the processes involved in the transformation of sulfate in soils (Chao *et al.*, 1962a,b,c; Parfitt and Smart, 1978; Couto *et al.*, 1979; Rajan, 1979; Singh, 1984a,b,c; Nodvin *et al.*, 1986). Mechanism of sulfate adsorption by iron oxide in two tropical soils has been reported recently (Parfitt and Smart, 1978; Curtin and Syers, 1990).

Sulfate is adsorbed in soils by replacing OH- groups (Chang and Thomas, 1963). To a certain extent, sulfate is retained by most soils and the S adsorption by soils depends on the physical and chemical characteristics of soils. Tropical soils tend to have lower levels of S compared to temperate soils due to the lower organic matter content (Blair, 1979). The effect of organic matter on sulfate adsorption is still a matter of debate. Singh (1984a) reported that organic matter had a negative effect on S adsorption. Other investigators reported that organic matter may increase sulfate adsorption (Harrison *et al.*, 1989).

Reactions of sulfate in soil are known to vary with the SO_4^{2-} activity, levels of available Al and equilibration time (Barrow and Shaw, 1977; Parfitt, 1978). While there are many rate studies dealing with reactions of phosphate with soil constituents, sulfate has received little attention. Sulfate is known to react more rapidly than phosphate (Parfitt and Smart, 1978), but like phosphate, slow adsorption reactions are also reported to occur over periods of weeks (Barrow and Shaw, 1977).

In aluminium silicates the terminal Al atoms, which normally complete their coordination shells with hydroxyl groups, are responsible for sulfate adsorption (Rajan, 1978). Sulfate may be retained in soils by three mechanisms, namely, coulombic attraction on positively charged sites, formation of innersphere complexes with Fe or Al through replacement of surface water or hydroxyl groups and precipitation of basic Al-sulfates (Adams and Rawajfih, 1977; Parfitt, 1978).

Parfitt (1978) reported that hydrous oxides of iron and aluminium and poorly crystalline aluminosilicate material are the main sites for the sulfate retention. The dehydrated aluminium oxides are reported to adsorb more sulfate than iron minerals (Rajan, 1978).

The adsorption of sulfate is influenced by different soil properties. These are :

a. Type of clay

Harward and Reisenauer (1966) indicated that sulfate retention on different clays is in the order of kaolinite(1:1) > illite (2:1) > montmorillonite (2:1). The higher proportion of anion exchange sites on 1 : 1 type clays and higher negative charge with associated anion repulsion on 2:1 type clays cause the greater retention of sulfate by kaolinite than by illite or montmorillonite. Chao *et al.* (1962c) reported that Al-clays retained more sulfate than H-clays. The amount and type of cations and the amount of clay, which determines the amount of weathered clay edges, were also reported to affect sulfate adsorption (Tisdale and Nelson, 1975).

b. Soil pH

Sulfate adsorption capacity is pH dependent (Gebhardt and Coleman, 1974; Singh, 1984b); therefore, a change in soil pH will influence the adsorption of sulfate in soils with variable charge colloids. At low pH, anion exchange caused by positive charge develops on hydrous iron and aluminium oxides or on the crystal edges of clays, particularly kaolins. Sulfate adsorption decreases with increasing pH and it is generally insignificant at pH values above 6.5, because of the reduction in positive charge on the hydroxy complex and increased OH^- concentration (Chao *et al.*, 1963).

An experiment on the effect of pH on sulfate adsorption by forest soil was conducted by Nodvin *et al.* (1986) who found that the highest sulfate retention occurred at pH around 4.0.

Marsh *et al.* (1987) concluded that there is a very close direct relationship between sulfate sorbed by soils and surface positive charge. A similar dependence of sulfate adsorption on surface positive charge has been reported by Hingston *et al.* (1972) and Parfitt and Smart (1978). Agricultural practices such as liming can result in increased soil pH and decreasing sulfate sorption; decreased surface positive charge and increased surface negative charge. Therefore, very little or no sulfate is adsorbed by limed soils (Haynes, 1983).

c. Concentration of cations and anions in soils

Sulfate adsorption is directly affected by which cations are present. Chao *et al.* (1963) noted that the relative effects of different cations on the adsorption of sulfate is $Al^{3+} > Ca^{2+} > K^+$. The concentration of cations in solution also affects the adsorption of sulfate. Barrow (1972) found that sulfate adsorption increased as calcium concentration increased.

Parfitt (1982) studied the competitive adsorption of phosphate and sulfate on goethite (α-FeOOH) and stated that sulfate adsorption was strongly influenced by pH of the solution and a strong reduction in sulfate adsorption was found because of competition for adsorption sites by phosphate. This evidence suggests that the application of phosphate fertiliser may increase sulfate leaching in soils, as was observed by Barrow (1970).

2.6.2 Oxidation of Elemental Sulfur

It is generally accepted that the oxidation of inorganic sulfur in soils is mainly carried out by the autotropic bacteria of the genus *Thiobacillus* (Starkey, 1966). Many studies have shown that other microorganisms are also capable of oxidizing reduced-sulfur compounds, including the facultative autotrophic bacteria such as *Beggiatoa*, the aerobic heterotrophic fungi such as *Saccharomyces* and *Penicillium*, the aerobic and facultative aerobic heterotrophic bacteria such as *Bacillus* and *Aerobacter*, the anaerobic photoautotrophs such as the green sulfur bacteria *Chlorobium* and *Chlorobacterium*, and the purple sulfur bacteria such as *Chromatium* and *Thiocystis* (Vitolins and Swaby, 1969; Wainwright, 1984).

Vitolins and Swaby (1969) isolated 206 strains of sulfur-oxidizing microorganisms in their experiment. They found that facultative autotrophs or heterotrophs were the major strains which were capable of oxidizing sulfur to sulfate.

(a) Measurement of Elemental Sulfur Oxidation

The oxidation of elemental S in soils can be measured by three different techniques (Blair, 1987a) : appearance of sulfate (Li and Caldwell, 1966); S-uptake studies (Fox *et al.*, 1964); and disappearance of elemental S (Shedley, 1982).

Appearance of sulfate

Li and Caldwell (1966) conducted an incubation study on soils using S of different particle sizes for various lengths of time. The appearance of SO_4^{2-} in an extractable soil pool was used as a measure of S oxidation. Oxidation rate increased as particle size decreased and oxidation rate (as a percentage of applied S oxidized per day) decreased with time. The application of unlabelled elemental S in this study might have resulted in an underestimate of S oxidation due to the S immobilization (Blair, 1987a).

Sulfur-uptake studies

In the study of Fox *et al.* (1964) S oxidation was determined by the measurement of S-uptake by corn and they found a linear relationship between the estimated specific surface area of the elemental S and the S yield. Blair (1987a) plotted these results against the reciprocal of particle diameter and found a curvilinear relationship between oxidation rate and the reciprocal of particle diameter. The study by Fox *et al.* (1964) measured a higher oxidation rate compared to the results of Li and Caldwell (1966) and Blair (1987a) suggested that the higher oxidation rate was due to the presence of plants in the system acting as a sink for sulfate, minimizing the amount of S in the system that could be immobilized, and maintaining a low soil solution concentration.

Disappearance of elemental sulfur

Blair (1987a) stated that measuring the disappearance of elemental sulfur is the most accurate technique for measuring the oxidation rate of elemental S because it overcomes the underestimations that may arise when measuring the production of sulfate or plant uptake of S methods. A range of solvents has been used to extract elemental S from soils. Shedley (1982) used acetone and recovered almost 100 % of freshly applied elemental S and no sulfate or organic S compound. Using this technique he found a linear relationship between the reciprocal of particle diameter and oxidation rate over a 140-day period.

(b) Factors Affecting Elemental Sulfur Oxidation

Temperature

The effect of temperature on microbial oxidation of elemental S has been studied by Nor and Tabatabai (1977). They found that the mean oxidation of S applied to five soils was 8, 22 and 47 % at temperature of 5, 15 and 30 °C, respectively, after 56 days of incubation.

Li and Caldwell (1966) found that microbial oxidation of S occurred very slowly at temperatures below 4 °C, and increased until 40 °C. Similar results were reported by Janzen and Bettany (1987b) who found that oxidation rate of elemental S was exponentially related to temperature.

Janzen and Bettany (1987b) stated that the relationship between oxidation rate of elemental S and temperature up to 30 °C at a given water potential can be described by the following equation.

$$K = a.b^{T}$$

where, K = oxidation rate, a and b = constants for water potential and temperature, respectively and T = temperature (°C).

Shedley (1982) found that maximal S oxidation rate occurred at 24/18 °C day/night temperature for 0.04 mm particles.

Soil moisture and aeration

Aeration and moisture in the soil are closely interrelated. Most S-oxidizing bacteria are aerobic so their activity declines when oxygen is lacking due to waterlogging (Jones *et al.*, 1971). Oxidation of elemental S is most rapid at a soil moisture content near to field capacity (Janzen and Bettany, 1987b). Kittams and Attoe (1965) reported this to be at 87.5 % of field capacity and decline rapidly at low moisture content (less than 18 %)().

In a pot experiment, Barrow (1971) compared the effects of waterlogging on Yarloop subterranean clover yield in sulfate and elemental S fertilised pots and indicated that plant yield was more depressed by waterlogging in the sulfate treatments. A greater depression in the sulfate treatment suggesting that the depression of elemental S oxidation at high moisture contents was not significant relative to the depression in availability of soil sulfate under the same conditions.

Soil pH

Nor and Tabatabai (1977) found that the rates of oxidation of elemental S were lower in acid soils than in alkaline soils, and the rates of sulfate formation were higher in alkaline soils (average 69 %) compared with those of the acid soils (average 52 %). A similar result was reported by Janzen and Bettany (1987a).

Vitolins and Swaby (1969) surveyed a range of soils and failed to find any relationship between S-oxidizing ability and pH of the soils, except at pH higher than 8. These soils often had a very poor S-oxidizing ability.

Soil texture

The effect of soil texture on S oxidation rates was studied by Rehm and Caldwell (1969) at a moisture content of 50 % of field capacity. They did not find a significant relationship. Similar results were reported by McCaskill and Blair (1987) who studied the effects of particle size and soil texture on elemental S oxidation and indicated that no relationship existed between soil texture and conversion of elemental S to sulfate over a range of clay contents from 9 to 52 %.

The status of nutrient and organic matter in soils

The nutrient requirements of microorganisms are not fully understood but are probably similar to those of higher plants (Weir, 1975). Bloomfield (1967) reported a more than two fold increase in S oxidation rate in the presence of phosphate fertiliser compared to the rate in the absence of added phosphate.

The effect of organic matter on elemental S oxidation is not fully understood. Wainwright *et al.* (1986) found that the addition of wheat straw into a loam soil stimulated elemental S oxidation, suggesting that this was probably due to the increased availability of carbon.

Particle size of elemental sulfur

Since direct contact between S-oxidizing microorganisms and the elemental S is necessary for S oxidation, the amount of S oxidized should be directly related to the surface area of the S particles (Li and Caldwell, 1966).

A linear relationship was reported between the specific surface area of S particles and S uptake by corn (Fox *et al.*, 1964). This general relationship means that the release rate is inversely proportional to the particle diameter. Field studies, subsequent incubation and pot experiment have confirmed this general relationship for the initial release period (Kittams and Attoe, 1965; Li and Caldwell, 1966 and Shedley, 1982).

Blair (1987a) compared S oxidation rates on different particle sizes obtained by Shedley (1982); Fenster (1965) and Li and Caldwell (1966), and stated that similar results were found for particle sizes from 1 to 0.1 mm. In contrast, a greater oxidation rate was reported by Shedley (1982) for 0.05 mm particle sizes using the disappearance of elemental S method, than that reported by Fenster (1965), using the plant-uptake technique. Blair (1987a) suggested that this difference was due to an underestimation of oxidation rate in the plant uptake method since some oxidized elemental S is not taken up.

Modelling S release from elemental S

Based on the spherical-particle model, McCaskill and Blair (1989) created a model for the release of sulfate from elemental S and superphosphate. They reported that the release of S from elemental S is dependent on the particle diameter and time of application. The calculation of the release rate can be made by using the following equation :

$$\Delta r = r_{t-1} - r_t$$

where, Δr = release rate

r_{t-1} = initial radius of particles

r_t = particle radius at time t

$r_t = (M_{t-1} - R_t/(\rho\ 4/3\ \pi))^{1/3}$

$R_t = (\rho\ 4/3\ \pi\ r_{t-1}^3 - \rho\ 4/3\ \pi\ r_t^3)/\Delta t$

$A = 4\ \pi\ r^2 \quad M = \rho\ 4/3\ \pi\ r^3 \quad R_A = R_t/A$

where, A = surface area M = mass r = particle radius

ρ = density (2 kg L^{-1} or 2 ng mm^{-3})

R_t = release of the particle on day t

R_A = release per unit surface area

From this equation it can be predicted that the release from the particle on day t and the release per unit surface area will decline with time according to a curvilinear relationship, while the particle radius at time t will decrease at a constant rate and specific surface area will increase exponentially (Figure 2.4) (Blair, 1987a).

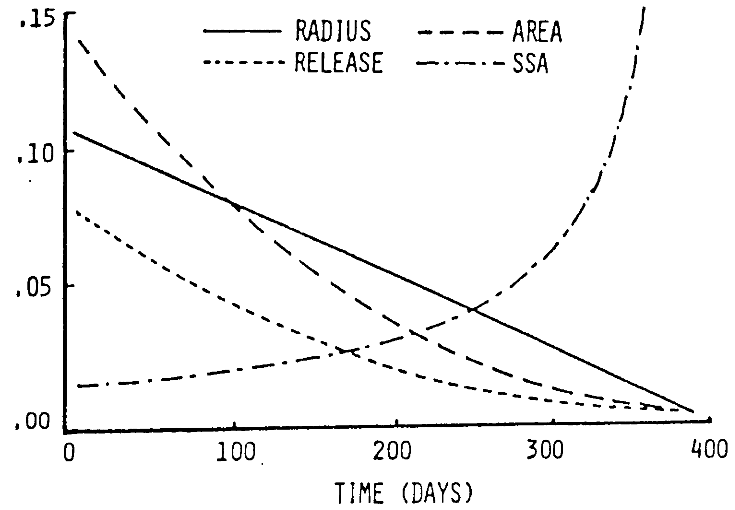


Figure 2.4 Change in particle radius (mm), surface area (mm^2), S release (ng day^{-1}) and specific surface area for a constant unit release rate using the spherical-particle model.

McCaskill and Blair (1989) developed a mechanistic model relating S oxidation to temperature and soil moisture and indicated that the maximum release rate (Δr_{max}) can be calculated by the following equation :

$$\Delta r = \Delta r_{max} \cdot f_T \cdot f_\theta$$

where, Δr = S release Δr_{max} = maximum S release

$f_T = \max(0, -0.103 + 0.0315\ Ts); f_T \leq 1$

$f_\theta = -0.386 + 2.37\ F_\theta - 0.945\ (F_\theta)^2$

where, Ts = Soil temperature. F_θ = current volumetric soil moisture / volumetric soil moisture at field capacity.

The maximum release rate (Δr_{max}) can also be calculated based on the particle diameter remaining after t days of application (McCaskill and Blair, 1989). However, the particle diameter at time 0 should be known. Since the proportion of added elemental S remaining after digestion with chloroform or acetone at t days is the fraction of (current mass)/(initial mass) and the equation is expressed as :

$$\Delta r = (r_0 - r_t)/t$$

where, r_0 = initial radius (mm)

r_t = the radius after t days (mm)

2.6.3 Sulfur from Fertilisers

The application of ammonium or potassium sulfate, as nitrogen or potassium sources, and the utilization of superphosphate as a source of P in agriculture has often masked S deficiency. There has been a gradual replacement of these fertilisers by high-analysis materials such as triple superphosphate, urea and mono- and diammonium phosphate, all of which contain little or no S. This has changed the S balance and resulted in increased S deficiency (Lefroy, 1989).

A wide range of S-containing fertilisers is available. Many liquid and dry materials have been produced to which some form of S has been added either deliberately or as a counter ion to other nutrients. A wider range of S-containing fertiliser materials is available than any other major or secondary plant nutrient.

Beaton and Fox (1971) stated that 16 dry and fluid sources of S fertiliser products are available, whilst Blair (1979) listed 40 materials available as a source of S (Table 2.2). The suitability of these products depends on climatic conditions, yield and type of crop, crop and soil management systems and soil properties (Beaton, 1987). Fertilisers which supply S in the sulfate form have the advantage of being immediately available to the plants (Friesen and Chien, 1986); however, in soils with a low sulfate retention capacity and in areas with high rainfall, sulfate can be readily leached from root zone (Blair, 1979). Leaching losses of fertiliser S may be reduced by applying S in the elemental form, but this form needs to be oxidized to sulfate to become available for the plant (Janzen and Bettany, 1987b).

Reactions of fertiliser sulfate in soils have been reviewed by Barrow (1975). These reactions were divided into two groups : movement of sulfate fertilisers into the soil and reaction of sulfate ions in the soil. Both of these are dependent on the solubility of the materials in the soil solution.

Blair (1987b) revealed that many factors should be considered in making a decision as to which S sources are most appropriate to be utilized, but the main factor is the cost per effective unit of S. Furthermore, he stated that such considerations should include both the initial response to and the residual value of the applied fertilisers.

Much research has been conducted on the effectiveness of sulfate and elemental S fertilisers. Shedley (1982) found that 20 kg S ha^{-1} applied as gypsum and elemental S resulted in similar responses in animal liveweight gain, although the pattern of sulfate release for the two fertilisers was different.

The importance of S in agricultural production has never been in greater evidence than today, particularly in tropical regions. If S is ignored where needed, it will severely limit current and future crop production.

There are many aspects of S nutrition of flooded and non-flooded rice and on pastures that require further investigation. The complex global S cycle and the impact of human activities in the system require a better understanding of the transformation of S from the earth, atmosphere and hydrosphere in relation to the availability of S for agriculture. The experiments reported in this thesis were undertaken to develop a better knowledge of the usefulness of different S sources for flooded and non-flooded rice and for pastures. These results can be used to develop more efficient sulfur fertilising for a wide range of crops.

Table 2.2 The S Content of Fertiliser S Sources Available.

Source	per cent
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 superphospate	11-13
Diammonium phosphate-sulfate	10-15
Magnesium sulfate	23
Potassium-magnesium sulfate	22
Ammonium phosphate-sulfate-gypsum	8
Ammonium phosphate-sulfate-urea	6
Urea-ammonium sulfate	4-13
Elemental S Containing	
Diammonium phosphate-S	12-15
Elemental S	100
Diammonium polyphosphate S	15
Diammonium phosphate-urea phosphate-S	5-20
Urea-S	10
KCl-Urea-S	Varies
S-coated urea	Varies
Rock P-S	7-16
S-bentonite	90
S-fortified superphosphate	27
Ammonia-S solution	10
Other Inorganic Forms	
Ammonium thiosulfate solution	26
S dioxide	50
Ammonium bisulphite polyphosphate	3-5
Ammonium polysulfide	40-45
$NH_4P_2S_5$	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

Source : Blair (1979).

CHAPTER 3

SULFUR SOURCES FOR FLOODED AND NON-FLOODED RICE

3. 1 INTRODUCTION

Rice plants are grown both under flooded and non-flooded conditions on a wide range of soils. The most distinctive difference between flooded and non-flooded rice is the presence of a continuous water layer over the soil surface which modifies the chemical, physical and biological characteristics of the soils (Ponnamperuma, 1975 and Yoshida, 1975). Because of these differences experiences in flooded soils cannot be extrapolated to non-flooded soils and vice versa, and therefore research needs to be undertaken under the appropriate soil conditions.

Rice is the main source of carbohydrate in the diet for over 50 % of the world population (Grist, 1986) and the demand has been increasing in recent years largely because of a growing rice-consuming population. In Indonesia, prior to 1970, rice demand exceeded production due to the relatively low yield and as a result, the country was the biggest importer in the world. The introduction of "Pelita", a five-year development program in 1969, resulted in an increase in production of flooded rice from 11.2 to 42.4 Mt in 1989 with an expansion in production area of only 2.8 Mha. The production area of non-flooded rice declined from 1.5 Mha in 1969 to 1.2 Mha over the same period but the production increased from 2.1 to 2.4 Mt (Directorate General of Food Crops, Ministry of Agriculture, 1986, 1990).

To support this program, there has been a move from the use of ammonium sulfate (21% N and 24% S) to urea (46% N and 0% S) and from single superphosphate (SSP) (9% P and 13% S) to triple superphosphate (TSP) (20% P and 1% S) (Blair, 1979). This reduction of fertiliser S input in addition to the higher S offtake associated with higher yields, has led to an increase in the incidence of sulfur deficiency (Blair, 1979, 1983, 1987b; Blair and Lefroy, 1987; Ismunadji, 1987).

Recently, a wide range of sulfur-containing fertilisers has become commercially available. Information on the effectiveness of S from different sources under different cropping conditions is required to develop effective S-fertiliser management strategies to overcome the increasing S-deficiency problem.

The Indonesian fertiliser industry is based on urea and TSP (Suryosunarko, 1989) so these fertilisers provide the most suitable vehicle for the re-introduction of S into fertiliser programs (Lefroy, 1989). Several products are available for this but little is known of the S availability from such products. In consequence, a range of commercially and developmental S-containing fertilisers was investigated to study their short and longer term agronomic effectiveness in providing S to rice under flooded and non-flooded conditions.

3. 2 MATERIALS AND METHODS

3.2.1 Soil and Pot Preparations

A S-deficient granitic Aquic Haplustalf soil from Uralla, NSW, was collected from an unfertilised pasture site, air-dried and processed through a Royer shredder. This achieved a relatively uniform particle size, with good mixing, and allowed the easy removal of plant debris. The soil was then passed through a 3 mm sieve before being used in the experiment.

Pots, 30 cm deep, were made from 15 cm internal diameter polyvinyl chloride (PVC) pipe fitted with PVC end caps and sealed with silastic silicone. The pots were filled to a depth of approximately 25 cm, with 6.9 kg of air-dried soil (4.5 % moisture content). The chemical properties of the soil are presented in Table 3.1.

Table 3.1 Soil Characteristics.

Soil characteristic	Value	
Colwell P	17.0	μg P g^{-1} soil
Organic P	135.8	μg P g^{-1} soil
Total P	275.0	μg S g^{-1} soil
Extractable S	6.9	μg S g^{-1} soil
pH (1 : 5 H_2O)^A	6.1	
pH buffer capacity	0.01	(mol kg^{-1} dry soil)
Organic Carbon	0.87	%
ECEC	32.0	mmol (p^+) kg^{-1}
Exchangeable cations		
Ca	69.9	% of ECEC
Mg	10.2	% of ECEC
K	4.9	% of ECEC
Na	5.4	% of ECEC
Al	9.5	% of ECEC

Source : Anderson (1988).

^{A} *measured at start of present experiment*

3.2.2 Treatments, Experimental Design and Statistical Analysis

Two separate main experiments were conducted with rice using flooded and non-flooded soils. The experiments were conducted in a heated glasshouse, of the Department of Agronomy and Soil Science, University of New England, Armidale. Within each main experiment there was a nested experiment, the components being S rate and S source, each with two consecutive crops. Each component consisted of 3 replicates in a randomized block design.

The first experiment was an S-application rate study, where S was applied as gypsum at rates of 0, 2.5, 5 and 10 mg S kg^{-1} soil (approximately equal to 0, 5, 10 and 20 kg S ha^{-1} respectively, assuming that 1 ha of soil is equal to 2,000,000 kg, Donahue *et al.*, 1983). These units were used throughout this thesis. Yield and S content were determined at active tillering (AT), 59 days after transplanting (dat), maximum tillering (MT, 89 dat) and maturity (M, 144 dat). These treatments (Table 3.2) were applied to pots which were maintained under both flooded and non-flooded (field capacity) conditions.

The treatments in the major experiment consisted of the factorial combination of 9 fertilisers and a control (C) and three times of harvesting (AT, MT and M). The fertiliser treatments included six commercial S-containing fertilisers : gypsum (G) of particle size < 0.01 mm, elemental sulfur (E) of particle size < 0.01 mm, urea-S melt (US) manufactured by Cominco Ltd., Calgary, Alberta, Canada, sulfur-coated urea (SCU) manufactured by Tennessee Valley Authority, National Fertiliser Development Center, Muscle Shoals, Alabama, USA, TSPS-Hifert (HF) manufactured by Hi-Fert Pty. Ltd., Portland, Victoria, Australia and S-bentonite (SB) manufactured by Degra-Sul Fertiliser Production Ltd., Calgary, Alberta, Canada. These fertilisers were compared with three TSPS fertilisers which were made at UNE using a rotating drum seed-coating device (Scott, 1986). Slack wax (SW), calcium ligno sulfonate (LS) and polyvinyl alcohol (PVA) were used as adhesive materials to bind elemental S (with particle size less than 0.01 mm) to the surface of 2 to 4 mm diameter TSP granules. The S was applied at a rate of 10 % of total TSP-S weight. Each of the 9 products was applied at a rate of 10 kg S ha^{-1}. The fertilisers were applied by mixing thoroughly with the soil two days before transplanting.

Table 3.2 Source and rate of applied fertiliser.

Form of fertiliser	Source	Treatment code	Application kg S ha^{-1}	Application mg product pot^{-1}
Nil	Nil	C	0	0
sulfate-sulfur	Gypsum	G_1	5	89
	Gypsum	G_2 or G	10	178
	Gypsum	G_3	20	356
Triple super phosphate + elemental S	TSPS-PVA	PVA	10	330
	TSPS-Ca ligno sulfonate	LS	10	330
	TSPS-Hifert	HF	10	330
	TSPS-S.wax	SW	10	330
Nitrogen-sulfur	Urea-S melt	US	10	165
	Sulfur-coated Urea	SCU	10	206
Elemental sulfur	Elemental S	E	10	33
	S-bentonite	SB	10	37

Data were analysed by analysis of variance using the NEVA computer program (Burr, 1982). At each harvest, data from the S source and S rate as well as flooded and non-flooded components of the experiment were analysed separately. Data of C and G_2 treatments from the S rate experiment were used in the S-source experiment. In the S source experiment the G_2 treatment is referred to as G. In addition, data of percentage of S derived from the fertilisers and fertiliser S recovery in plant and soil fractions as well as data of rate of elemental S oxidation at AT, MT and M were combined and were analysed to study the effect of S source × harvest time interaction. An example of the analysis of variance for each experiment is presented in appendix 3.1.

Throughout this thesis, the differences between treatment means are deemed to exist when they are significant at the 5 % level ($P < 0.05$) of probability.

3.2.3 Basal Nutrients and ^{35}S Labelling

Basal nutrients (Table 3.3) were thoroughly mixed with the soil prior to potting. Fertiliser K, P and Mg were applied in two equal applications 14 and 2 days before transplanting and fertiliser N was applied half one day before transplanting and the rest 21 days after transplanting. Other basal fertilisers (Zn, Cu, Mo and B) were applied 2 days before transplanting. Calcium additions were equalized between pots by adding $CaCl_2$ to the C, PVA, LS, HF, SW, US, SCU, E and SB and applied 14 days before transplanting. To balance the P and N in each pot, a different amount of these nutrients was added, as presented in Table 3.4.

The reverse-dilution technique developed at UNE and CSIRO has proven to be a useful method to study the fate of nutrients in soil and plant systems (Shedley *et al.*, 1979; Shedley, 1982). This technique was used to study the release of S from the different sources because of the impossibility of labelling the manufactured fertilisers.

Carrier free $Ca^{35}SO_4$ was obtained from Amersham Australia Pty. Ltd. and diluted with distilled water to give a solution containing 1.08 MBq mL^{-1}. A syringe was used to apply 5 mL of the labelled solution to the soil and mixed thoroughly in a large plastic bag two weeks before transplanting. For the flooded experiment the soils were placed in the pots and flooded with distilled water and incubated for two weeks prior to transplanting to allow the equilibration of ^{35}S with the native sulfate and rapidly turning over organic S in the soil. Puddling was also conducted three days after flooding by stirring the soil with a plastic spatula. For the non-flooded experiment, 500 mL of distilled water was added to the soil to achieve a water content equal to field capacity and then mixed thoroughly. The soil was incubated for two weeks in a plastic bag. After incubation the soil was placed in the pots and both the flooded and non-flooded pots placed in the glasshouse. The treatments listed in Table 3.2 were incorporated into the soil two days before transplanting.

In order to calculate the recovery of fertiliser S by the plant, radioactivity data were converted to specific radioactivity ratio (SRR). SRR is the ratio of the treatment to the control specific radioactivity (SR) and SR is the ^{35}S activity (MBq pot $^{-1}$) expressed per unit of total S content of the plant (mg pot $^{-1}$). The rate of fertiliser S uptake (% day^{-1}) was determined by dividing % of fertiliser S present in the plant at each growth period by the length of the period in days.

In the original paper of Shedley *et al.* (1979), the reverse dilution results were presented as SRR data. Boswell (1983) made a comparison of the release of S from dung, urine and litter using both the reverse-dilution and direct-labelling techniques and found that "there was general agreement in the patterns of S uptake and S release rates as measured by the tracer techniques". In order to assist in understanding the results reported in this study, sulfur input from the fertiliser was estimated as (1-SRR) × 100 %.

Table 3.3 Basal nutrient application rates.

Nutrients	Source	Application kg ha^{-1}	 mg product pot^{-1}
N	$CO(NH_2)_2$	60.0	430.5
K	KCl	50.0	314.6
P	$Ca(H_2PO_4)_2.H_2O$	60.0	805.0
Mg	$Mg(NO_3)_2.6H_2O$	12.0	417.8
Zn	$ZnCl_2$	1.92	13.2
Cu	$CuCl_2.H_2O$	1.52	13.5
Mo	$(NH_4)_2Mo_7O_{24}.4H_2O$	0.08	3.4
B	H_3BO_3	0.12	2.3

Table 3.4 Amount of N and P added to balance the nutrients in each pot.

Treatments	Application (mg product pot^{-1}) $CO(NH_2)_2$	 $Ca(H_2PO_4)_2.H_2O$
C	430.5	805.0
G	430.5	805.0
PVA	430.5	563.5
LS	430.5	563.5
HF	430.5	563.5
SW	430.5	563.5
US	298.5	805.0
SCU	257.4	805.0
E	430.5	805.0
SB	430.5	805.0

3.2.4 Crop Management

Seeds of IR 43 rice (*Oryza sativa L.*), which is commonly cultivated under flooded and non-flooded conditions, were germinated and grown for 2 weeks in quartz sand. One healthy seedling was transplanted to each pot. For the flooded treatment, the depth of water was maintained at approximately 5 cm above the soil surface and the soil was dried one week before the end of the experiment. For non-flooded rice, the water status of soil was maintained at or near field capacity by weighing. The temperature in the glasshouse was maintained between 20 and 35 °C throughout the experiment.

In this study, two crops were grown with the same water regime to investigate the initial and residual effects of the fertiliser application under flooded and non-flooded conditions. No S was added to the second crop but basal nutrients were re-applied at the same rate as for the first crop. The plant parameters recorded were tiller number, and at maturity panicle number, dry weights of stem + leaf, root, grain, grain per panicle and 100 grains, percentage of empty grains; harvest index and S content of stem + leaf, grain and root.

At harvest, the plants were cut approximately 1 cm above the soil surface and the tops were separated into grain and stem + leaf. After harvest the soil was pushed out of the pot and laid in a plastic tray and the roots were removed and washed. The soil was then thoroughly mixed and an approximately 500 g sample taken, air-dried, ground and passed through a 2 mm sieve and analysed for total S (Till *et al.*, 1984), acetone extractable elemental S (Shedley, 1982) and $Ca(H_2PO_4)_2$ extractable S (ES)(Barrow, 1967). The S in these extracts was determined by Inductively Coupled Plasma (ICP) Spectrometry and ^{35}S determined by Liquid Scintillation Counting. The oxidation rate of elemental S was determined from the difference between elemental S added and elemental S remaining in the soil as determined by acetone. The organic S (OS) content was estimated by subtracting the amount of elemental S remaining in the soil plus phosphate extractable S from the total S content of the soil.

The plant materials were dried at 80 °C until a constant dry weight was achieved and ground to pass 1 mm screen. A subsample of each plant component was taken (0.2 g), digested in a sealed container with $HClO_4$ and H_2O_2 (Anderson and Henderson, 1986) and measured for total S by ICP spectrometry and ^{35}S content by Liquid Scintillation Counting.

After the first crop was harvested, the soil was mixed thoroughly and returned to the same pot. The pots were re-wetted and kept in the glasshouse for two weeks. For the flooded rice the soil was flooded with distilled water and for the non-flooded the soil moisture content was maintained at or near field capacity with distilled water. One week prior to harvesting of the first crop, seeds of the same variety of rice were germinated in the quartz sand. One healthy seedling was transplanted to each pot two weeks after the first crop had been harvested. The experimental procedures and measurements were the same as in the first crop, except that the crop was harvested only at maturity.

3.3 RESULTS - FIRST FLOODED CROP

3.3.1 Response to Gypsum

a. Tiller and panicle number and yield

Tiller number increased with S-application rate at each observation and harvest time. As early as 31 dat S the application of S had resulted in increased tiller number from 1.3 plant^{-1} in the C up to 5.0 plant $^{-1}$ in the G_3 treatment. At M, panicle number was 8.7 and 17.7 plant $^{-1}$ in the corresponding treatments (Appendix 3.2).

At each harvest, leaf + stem, root and total yields increased with increasing S-application rate (Table 3.5). However, the difference in root yield recorded between G_2 and G_3 treatments at MT and M was not significant. At M, grain yield also responded to S-application rate up to 20 kg S ha^{-1} (Table 3.5).

Table 3.5 The effect of S-application rate on the dry matter yield (g pot $^{-1}$) of plant components at different growth stages under flooded conditions.

Growth stages	Yield (g pot $^{-1}$)	Treatment C	G_1	G_2	G_3
AT	leaf + stem	4.2 d^A	10.4 c	14.4 b	18.7 a
	root	1.5 d	4.1 c	8.7 b	9.1 a
	total	5.7 d	14.5 c	23.1 b	27.8 a
MT	leaf + stem	16.7 d	26.3 c	36.9 b	41.9 a
	root	6.4 c	11.7 b	18.5 a	21.7 a
	total	23.1 d	38.0 c	55.4 b	63.6 a
M	grain	15.6 d	25.5 c	30.7 b	35.6 a
	leaf + stem	18.8 d	28.3 c	37.2 b	42.4 a
	root	8.7 c	15.1 b	22.2 a	22.7 a
	total	43.1 d	68.9 c	90.1 b	100.7 a

^{A} Data followed by the same letter in the same row are not significantly different ($P > 0.05$) (Duncan's multiple range test).

There were no significant differences in dry weight or number of grains per panicle recorded among G_1, G_2 and G_3 treatments. However, these were significantly greater than those of C (Appendix 3.2). S application had no significant effect on the 100 grain dry weight or harvest index. The percentage of empty grains declined significantly when S was applied (Appendix 3.2).

b. S content, percentage of S derived from the fertiliser and recovery of fertiliser S

At each harvest, S content of the root, stem + leaf and the whole plant increased significantly with increasing S-application rate. A similar response was recorded in the grain at M (Table 3.6).

Increasing S-application rate resulted in an increasing proportion (%) of the plant S being derived from the fertiliser in root, stem + leaf as well as in grain components at each harvest (Figure 3.1). At each growth period, increasing S-application rate above G_1 resulted in a lower recovery of applied fertiliser in root, stem + leaf and the whole plant. A similar trend was recorded in grain yield at M (Figure 3.2).

Table 3.6 The effect of S-application rate on S content of rice (mg pot^{-1}) at different growth stages under flooded conditions.

Growth stages	S content (mg pot^{-1})	Treatment			
		C	G_1	G_2	G_3
AT	leaf + stem	4.4 d[A]	10.9 c	13.6 b	20.1 a
	root	1.1 d	3.0 c	4.7 b	6.9 a
	total	5.5 d	13.9 c	18.3 b	27.0 a
MT	leaf + stem	10.3 d	16.2 c	24.3 b	30.9 a
	root	2.7 d	6.5 c	8.6 b	11.9 a
	total	13.0 d	22.7 c	32.9 b	42.8 a
M	grain	11.0 d	16.3 c	24.4 b	30.0 a
	leaf + stem	10.5 d	16.7 c	24.7 b	30.4 a
	root	3.2 d	7.3 c	10.2 b	12.8 a
	total	24.7 d	40.3 c	59.3 b	73.2 a

[A] Data followed by the same letter in the same row are not significantly different (P > 0.05) (Duncan's multiple range test).

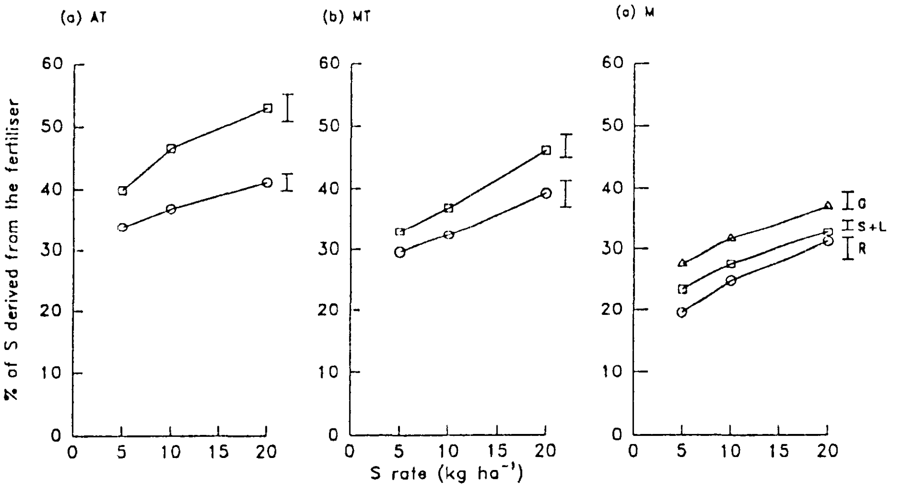


Figure 3.1 The effect of S-application rate on percentage of S derived from the fertiliser in different plant parts at different growth stages under flooded conditions. Vertical bars indicate LSD (P = 0.05) at each observation time.

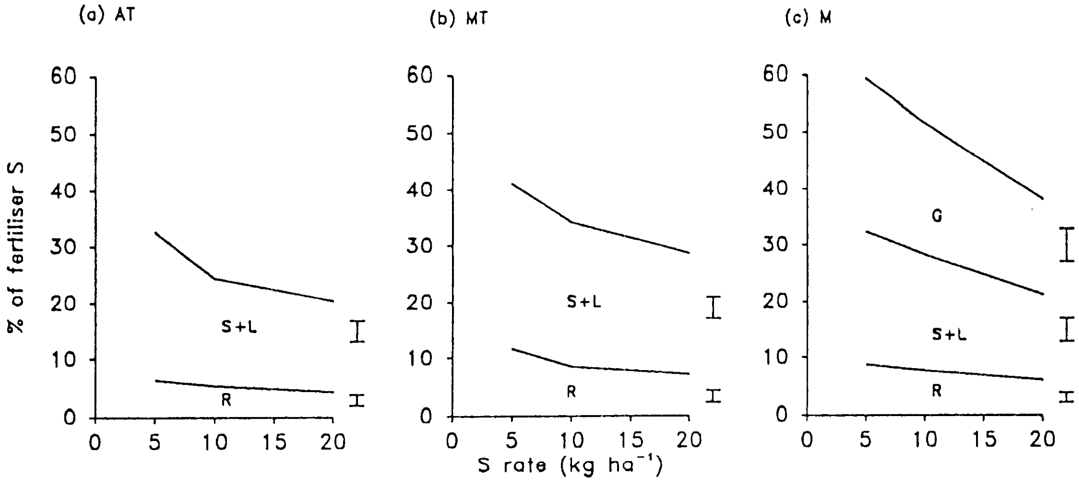


Figure 3.2 The effect of S-application rate on percentage of the fertiliser S incorporated into the plant components at different growth stages under flooded conditions. Vertical bars indicate LSD (P = 0.05) at each observation time.

c. Soil S pools

At AT and MT, increasing extractable S and organic S levels were recorded with increasing S-application rate (Appendix 3.3). At M, the highest extractable S level was recorded in the G_3 treatment, although this was not significantly different from the G_2 (Appendix 3.3).

The highest percentage of fertiliser S which was recovered in the extractable S fraction at AT was in the G_3 treatment, although this was not significantly different from that of G_2 (Table 3.7). There were no significant differences in percentage of fertiliser S that was recovered in this fraction at MT or at M. At each harvest, S-application rate had no significant effect on the percentage of fertiliser S that was recovered in the OS fraction (Table 3.7).

Table 3.7 The effect of S-application rate on the percentage of fertiliser S incorporated into the extractable S (ES) and organic S (OS) at different growth stages under flooded conditions.

Treatment	------ AT ------		------ MT ------		------ M ------	
	ES (%)	OS	ES (%)	OS	ES (%)	OS
C	--	--	--	--	--	--
G_1	29.7 b[A]	39.0 a	17.6 a	41.7 a	2.2 a	38.2 a
G_2	38.6 a	37.4 a	19.5 a	46.7 a	3.6 a	43.9 a
G_3	42.5 a	35.8 a	23.5 a	48.5 a	5.8 a	53.7 a

[A] *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

3.3.2 Comparison of S Sources

a. Tiller and panicle number

At each observation time, tiller number was highest in the G treatment, although this was not significantly different from the PVA and LS at MT and M (Figure 3.3a).

There were no significant differences in the number of tillers recorded among the TSP-S treatments at the first observation (31 dat). PVA and LS produced the highest number of tillers after 45 days (Figure 3.3a).

There was no significant difference in number of tillers recorded between US and E. This was significantly higher than the SCU and SB from AT to M. At no growth stages were tiller numbers different between the control and SB or SCU (Figure 3.3b).

The highest panicle number was recorded in the G treatment although this result was similar to that of PVA. Among the TSP-S treatments PVA and LS produced a significantly higher number of panicles than the other treatments and there was no difference between HF and SW (Appendix 3.4).

A significantly higher number of panicles was recorded with US than with SCU, which together with SB was not greater than the control (Appendix 3.4).

There was no significant difference in dry weight of grains per panicle, 100 grain dry weight and harvest index recorded between the fertilised treatments and C. The percentage of empty grains was similar among the fertilised treatments and was significantly lower than that of C, except SB, which was similar to that of C (Appendix 3.4).

b. Yield

For ease of comparison data of dry matter yield and S content have been converted to that relative to gypsum. At all harvests yield was highest in the gypsum (G) treatment although yields were not significantly different from the PVA and LS treatments at MT and M (Table 3.8).

Among the TSP-S treatments, PVA resulted in the highest whole plant relative yield at AT and at the other harvests PVA and LS were not different from each other. Only at AT did the PVA and LS yield less than the G. Lower yields were recorded for HF and SW and also for SCU and SB. The yields of SCU and SB were not different from the control. These differences were generally reflected in each plant part (Appendix 3.5). Grain and total plant yields at M followed similar trends (Table 3.8).

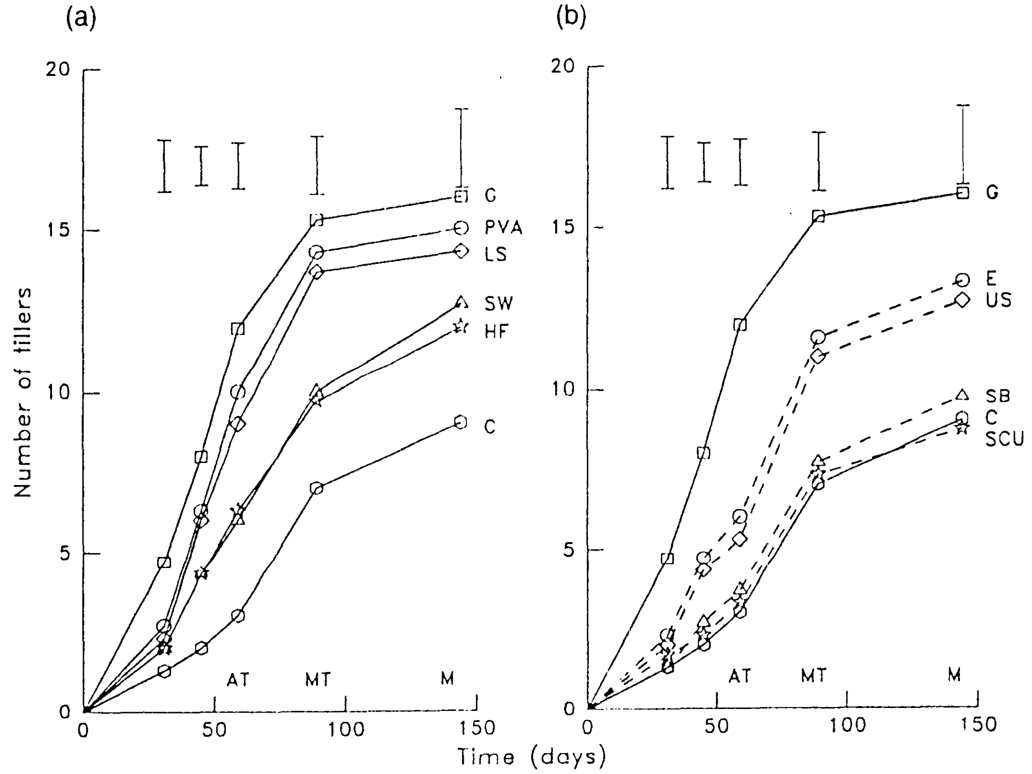


Figure 3.3 The effect of different S sources on number of tillers at different growth stages under flooded conditions. Comparison of G and C treatments with a) TSP-S sources and b) non TSP-S sources. Vertical bars indicate LSD (P = 0.05) at each observation time.

Table 3.8 The effects of different S sources on relative yield of the whole plant and grain at different growth stages under flooded conditions.

Source of S	Relative yield (%)			
	AT	MT	M	
			grain	total
C	24.8 f[A]	41.8 e	50.7 d	47.9 e
G	100.0 a	100.0 a	100.0 a	100.0 a
PVA	72.6 b	92.2 ab	94.5 ab	90.3 ab
LS	66.1 c	89.0 a-c	93.8 ab	89.7 ab
HF	49.2 e	64.4 d	86.1 b	75.7 c
SW	49.5 e	75.6 cd	85.8 b	77.9 c
US	50.5 de	74.8 cd	84.7 b	80.8 c
SCU	25.0 f	49.7 e	69.4 c	61.7 d
E	56.3 d	80.9 bc	87.2 b	82.8 bc
SB	30.8 f	49.0 e	61.5 cd	55.3 de

[A] *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

c. S Content

At each harvest, there was a similar trend in relative S content of the whole plant to that of relative plant yield (Table 3.9).

Among the TSP-S treatments, PVA produced the highest whole plant S content at each harvest as well as grain S content at M, although these results were not significantly different from LS except at AT. The S content of G was only significantly greater than PVA at AT, but always greater than all other treatments. Among the N-S treatments, SCU resulted in a significantly lower whole plant S content as well as grain S content than did US. The S content with SB was always lower than with E. The lowest whole plant and grain S content was recorded in the control, although plant S content in the SCU and SB treatments at AT and MT were not significantly different from the control (Table 3.9). These differences were generally reflected in each plant component (Appendix 3.6).

Table 3.9 The effect of different S sources on relative S content of rice at different growth stages under flooded conditions.

Source of S	Relative S content (%)			
	AT	MT	M	
			grain	total
C	30.1 e[A]	39.5 e	45.0 e	42.0 e
G	100.0 a	100.0 a	100.0 a	100.0 a
PVA	83.3 b	90.9 ab	94.2 ab	95.2 ab
LS	72.4 c	84.4 b	89.9 b	91.9 b
HF	57.9 d	63.3 d	76.6 c	73.9 c
SW	57.3 d	67.8 cd	74.4 c	75.7 c
US	60.0 d	70.4 cd	79.5 c	77.4 c
SCU	31.2 e	47.5 e	62.7 d	60.0 d
E	64.9 cd	72.5 c	79.4 c	79.3 c
SB	35.5 e	45.0 e	54.9 d	55.7 d

[A] *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

d. Percentage of plant S derived from the fertiliser

There was a significant harvest time × S source interaction in the percentage of S in the whole plant derived from the fertiliser. In general, the percentage with gypsum declined significantly with time (Table 3.10). In contrast, the percentage in the elemental S treatments increased significantly with time, except PVA, which did not differ with time, and LS and E, which increased up to MT. At each harvest the G treatment had the highest percentage of plant

S derived from the fertiliser, although the value was similar to that from PVA, LS and E at MT and only differed significantly from SCU and SB at M (Table 3.10).

Among the TSP-S treatments the PVA and LS treatments had the highest percentage of plant S derived from the fertiliser at AT and MT. HF and SW performed similarly at each harvest. There were no differences recorded among the TSP-S treatments at M (Table 3.10).

At each harvest US resulted in a significantly higher percentage of plant S derived from the fertiliser than did SCU. The percentage of plant S derived from the fertiliser was lower with SB than with E (Table 3.10).

At M, there were no significant differences in plant S derived from the fertiliser in the whole plant recorded among the treatments except from SCU and SB which were significantly lower than the other treatments (Table 3.10).

Table 3.10 The effect of different S sources on percentage of S derived from the fertiliser in the whole plant at different growth stages under flooded conditions.

Source of S	S derived from the fertiliser (%) AT	MT	M
G	41.7 a[A]	33.6 b	28.0 c-f
PVA	28.4 c-f	30.5 cd	28.3 c-f
LS	26.6 e-g	29.8 cd	28.5 c-f
HF	16.9 j	26.1 f-h	29.9 cd
SW	17.1 j	25.2 g-i	30.0 cd
US	18.4 j	27.9 d-f	30.8 c
SCU	8.1 k	17.4 j	23.7 hi
E	24.3 g-i	29.0 c-e	30.7 cd
SB	9.7 k	17.1 j	22.8 i

[A] Data followed by the same letter are not significantly different ($P > 0.05$) (Duncan's multiple range test).

e. Fertiliser-S uptake

There was a significant harvest time × S source interaction on the rate of fertiliser-S uptake. In general, the rate of fertiliser-S uptake by the rice was higher between AT and MT than between transplanting and AT. Uptake rate remained relatively constant between MT and M. An exception was recorded in the G treatment, where the rate of fertiliser-S uptake was significantly greater than all other treatments at AT and gradually declined, although not significantly at MT and M (Table 3.11).

Among the TSP-S treatment, PVA resulted in the highest rate of fertiliser-S uptake up to AT, although this did not differ significantly from LS. No significant differences were recorded between HF and SW. Fertiliser-S uptake did not differ significantly among the TSP-S treatments between AT to MT and MT to M (Table 3.11).

The rate of fertiliser-S uptake from SCU and SB were lower than all other treatments at all times although only significantly lower than some treatments (Table 3.11).

Table 3.11 Rate and total of fertiliser-S uptake by rice at different growth stages as affected by different sources of S under flooded conditions.

Source of S	Rate of fertiliser-S uptake ---------- (% day^{-1}) --------------			Total fertiliser-S uptake ---------- (% of applied) ------------		
	Trans. - AT	AT - MT	MT - M	AT	MT	M
G	0.41 a-d[A]	0.33 b-e	0.32 c-f	24.2 g	34.2 e	51.6 a
PVA	0.22 f-i	0.48 a	0.38 a-d	13.1 k	27.7 f	48.4 b
LS	0.18 h-j	0.48 a	0.40 a-d	10.6 kl	25.1 fg	46.9 b
HF	0.09 jk	0.38 a-d	0.41 a-d	5.4 no	16.9 j	39.6 d
SW	0.08 jk	0.41 a-d	0.43 a-c	5.0 o	17.6 j	41.2 cd
US	0.10 jk	0.44 ab	0.43 a-c	6.2 m-o	19.4 ij	42.9 c
SCU	0.03 k	0.24 e-i	0.30 d-g	1.2 p	8.8 lm	25.5 fg
E	0.15 ij	0.41 a-d	0.41 a-d	8.7 lm	21.0 hi	43.8 c
SB	0.03 k	0.21 g-i	0.27 e-h	1.9 p	8.2 l-n	23.1 gh

[A] *Data followed by the same letter are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

There was a significant harvest time × S source interaction in total fertiliser-S uptake by the whole plant. Total recovery of fertiliser S in the whole plant increased significantly with time in all treatments (Table 3.11). At each harvest, the highest recovery of fertiliser S in the whole plant was recorded in the G treatment. The lowest recoveries were recorded with the SCU and SB treatments at all harvest (Table 3.11).

At each growth period, PVA and LS resulted in a significantly higher recovery of fertiliser S in the whole plant than HF and SW. This was also higher than that of elemental S alone at MT and M.

Among the N-S treatments, US resulted in a greater total fertiliser-S uptake by the whole plant than did SCU. The recovery of fertiliser S in the plant was higher from E than with SB (Table 3.11).

f. Soil S pools

There was a significant S source × harvest time interaction on ES (Appendix 3.7). In general, the ES level in soil extracts declined significantly at later harvests. An exception was found with SCU and SB, where ES levels from these treatments decreased significantly from AT to MT and were relatively constant from MT to M (Appendix 3.7).

At AT, the G produced the highest level of ES which was significantly greater than all other treatments. Among the TSP-S treatments, similar results were recorded for the PVA and LS treatments and these were significantly greater than those of HF and SW. A non-significant difference in ES level was recorded between E and SW as well as among HF, US and SB treatments. The lowest level of ES was recorded in the control (Appendix 3.7).

At MT, the highest ES level was recorded in the PVA treatment, although this was not significantly different from that in the G, LS, HF, SW, US and E treatments. The ES levels of the SCU and SB treatments did not differ from each other but were lower than for the other fertilised treatments and greater than the control (Appendix 3.7).

At M, the highest ES level was recorded in the SB treatment although this was not significantly different from that of the SCU treatment. The ES level of all other fertilised treatments did not differ significantly from each other and were lower than the SB and SCU treatments. The lowest ES level was recorded in the control (Appendix 3.7).

There was a significant harvest time × S source interaction recorded on the percentage of fertiliser S in the ES fraction. In general, the recovery of fertiliser S in this fraction increased from AT to MT and declined from MT to M. An exception was found in the G treatment, where the recovery declined significantly with time (Table 3.12).

At AT, 38.6% of S from the G treatment was measured in the ES pool and this was significantly higher than any other treatment. This value declined to 3.6 % at M. This contrast with SB or SCU where the level was low at AT and increased at the last two harvests (Table 3.12).

Among the TSP-S treatments the highest amount of fertiliser S was found in the ES pool at AT with PVA and LS and no differences were observed at M (Table 3.12).

There was no significant S source × harvest time interaction on OS. In general, the OS content declined with time (Appendix 3.8). At each harvest, there was no difference recorded in organic S among the treatments (Appendix 3.8).

There was a significant S source × harvest time interaction recorded in the recovery of fertiliser S in the OS fraction (Table 3.12). The percentage of fertiliser S recovered in this fraction increased with time in each treatment. At AT, 37.4% of the S from G was in the OS pool compared to levels of less than 10 % for all other treatments. At M, the recovery of fertiliser S was highest in the G treatment but the recovery of fertiliser S had increased more with the other sources. The lowest recovery was recorded in the SCU treatment (Table 3.12).

Table 3.12 The effect of different sources of S on percentage of the fertiliser S incorporated into the extractable S (ES) and organic S (OS) at different growth stages under flooded conditions.

Source of S	ES (% applied) AT	MT	M	OS (% applied) AT	MT	M
G	38.6 a[A]	19.5 a	3.6 b	37.4 b	46.7 a	43.8 a
PVA	11.0 c-f	12.3 c	5.2 i-k	7.0 f	8.7 f	28.5 cd
LS	10.0 c-g	12.2 c	5.1 i-k	8.7 f	9.3 f	28.8 c
HF	8.1 f-i	11.3 c-e	6.0 h-k	9.0 f	9.4 f	27.9 cd
SW	7.1 g-j	10.6 c-f	7.1 g-j	7.7 f	9.6 f	23.1 de
US	9.1 d-g	11.4 c-e	5.0 jk	8.4 f	7.5 f	24.3 c-e
SCU	5.3 i-k	10.3 c-f	8.9 d-h	6.8 f	8.9 f	21.1 e
E	10.1 c-g	11.9 cd	5.4 i-k	8.8 f	10.4 f	28.5 cd
SB	5.5 i-k	10.5 c-f	8.8 e-h	7.1 f	8.5 f	26.4 c-e

[A] Data followed by the same letter are not significantly different ($P > 0.05$) (Duncan's multiple range test).

Acetone-extractable elemental S

There was no significant S source × harvest time interaction on elemental S oxidation. In all treatments, the amount of elemental S oxidized increased significantly with time. Among the TSP-S treatments, the PVA and LS treatments had the highest elemental S oxidation levels. No significant differences were recorded between the HF and SW treatments except at AT. The elemental S oxidation level was greater with US than with SCU and the SB treatment had significantly less elemental S oxidation level than did E. The lowest levels were always recorded in the SB and SCU treatments (Table 3.13).

There was no significant S source × harvest time interaction on elemental S oxidation rate. With all sources the rate increased from AT to M (Table 3.13). Among the TSP-S treatments, the PVA and LS resulted in the highest oxidation rates at AT and MT, although these were not always significantly greater than the HF and SW treatments. There were no differences among the TSP-S treatments at M (Table 3.13).

The elemental S oxidation rate with US was higher than with SCU at AT. However, they were similar at MT and M. The rate with E was higher than with SB at AT and MT but was similar at M (Table 3.13).

Table 3.13 Total oxidation and oxidation rate of elemental S as affected by different sources of S at different growth stages under flooded conditions.

Source	Oxidation of elemental S			Oxidation rate		
	------- (% applied) ----------			------------------- (% day^{-1}) ------------------		
of S	AT	MT	M	Trans. - AT	AT - MT	MT - M
PVA	30.0 i^A	48.6 f	84.5 a	0.51 c-f	0.62 a-c	0.65 ab
LS	29.0 ij	46.6 fg	83.6 ab	0.49 d-g	0.58 cd	0.67 a
HF	24.1 k	37.8 h	72.8 d	0.41 f-h	0.46 e-h	0.64 ab
SW	23.0 m	37.6 h	72.2 d	0.39 g-i	0.49 d-g	0.63 ab
US	24.1 k	38.5 h	72.9 cd	0.41 f-h	0.48 d-g	0.62 a-c
SCU	16.4 l	28.3 ij	60.4 e	0.28 i	0.40 f-h	0.58 a-d
E	26.9 j	43.5 g	78.3 bc	0.45 e-h	0.55 b-e	0.63 ab
SB	16.7 l	27.5 ij	59.3 e	0.28 i	0.36 hi	0.58 a-d

^{A} *Data followed by the same letter are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

3.4 RESULTS - SECOND FLOODED CROP

3.4.1 Response to gypsum

a. Tiller and panicle number and yield

As for crop 1, tiller and panicle number (Appendix 3.9) and yield of each component (Table 3.14) increased and the percentage of empty grains (Appendix 3.9) decreased with increasing S-application rate; however, the significant differences were only between G_3 and the control or G_3 and G_1. S-application rates had no significant effect on number of grains per panicle, dry weight of grains per panicle and dry weight of 100 grains. In the second crop, the harvest index increased with S-application rate with the significant difference between C and G_3 (Appendix 3.9).

Table 3.14 The residual effect of S-application rates on dry matter yield of plant components under flooded conditions.

	Dry matter yield (g pot^{-1})			
Treatment	grain	stem + leaf	root	total
C	8.0 b^A	20.0 b	4.7 b	32.7 b
G_1	10.4 ab	20.6 b	5.0 b	36.0 b
G_2	10.7 ab	21.7 ab	5.5 ab	37.9 ab
G_3	12.3 a	23.6 a	6.2 a	42.1 a

^{A} *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

b. S content, percentage of S derived from the fertiliser and recovery of fertiliser S

As for the yield parameters, plant S content increased with S-application rate with the difference between G_3 and C or G_1 being significant in all plant parts except the root and stem + leaf (Table 3.15).

Table 3.15 The residual effect of S-application rates on S content of plant components under flooded conditions.

	S content (mg pot $^{-1}$)			
Treatment	grain	stem + leaf	root	total
C	7.0 c[A]	9.9 b	3.4 a	20.3 c
G_1	8.7 bc	11.0 ab	3.5 a	23.2 bc
G_2	9.4 ab	11.8 ab	3.6 a	24.8 ab
G_3	11.0 a	13.5 a	4.4 a	28.9 a

[A] Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).

Percentage of S derived from the fertiliser in each plant component increased significantly with increasing S-application rate except in the root where the difference between the G_1 and G_2 treatments was not significant (Figure 3.4).

Among the fertilised treatments, the lowest total fertiliser-S uptake of the whole plant and stem + leaf components was recorded in the G_3 treatment. In the grain and root components no significant differences were recorded among the fertilised treatments (Figure 3.5).

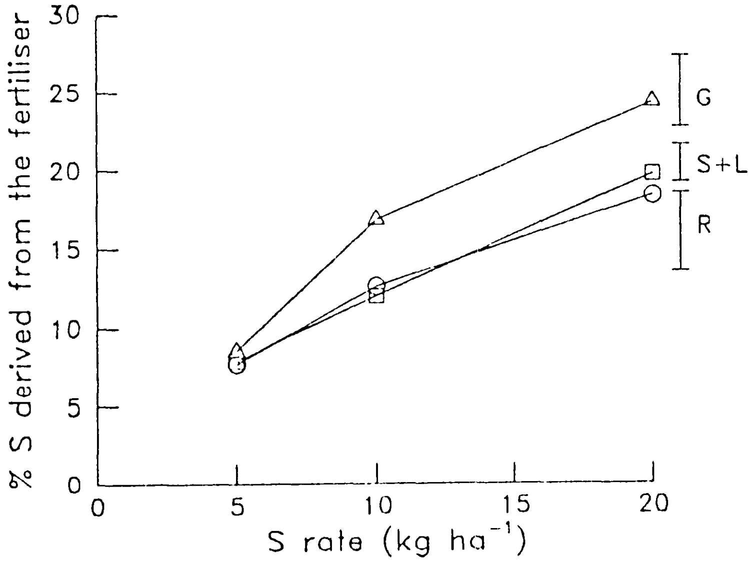


Figure 3.4 The residual effect of S-application rate on percentage of S derived from the fertiliser in different parts of plant under flooded conditions. Vertical bars indicate LSD ($P = 0.05$).

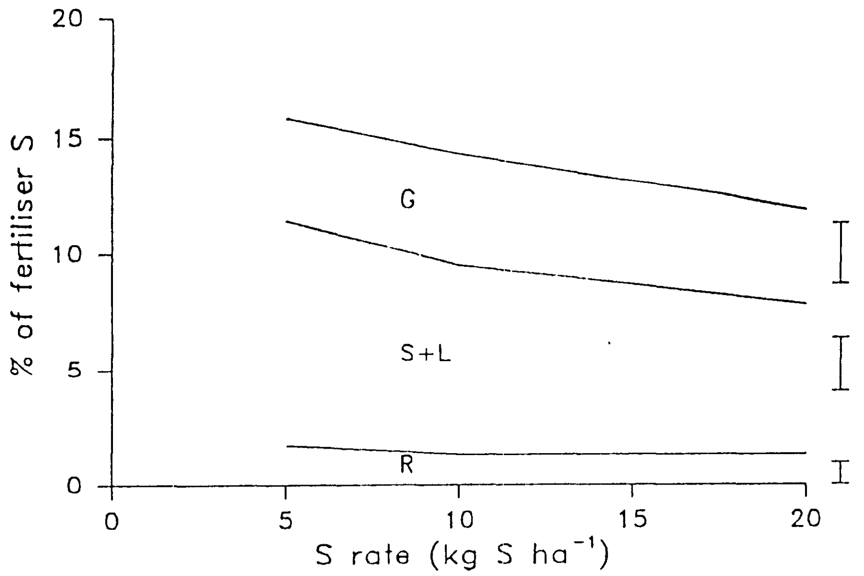


Figure 3.5 The residual effect of S-application rate on percentage of the fertiliser S incorporated into the plant components under flooded conditions. Vertical bars indicate LSD (P = 0.05).

c. Soil S pools

There was no strong effect of residual treatments on ES level at the end of the second crop (Appendix 3.10). The G_3 treatment resulted in a significantly higher ES level than C. There was no significant difference in ES level observed among the fertilised treatments. A similar OS level was recorded from the fertilised treatments and control (Appendix 3.10). The S-application rate had no significant effect on the recovery of fertiliser S that was incorporated into the ES and OS fractions (Appendix 3.11).

3.4.2 Comparison of S Sources

a. Tiller and panicle number and yield

The highest number of tillers was recorded in the SB treatment, although this was not significantly different from any of the elemental S sources, only greater than the G and C treatments. These differences were reflected in the number of panicles (Appendix 3.12).

The lowest yield was recorded in C but this was not significantly different from the G treatment for each parameter. By contrast, the highest relative plant yield was recorded in the

SB treatment although this did not differ significantly from any of the elemental S sources for grain and leaf + stem yield (Table 3.16).

There were no significant differences in total plant yield recorded among the TSP-S treatments and also among the N-S treatments (Table 3.16).

Table 3.16 The residual effect of different sources of S on relative dry matter yield of plant components under flooded conditions.

Source of S	Relative yield (%) grain	stem + leaf	root	total
C	75.5 c[A]	93.0 b	85.3 c	86.8 d
G	100.0 bc	100.0 b	100.0 bc	100.0 cd
PVA	103.8 ab	103.4 ab	101.2 bc	103.1 c
LS	101.6 ab	103.1 ab	103.4 a-c	102.5 c
HF	109.7 ab	108.9 ab	108.3 ab	108.6 a-c
SW	112.9 ab	108.1 ab	106.6 ab	108.9 a-c
US	108.3 ab	108.5 ab	104.6 a-c	107.5 bc
SCU	120.6 ab	118.3 a	119.0 ab	118.8 ab
E	106.3 ab	105.4 ab	100.9 bc	104.8 c
SB	124.0 a	119.5 a	121.0 a	120.9 a

[A] Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).

The S applied to the previous crop had no significant effect on dry weight of grain per panicle or dry weight of 100 grains in the second crop (Appendix 3.12). There was no significant difference in percentage of empty grains recorded among the fertilised treatments. The highest percentage was recorded in the control, but this was not significantly different from that of G, PVA, SW, US and E (Appendix 3.12).

b. S Content

The highest relative S contents of the whole plant, grain, stem + leaf and root were recorded in the SB treatment, although these values were not significantly different from SCU, HF and SW in S content for any plant component or from any of the fertilised treatments for the stem + leaf. Among the fertilised treatments the G produced the lowest relative S contents for all plant components although this result was higher than that of control (Table 3.17).

There were no significant differences in relative S content of any plant component among the TSP-S treatments nor among the N-S treatments (Table 3.17).

Table 3.17 The residual effect of different sources of S on relative S content of plant components under flooded conditions.

Source of S	Relative S content (%) grain	stem + leaf	root	total
C	75.5 d[A]	84.5 b	98.5 c	82.9 e
G	100.0 c	100.0 ab	100.0 c	100.0 d
PVA	105.3 bc	101.7 ab	104.8 c	102.9 cd
LS	104.0 c	104.1 ab	108.8 bc	104.3 cd
HF	120.1 a-c	119.6 a	115.8 a-c	118.2 a-c
SW	122.6 a-c	114.7 a	118.6 a-c	117.8 a-c
US	112.7 a-c	113.5 ab	113.1 a-c	112.7 b-d
SCU	129.0 ab	124.3 a	142.0 ab	128.7 ab
E	108.3 a-c	110.9 ab	104.0 c	108.8 cd
SB	132.3 a	128.0 a	145.0 a	131.8 a

[A] *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

c. Percentage of plant S derived from the fertiliser

The SB treatment resulted in the highest percentage of S derived from the fertiliser in the grain component, although this was not significantly different from that with SCU. The lowest level was recorded in the G treatment, although this did not differ significantly from that with PVA, LS and E. A similar trend was recorded in the root and stem + leaf components (Table 3.18).

Table 3.18 The residual effect of different S sources on percentage of S derived from the fertiliser in plant components under flooded conditions.

Source of S	Percentage of S derived from fertiliser (%) grain	stem + leaf	root
G	16.8 d[A]	12.6 c	12.0 c
PVA	18.2 cd	13.7 c	14.0 c
LS	19.7 b-d	14.3 c	15.3 bc
HF	24.1 b	18.6 b	19.7 b
SW	25.2 b	19.9 b	20.3 b
US	22.9 bc	15.1 c	16.3 bc
SCU	33.3 a	28.9 a	27.3 a
E	20.3 b-d	15.0 c	15.3 bc
SB	33.9 a	28.6 a	29.3 a

[A] *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

d. Fertiliser-S uptake

Lowest total fertiliser-S uptake was recorded in the G treatment although this was not significantly different from PVA, LS and E. The highest recovery was obtained in the SB treatment. These differences were generally reflected in the other plant components (Table 3.19).

Table 3.19 The residual effect of different S sources on recovery of the fertiliser S in different plant parts under flooded conditions.

Source of S	Total fertiliser-S uptake (% applied) grain	stem + leaf	root	total
G	4.8 d[A]	8.2 c	1.3 d	14.3 e
PVA	5.4 cd	9.4 c	1.5 cd	16.3 de
LS	5.7 cd	9.5 c	1.8 b-d	17.0 de
HF	8.0 bc	13.3 b	2.4 bc	23.7 bc
SW	8.7 b	14.1 b	2.6 b	25.4 b
US	7.2 b-d	10.7 c	1.9 b-d	19.8 cd
SCU	12.2 a	22.3 a	4.2 a	38.7 a
E	6.2 b-d	10.3 c	1.8 b-d	18.3 de
SB	12.7 a	22.4 a	4.5 a	39.6 a

[A] *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

e. Soil S pools

At the end of the second crop, the highest ES level was recorded in the SB treatment, although this was not significantly different from that with SCU, HF, SW, US and E. Only the SB and SCU treatments were significantly higher than the C (Appendix 3.13). The recovery of fertiliser S in the ES fraction was similar to the levels of ES. The same 5 treatments had the highest recoveries with only the SCU and SB being significantly greater than the PVA, LS and G treatments (Table 3.20).

There were no significant differences in OS level (Appendix 3.13) and recovery of fertiliser S in the OS fraction (Table 3.20) among the fertilised treatments. Only the SB and SCU treatments had significantly higher OS than the C.

Table 3.20 The residual effect of different sources of S on the percentage of fertiliser S incorporated into the extractable S (ES) and organic S (OS) under flooded conditions.

Source of S	Recovery of fertiliser S (%) ES	 OS
G	0.9 d[A]	32.3 a
PVA	1.5 b-d	29.8 a
LS	1.4 cd	28.9 a
HF	2.8 ab	32.1 a
SW	2.5 a-c	26.6 a
US	2.1 a-d	31.5 a
SCU	3.1 a	29.3 a
E	1.9 a-d	33.3 a
SB	3.0 a	27.8 a

[A] *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

At the end of the second crop, most of the elemental S from the different S sources applied in the first crop had been oxidized (Appendix 3.13). In all elemental S treatments, in excess of 94.6% of the elemental S had been oxidized during the experiment .

3.5 RESULTS - FIRST NON-FLOODED CROP

3.5.1 Response to Gypsum

a. Tiller and panicle number and yield

Tiller number increased with S-application rate at each observation and harvest time. As early as 31 dat the application of S had increased tiller number from 2.3 pot^{-1} in the C up to 5.7 pot $^{-1}$ in the G_3 treatment. At M, number of panicles were 10.7 and 19.0 pot $^{-1}$ in the corresponding treatments (Appendix 3.14).

At each harvest, dry matter yield of all components increased significantly with increasing S-application rate. At M, grain yield also responded to S up to 20 kg S ha^{-1} (Table 3.21).

Table 3.21 The effect of S-application rate on dry matter yield of plant components at different growth stages under non-flooded conditions.

Growth stages	Yield (g pot^{-1})	Treatment C	G_1	G_2	G_3
AT	leaf + stem	7.9 c^{A}	9.2 bc	12.2 ab	14.9 a
	root	3.6 c	4.5 bc	6.0 ab	7.4 a
	total	11.5 c	13.7 c	18.2 b	22.3 a
MT	leaf + stem	24.6 b	28.3 b	38.5 a	42.5 a
	root	6.1 b	7.2 b	9.9 a	10.9 a
	total	30.7 d	35.5 c	48.4 b	53.4 a
M	grain	11.5 d	14.0 c	16.1 b	18.4 a
	leaf + stem	36.3 b	40.6 b	49.3 a	52.3 a
	root	5.5 c	6.4 bc	7.8 ab	8.9 a
	total	53.3 d	61.0 c	72.3 b	79.6 a

^{A} *Data followed by the same letter in the same row are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

There was no significant difference in number of grains per panicle, dry weight of grains per panicle, dry weight of 100 grains and harvest index between the C and the fertilised treatments. The percentage of empty grains declined significantly with addition of S (Appendix 3.14).

b. S content, percentage of S derived from the fertiliser and recovery of fertiliser S

At each growth stage, S content (Table 3.22) and the percentage of S derived from the fertiliser (Figure 3.6) in all plant components increased with S-application rate. The percentage of fertiliser S taken up by the plant components declined significantly with increasing S-application rate at each growth period (Figure 3.7).

Table 3.22 The effect of S-application rate on S content of plant components at different growth stages under non-flooded conditions.

Growth stages	S content (mg pot^{-1})	Treatment C	G_1	G_2	G_3
AT	leaf + stem	9.1 d^{A}	12.0 c	15.0 b	18.6 a
	root	3.3 b	3.8 b	5.3 a	5.9 a
	total	12.4 d	15.8 c	20.3 b	24.5 a
MT	leaf + stem	16.3 c	20.3 c	26.3 b	33.2 a
	root	4.5 c	5.6 bc	7.0 ab	8.0 a
	total	20.8 d	25.9 c	33.3 b	41.2 a
M	grain	10.0 d	12.3 c	15.8 b	18.4 a
	leaf + stem	21.9 c	25.6 b	31.1 a	32.8 a
	root	5.2 b	6.3 b	8.0 a	9.1 a
	total	37.1 d	44.2 c	54.9 b	60.3 a

^{A} *Data followed by the same letter in the same row are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

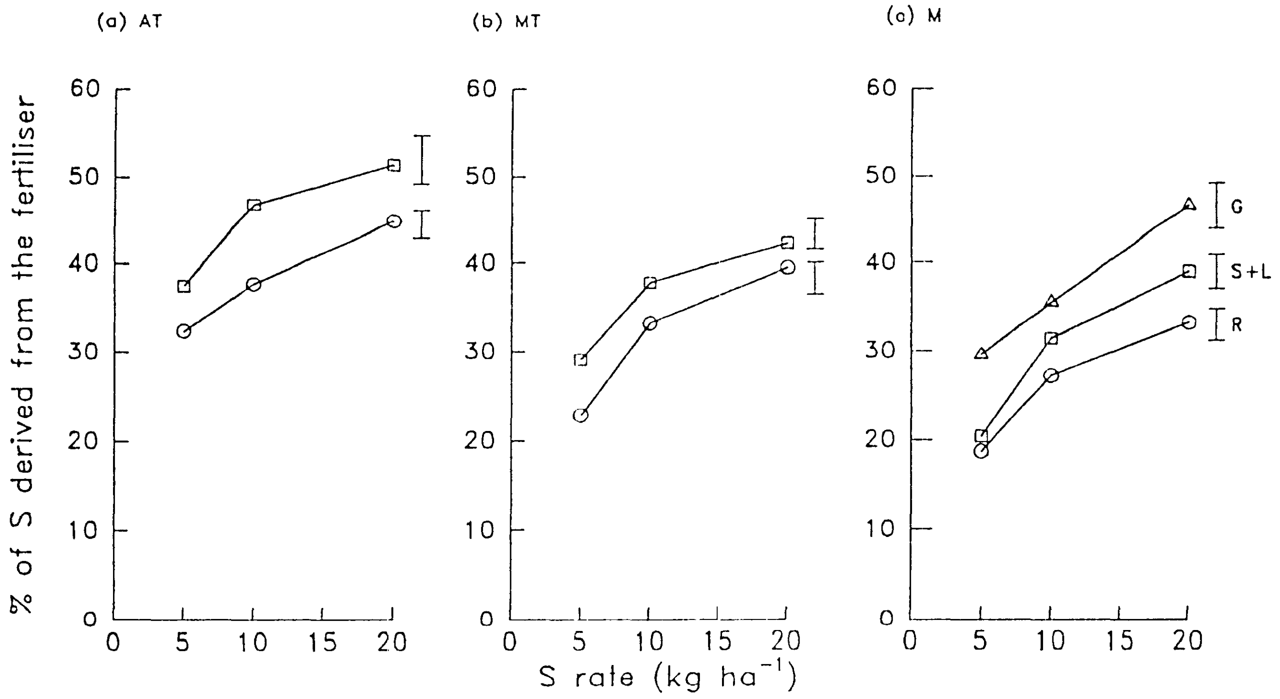


Figure 3.6 The effect of S-application rate on percentage of S derived from the fertiliser in different parts of the plant at different growth stages under non-flooded conditions. Vertical bars indicate LSD (P = 0.05) at each observation time.

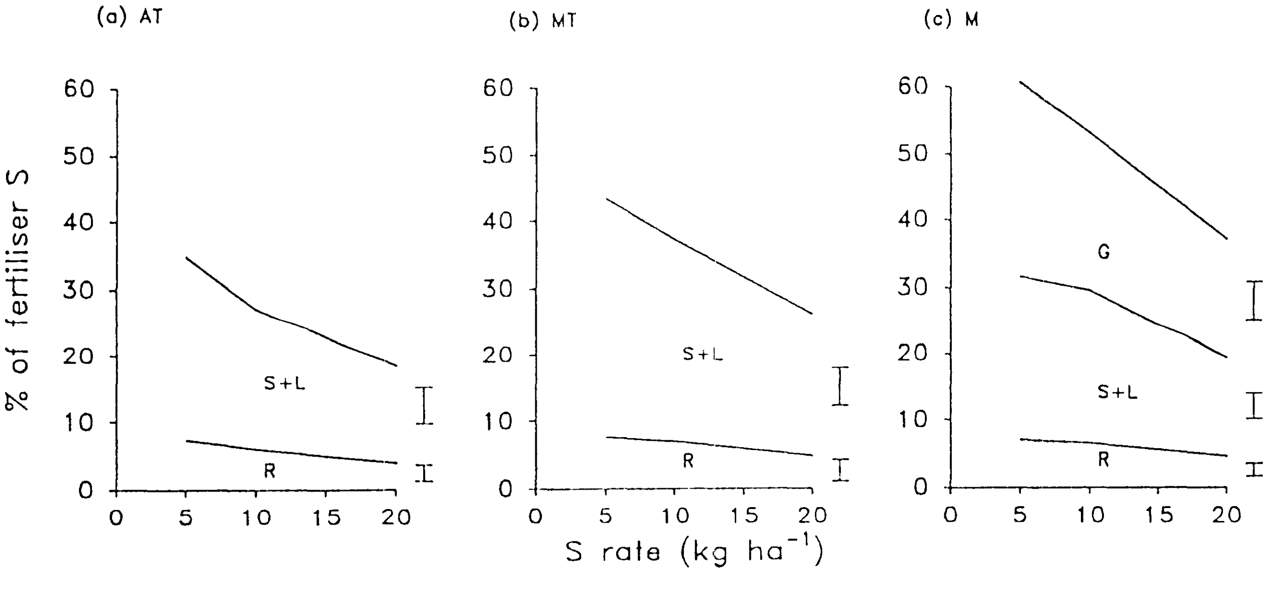


Figure 3.7 The effect of S-application rate on percentage of the fertiliser S incorporated into the plant components at different growth stages under non-flooded conditions. Vertical bars indicate LSD (P = 0.05) at each observation time.

c. Soil S pools

At each harvest, ES levels increased with S-application rate (Appendix 3.15). At AT, the percentage of fertiliser S that was recovered in this fraction increased significantly with increasing S-application rate; however, by MT and M, increasing S-application rate up to 20 kg S ha^{-1} had no significant effect on incorporation of fertiliser S into this fraction (Table 3.23). The level of OS increased significantly with S-application rate at both AT and MT (Appendix 3.15). The percentage of fertiliser S that was recovered in this fraction did not differ significantly between S-application rates at any harvest (Table 3.23).

Table 3.23 The effect of S-application rate on the percentage of fertiliser S incorporated into the extractable S (ES) and organic S (OS) at different growth stages under non-flooded conditions.

	----- AT -----		----- MT -----		----- M -----	
Treatment	ES	OS	ES	OS	ES	OS
C	--	--	--	--	--	--
G_1	24.6 b[A]	39.3 a	12.7 a	43.2 a	1.6 a	39.7 a
G_2	33.5 a	39.7 a	17.6 a	45.9 a	2.3 a	45.0 a
G_3	38.9 a	43.5 a	19.5 a	53.0 a	3.8 a	58.9 a

[A] *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

3.5.2 Comparison of S Sources

a. Tiller and panicle number

At each observation time, the highest number of tillers was recorded in the G treatment, although these were not significantly different from the PVA, LS, SCU and E treatments at AT up to M (Figure 3.8). Among the TSP-S treatments, PVA resulted in a higher number of tillers than HF. At MT and M the number of tillers was not significantly different between the TSP-S sources (Figure 3.8). At each observation time, there were no significant differences in the number of tillers in the N-S treatments. The number of tillers with SB was less than with E at MT, but was similar at AT and M (Figure 3.8).

The highest number of panicles was recorded in the G treatment, although this was not significantly different from the PVA, LS, SCU and E treatments. PVA and LS produced a higher number of panicles than did HF and SW (Appendix 3.16). There were no significant differences in the number of panicles among the N-S treatments. The SB treatment resulted in a lower number of panicles than did E. The lowest number of panicles was recorded in the C, although this did not differ significantly from that of SB, SW and HF (Appendix 3.16). There were no significant differences in harvest index, dry weight of grains per panicle and dry weight of 100 grains recorded among the treatments. The percentage of empty grains was similar in the C and elemental S treatments. There was a lower percentage of empty grains in the G compared to the C treatment although none of the elemental S treatments had significantly higher number of empty grains than the G treatment (Appendix 3.16).

b. Yield

At each harvest, the G treatment resulted in the highest relative whole plant yield, although this was not significantly different from that of PVA and E at MT and PVA, LS, SCU and E at M (Table 3.24). At AT, there was no significant difference in relative plant yield recorded among the TSP-S treatments. However, at MT and M, PVA resulted in the highest yield, although this was not significantly different from LS and SW at MT and LS at M. There was no significant difference in relative yield recorded among the N-S treatments at any stage. The relative yield with E was higher than with SB which did not differ from C (Table 3.24). These differences were generally reflected in each plant component (Appendix 3.17).

At M, the highest grain yield was recorded in the G treatment, although this was not significantly different from that of PVA, LS, SCU and E treatments, the SW and HF treatments were lower although not significantly lower than the LS. Among the TSP-S treatments, PVA and LS resulted in similar grain yields. There was no significant difference between the N-S treatments. The relative grain yield with E was higher than with SB. As in the earlier harvests (AT and MT) the lowest yield was recorded in the SB treatment and this was not different from that in C (Table 3.24).

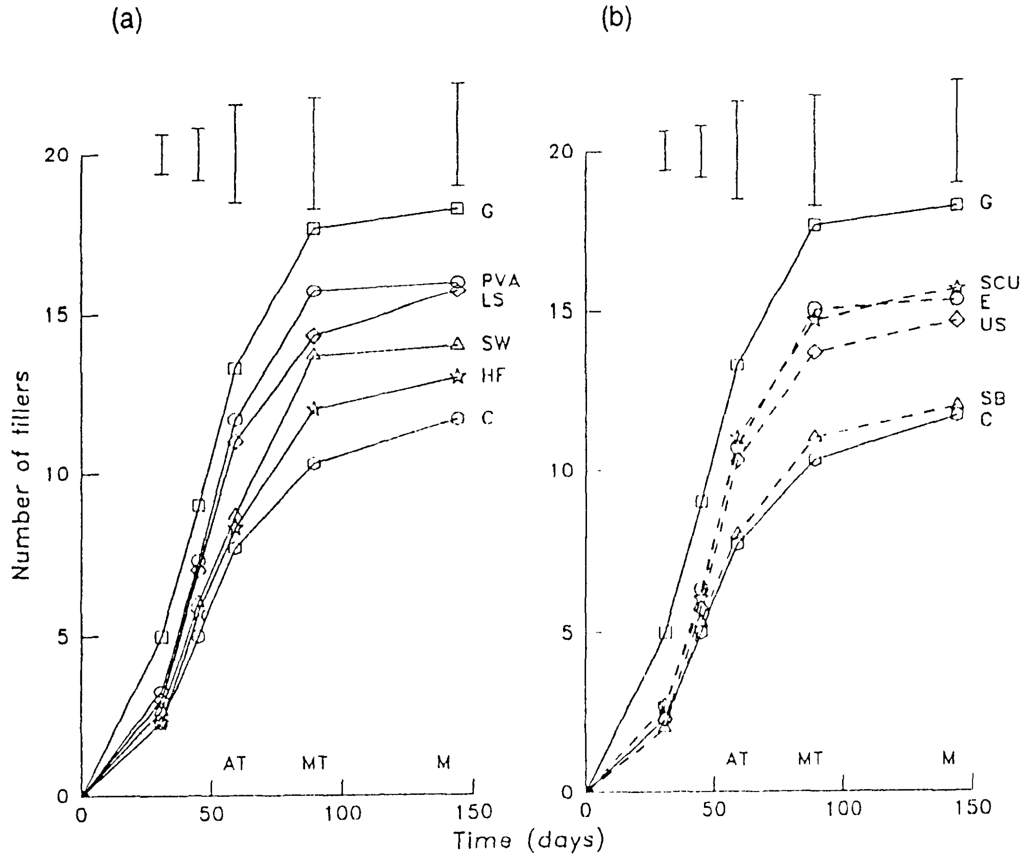


Figure 3.8 The effect of different S sources on number of tillers at different growth stages under non-flooded conditions. Comparison of G and C treatments with a) TSP-S sources and b) non TSP-S sources. Vertical bars indicate LSD (P = 0.05) at each observation time.

Table 3.24 The effect of S source on relative plant yield at different growth stages under non-flooded conditions.

Source of S	Relative yield (%)			
	AT	MT	M grain	M total
C	63.4 c[A]	63.5 e	71.6 e	72.8 f
G	100.0 a	100.0 a	100.0 a	100.0 a
PVA	84.0 b	92.8 ab	95.0 ab	94.9 ab
LS	79.8 b	87.7 bc	94.2 a-c	94.1 ab
HF	71.0 bc	77.3 c-e	85.9 cd	83.3 de
SW	74.2 bc	81.2 b-d	86.3 c	84.8 d
US	71.3 bc	81.6 b-d	88.0 bc	87.3 cd
SCU	75.8 bc	86.2 bc	93.2 a-c	93.5 a-c
E	74.4 bc	89.4 ab	93.0 a-c	93.0 a-c
SB	63.0 c	72.7 de	77.8 de	77.0 ef

[A] Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).

c. S Content

At each harvest, the highest whole plant S content was recorded in the G treatment, although this was not significantly different from that with PVA at MT and from PVA, LS and SCU at M (Table 3.25). The G treatment also produced the highest grain S content although it did not differ from those with the PVA, LS, SCU and E treatments.

Among the TSP-S treatments, the highest grain S contents were recorded with PVA and LS. The SCU produced a significantly higher S content in the grain than US, the other N-S source, although this was not the case at other harvests or for other plant components. Relative grain S content was higher with E and with SCU compared to SB, which did not differ from the control (Table 3.25). These differences were generally reflected in each plant part (Appendix 3.18).

Table 3.25 The effect of S source on relative S content of plant at different growth stages under non-flooded conditions.

Source of S	Relative S content (%)			
	AT	MT	M	
			grain	total
C	61.5 f[A]	62.5 f	62.9 f	67.5 f
G	100.0 a	100.0 a	100.0 a	100.0 a
PVA	82.1 b	91.7 ab	95.6 ab	95.5 ab
LS	79.8 bc	87.5 bc	93.1 a-c	93.6 a-c
HF	69.6 de	78.3 cd	82.9 c-e	81.4 de
SW	70.5 de	74.5 de	84.5 b-d	85.0 cd
US	73.4 c-e	80.8 cd	81.5 de	84.8 c-e
SCU	72.1 de	85.0 bc	93.4 a-c	92.4 a-c
E	76.3 b-d	85.6 bc	90.3 a-d	89.3 b-d
SB	66.0 ef	67.5 ef	71.9 ef	75.6 ef

[A] Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).

d. Percentage of plant S derived from the fertiliser

There was a significant S source × harvest time interaction recorded in the percentage of S derived from the fertiliser, which in general increased with time, except in the G treatment, which declined significantly with time (Table 3.26). At AT and MT, the highest percentage of S derived from the fertiliser in the whole plant was recorded in the G treatment (Table 3.26). By maturity, the G treatment was less than US, still greater than the SB and not significantly different from the rest.

Among the TSP-S treatments, PVA and LS had significantly higher percentages of S derived from fertiliser at AT and MT than did the other treatments. No differences were recorded at M. There was no significant difference in percentage of S derived from the fertiliser recorded in the N-S treatments. The percentage of S derived from fertiliser in the whole plant with SB was significantly lower than for all other treatments (Table 3.26).

Table 3.26 The effect of S source on percentage of S derived from the fertiliser in the whole plant and grain at different growth stages under non-flooded conditions.

Source of S	Percentage of S derived from fertiliser (%) --------------- whole plant ---------------		
	AT	MT	M
G	42.2 a[A]	35.5 b	31.4 d-f
PVA	29.3 gh	30.9 e-g	32.1 c-e
LS	28.0 hi	30.5 e-g	32.0 c-e
HF	18.6 n	27.4 ij	30.9 e-g
SW	19.4 mn	26.5 i-k	30.7 e-g
US	21.5 l	30.0 fg	33.6 c
SCU	27.7 l	27.6 h-j	32.0 c-e
E	25.1 k	30.0 fg	33.1 cd
SB	13.8 o	20.9 lm	25.9 jk

[A] *Data followed by the same letter are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

e. Fertiliser-S uptake

There was a significant S source x harvest time interaction on the uptake rate of fertiliser S by the whole plant (Table 3.27). In general, the rate of fertiliser-S uptake increased up to MT and was relatively constant from MT to M. An exception was recorded in the G treatment, where the uptake rate was significantly greater than all other treatments up to AT and declined significantly between AT - MT and MT - M (Table 3.27).

Among the TSP-S treatments, the uptake rate was higher from PVA and LS compared to HF and SW up to MT. No differences were recorded among the TSP-S treatments in the MT - M period. In this period the lowest fertiliser-S uptake rate was recorded in the G and SB treatments (Table 3.27).

There was a significant harvest time x S source interaction on recovery of fertiliser S in the whole plant (Table 3.27). However, this interaction appears to be due to higher recovery from G at AT and MT relative to other sources as well as low recovery from E and SCU at AT but equal to PVA at M. At M, highest fertiliser S recoveries were in the G and PVA treatments and lowest with SB (Table 3.27).

Table 3.27 Rate and total of fertiliser-S uptake at different growth stages as affected by different sources of S under non-flooded conditions.

Source of S	Rate of fertiliser S uptake (% day^{-1}) Trans. - AT	AT - MT	MT - M	Total fertiliser-S uptake (% of applied) AT	MT	M
G	0.46 ab[A]	0.33 de	0.29 d-g	27.2 g	37.2 e	53.3 a
PVA	0.26 f-h	0.44 ab	0.41 bc	15.1 k	28.3 g	51.0 ab
LS	0.24 gh	0.41 bc	0.43 ab	14.4 k	26.6 gh	50.3 b
HF	0.14 ij	0.34 d	0.42 ab	8.3 no	18.5 j	41.3 d
SW	0.14 ij	0.35 cd	0.44 ab	8.6 n	19.0 j	43.1 d
US	0.16 i	0.44 ab	0.44 ab	9.7 mn	23.0 i	47.1 c
SCU	0.17 i	0.44 ab	0.49 a	10.2 mn	23.5 i	50.7 b
E	0.20 hi	0.42 ab	0.47 ab	11.8 lm	24.5 hi	50.4 b
SB	0.09 j	0.27 e-g	0.32 d-f	5.8 o	13.9 kl	31.5 f

[A] *Data followed by the same letter are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

f. Soil S pools

There was no significant S source x harvest time interaction on extractable S with the level declining with time (Appendix 3.19). Among the fertilised treatments G was in the group with the highest extractable S level at AT and the lowest group at M. This contrasts with SB which was in the lowest group at AT and the highest at M. Among the TSP-S treatments, extractable S levels were highest with PVA and LS at AT, there were no differences at MT and SW was greater than PVA at M. No differences were recorded between N-S sources at any harvest or between E and SB at AT and MT (Appendix 3.19).

There was a significant S source x harvest time interaction recorded on the percentage of fertiliser S recovered in the extractable S fraction. In general, the recovery of fertiliser S in this fraction declined with time. At AT, 33.4 % of S from the applied G fertiliser was recovered in the

ES pool and this was significantly higher than any other treatment. This value declined to 2.3 % at M. This contrasts with SB where the level was low at AT and did not change over time (Table 3.28). Among the TSP-S sources, the highest amount of fertiliser S was found in the extractable S pool at AT with PVA and LS, at M there were no differences among the TSP-S sources (Table 3.28).

There was no significant S source × harvest time interaction on organic S. In general, the organic S content of soil extracts declined with time (Appendix 3.20).

There was a significant S source × harvest time interaction recorded on the recovery of fertiliser S in the organic S pool. The percentage of fertiliser S recovered in the organic S pool increased with time in each treatment. At AT, 39.7 % of the S from G was in the organic S pool compared to levels of less than 10 % for all other treatments which did not differ from each other. At M, the recovery of fertiliser S was higher in G than SB with no differences between the other sources (Table 3.28).

Table 3.28 The effect of different sources of S on percentage of the fertiliser S incorporated into the extractable S (ES) and organic S (OS) at different growth stages under non-flooded conditions.

Source	ES			OS		
of S	AT	MT	M	AT	MT	M
G	33.4 a[A]	17.6 bc	2.3 k	39.7 c	45.9 a	45.0 ab
PVA	17.0 b-d	13.2 c-g	3.1 jk	8.7 f	20.7 d	40.8 bc
LS	18.3 b	14.1 b-f	3.6 jk	7.0 f	21.8 d	41.9 a-c
HF	12.4 d-g	10.9 e-h	5.4 i-k	7.7 f	17.5 de	39.4 a-c
SW	12.1 e-g	11.2 e-h	5.5 i-k	8.4 f	18.4 de	39.6 a-c
US	17.7 bc	11.2 e-h	3.7 jk	6.4 f	19.8 de	43.4 a-c
SCU	16.9 b-d	11.6 e-h	3.3 jk	8.2 f	19.3 d-e	40.5 a-c
E	15.6 b-e	12.0 e-g	3.5 jk	9.8 f	21.1 d	40.9 a-c
SB	8.9 g-i	9.7 f-i	7.2 h-j	9.2 f	15.2 e	38.7 c

[A] *Data followed by the same letter are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

Acetone-extractable elemental S

There was no significant S source × harvest time interaction on oxidation of elemental S with S oxidation increasing significantly with time in all treatments (Table 3.29).

At AT, oxidation was highest with PVA, LS, E, SCU and US. At M, lowest oxidation had occurred in the SB treatment with oxidation intermediate with HF and SW (Table 3.29).

The SB treatment had a significantly lower oxidation rate than the PVA treatment in the period from transplanting to AT and showed a significant increase in oxidation rate from the initial to the final period (Table 3.29). There were no other significant differences with time or between treatments.

Table 3.29 Total oxidation and oxidation rate of elemental S as affected by source of S at different growth stages under non-flooded conditions.

Source	Oxidation of elemental S			Oxidation rate		
	(% applied)			(% day^{-1})		
of S	AT	MT	M	Trans. - AT	AT - MT	MT - M
PVA	40.8 hi[A]	62.4 d	95.6 a	0.69 a-c	0.72 a-c	0.60 a-d
LS	39.3 ij	62.2 d	95.5 a	0.66 a-d	0.76 a	0.61 a-d
HF	28.0 lm	46.2 gh	85.5 b	0.47 b-d	0.61 a-d	0.71 a-c
SW	29.5 k-m	48.3 fg	87.0 b	0.50 a-d	0.62 a-d	0.70 a-c
US	33.6 j-l	52.4 ef	94.5 a	0.57 a-d	0.63 a-d	0.77 a
SCU	35.0 i-k	52.9 ef	93.5 a	0.59 a-d	0.60 a-d	0.74 ab
E	36.9 ij	56.3 e	95.6 a	0.62 a-d	0.65 a-d	0.71 a-c
SB	24.1 m	37.5 ij	79.1 c	0.41 d	0.45 cd	0.76 a

[A] Data followed by the same letter are not significantly different ($P > 0.05$) (Duncan's multiple range test).

3.6 RESULTS - SECOND NON-FLOODED CROP

3.6.1 Response to gypsum

a. Tiller and panicle number and yield

As for crop 1, number of tillers (Appendix 3.21) and yield of each component, except root (Table 3.30) increased, and the percentage of empty grain (Appendix 3.21) decreased, with increasing S-application rate with a significant difference between C and G_3. S-application rates had no significant effect on number of panicles, number of grains per panicle, dry weight of grains per panicle, harvest index and dry weight of 100 grains (Appendix 3.21).

Table 3.30 The residual effect of S-application rate on dry matter yield of plant components under non-flooded conditions.

	Dry matter yield (g pot^{-1})			
Treatment	grain	stem + leaf	root	total
C	4.0 b[A]	14.6 b	2.4 a	21.0 b
G_1	4.7 b	15.9 ab	2.4 a	23.0 b
G_2	5.5 ab	17.5 ab	2.5 a	25.5 ab
G_3	7.6 a	19.7 a	2.8 a	30.1 a

[A] Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).

b. S content, percentage of S derived from the fertiliser and recovery of fertiliser S

As for the yield parameters, plant S content increased with S-application rate with the difference between C and G_3 being significant in all plant components except root (Table 3.31).

Table 3.31 The residual effect of S-application rate on S content of plant under non-flooded conditions.

Treatment	S content (mg pot^{-1}) grain	stem + leaf	root	total
C	3.3 b[A]	8.4 b	2.6 a	14.4 b
G_1	4.0 b	8.9 b	2.8 a	15.7 b
G_2	4.5 ab	10.7 ab	2.9 a	18.1 ab
G_3	6.2 a	12.5 a	3.3 a	22.0 a

[A] *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

Percentage of S derived from the fertiliser in each plant part increased with increasing S-application rate with a significant difference between G_1 and G_3 (Figure 3.9).

Among the fertilised treatments, the lowest percentage of fertiliser-S recovered in the whole plant was recorded in the G_3 treatment. No differences were recorded among the treatments in the other plant components (Figure 3.10).

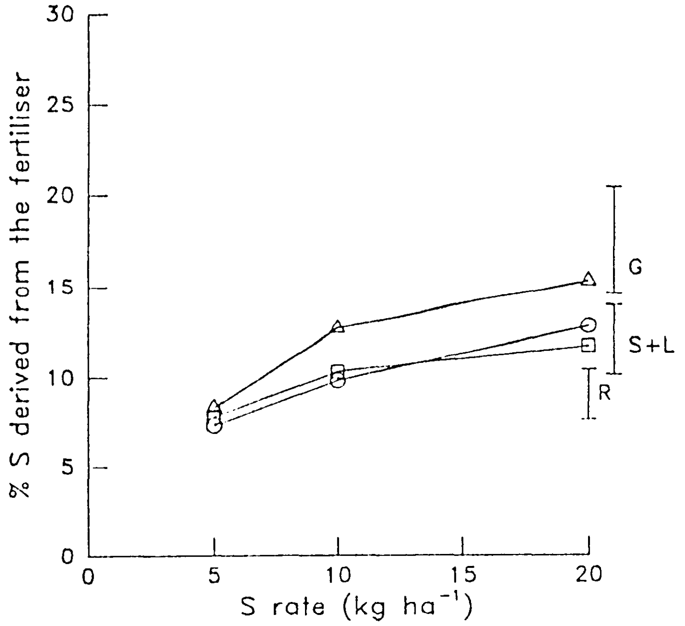


Figure 3.9 The residual effect of S-application rate on percentage of S derived from fertiliser by different plant parts under non-flooded conditions. Vertical bars indicate LSD (P = 0.05).

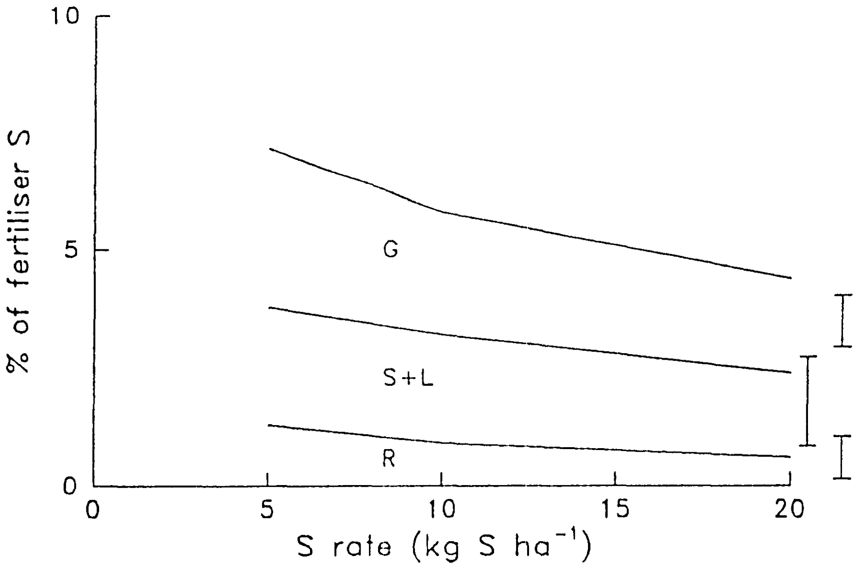


Figure 3.10 The residual effect of S-application rate on percentage of the fertiliser S incorporated into the plant components under non-flooded conditions. Vertical bars indicate LSD (P = 0.05).

c. Soil S pools

There were no significant differences in extractable S and organic S recorded among the treatments. The percentage of fertiliser S that was recovered in these fractions did not differ significantly among the treatments (Appendix 3.22).

3.6.2 Comparison of S Sources

a. Tiller and panicle number and yield

The highest number of tillers was recorded in the SB treatment, although this was not significantly different from the other treatments, except G and C treatments. There was no significant difference in number of panicles recorded among the fertilised treatments. The lowest number of panicles was recorded in the C, although this was only significantly lower than SB, HF and SCU (Appendix 3.23).

The lowest yield was recorded in the C but this was not significantly different from the G treatment for each parameter (Table 3.32). By contrast, the highest relative plant yield was recorded in the SB treatment, although this did not differ significantly from that of HF. In general, there were no significant differences in relative plant yield recorded among the TSP-S treatments and also among the N-S treatments.

Table 3.32 The residual effect of different S sources on relative dry matter yield of plant components under non-flooded conditions.

Source of S	Relative yield (%) grain	stem + leaf	root	total
C	75.6 c[A]	83.2 d	94.7 b	82.5 d
G	100.0 bc	100.0 cd	100.0 b	100.0 cd
PVA	117.5 a-c	103.3 cd	106.2 b	106.1 c
LS	112.6 a-c	112.2 bc	108.3 b	111.5 c
HF	141.7 ab	131.2 ab	126.3 ab	131.9 ab
SW	128.1 ab	114.5 a-c	116.6 ab	117.4 bc
US	115.2 a-c	114.7 a-c	114.1 b	114.4 bc
SCU	127.6 ab	115.2 a-c	115.6 b	116.9 bc
E	121.1 a-c	105.6 cd	103.7 b	108.9 c
SB	152.5 a	137.2 a	147.8 a	141.7 a

[A] Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).

b. S Content

Highest relative S content of the each plant component was recorded in the SB treatment, although the value was not significantly higher than with HF and SW (Table 3.33). Among the fertilised treatments, the G produced the lowest relative S content of the whole plant and this was not significantly different from that of C. Among the TSP-S treatments, HF produced the highest S content of the whole plant although this was not significantly different from LS and SW. No significant differences in the S content of the plant components were recorded among the N-S treatments (Table 3.33).

Table 3.33 The residual effect of S source on relative S content of plant components under non-flooded conditions.

Source of S	Relative S content (%) grain	stem + leaf	root	total
C	75.4 c[A]	79.1 d	95.4 b	79.8 e
G	100.0 bc	100.0 cd	100.0 b	100.0 de
PVA	114.7 a-c	103.2 cd	96.7 b	103.5 c-e
LS	130.3 ab	109.6 b-d	92.2 b	110.2 b-e
HF	157.7 a	141.5 ab	115.5 ab	138.6 ab
SW	151.2 ab	128.2 a-c	123.1 ab	131.6 a-c
US	122.2 a-c	118.7 a-c	105.9 b	116.2 b-d
SCU	139.8 ab	123.4 a-c	103.9 b	122.6 a-d
E	136.4 ab	107.5 b-d	104.5 b	112.4 b-d
SB	168.5 a	143.9 a	150.7 a	149.0 a

[A] Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).

c. Percentage of plant S derived from the fertiliser

The SB treatment resulted in the highest percentage of S derived from the fertiliser in each plant component. The lowest level was recorded in the G treatment, although this did not differ significantly from that with PVA, LS, SW, US, SCU and E. In the grain component, there was no significant difference in percentage of S derived from the fertiliser recorded among the TSP-S and N-S treatments (Table 3.34).

Table 3.34 The residual effect of different S sources on percentage of plant S derived from the fertiliser under non-flooded conditions.

Source of S	Percentage of S derived from the fertiliser (%) grain	stem + leaf	root
G	12.7 c[A]	9.8 c	10.3 c
PVA	14.3 bc	11.0 c	10.6 c
LS	14.7 bc	11.9 c	11.1 bc
HF	19.5 b	17.6 ab	16.3 ab
SW	17.1 bc	13.7 bc	14.6 bc
US	16.1 bc	12.5 c	14.1 bc
SCU	15.7 bc	13.5 bc	13.6 bc
E	14.5 bc	12.3 c	11.4 bc
SB	25.5 a	21.6 a	20.5 a

[A] Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).

d. Fertiliser-S uptake

Lowest total fertiliser-S uptake was recorded in the G treatment although this was not significantly different from PVA, LS, US and E. The highest recovery was recorded in the SB treatment. These differences were generally reflected in the other plant components (Table 3.35).

Table 3.35 The residual effect of different S sources on total fertiliser-S uptake by plants under non-flooded conditions.

Source of S	Total fertiliser-S uptake (% applied) grain	stem + leaf	root	total
G	1.7 c[A]	3.2 c	0.9 b	5.8 e
PVA	2.2 bc	3.7 c	0.9 b	6.7 de
LS	2.5 bc	4.3 c	0.9 b	7.6 c-e
HF	4.0 b	8.1 ab	1.6 b	13.6 b
SW	3.4 bc	5.6 bc	1.5 b	10.5 c
US	2.6 bc	4.8 c	1.2 b	8.7 c-e
SCU	2.9 bc	5.4 bc	1.2 b	9.5 cd
E	2.5 bc	4.3 c	1.0 b	7.8 c-e
SB	5.9 a	10.1 a	2.6 a	18.6 a

[A] *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

e. Soil S pools

At the end of the second crop the highest extractable S level was recorded in the SB treatment, although this was not significantly different from that of HF (Appendix 3.24). The highest recovery of fertiliser S that was incorporated in to the extractable S pool was recorded in the SB treatment and the lowest recovery was recorded in the G (Table 3.36).

There were no significant differences in organic S (Appendix 3.24) and recovery of fertiliser S (Table 3.36) in this pool recorded among the fertilised treatments. No elemental S was detected in the soil extracts after the second crop.

Table 3.36 The residual effect of different sources of S on the percentage of fertiliser S incorporated into the extractable S (ES) and organic S (OS) under non-flooded conditions.

Source of S	Recovery of fertiliser S (%) ES	OS
G	1.4 b[A]	36.8 a
PVA	1.9 ab	38.7 a
LS	1.9 ab	40.2 a
HF	2.6 ab	41.7 a
SW	2.7 ab	42.4 a
US	1.9 ab	41.2 a
SCU	2.0 ab	38.1 a
E	2.2 ab	38.6 a
SB	3.4 a	43.6 a

[A] *Data followed by the same letter in the same column are not significantly different ($P > 0.05$) (Duncan's multiple range test).*

3.7 DISCUSSION

The response to S in yield and S content recorded in the first crop in both flooded and non-flooded experiments can be related to the low inherent sulfur content of the soil. Chemical analyses of the soil before the experiment was undertaken showed that the organic S content was 103 ppm and the extractable S was 7.4 ppm. A strong S deficiency in the rice field of Pakistan was reported by Salim and Rahmatullah (1987) where the available S of the soil was reported to be less than 10 ppm. Visual observation during the course of the experiment indicated that in the C treatment the plants were stunted and the young leaves were slightly yellow. Tillering was also reduced, all symptoms of S deficiency (Yoshida and Chaudry, 1979).

Although the grain yield under non-flooded conditions (Table 3.21) was lower than that under flooded conditions (Table 3.5) when S was applied, the stem + leaf yield under non-flooded (Table 3.21) was higher than under flooded conditions (Table 3.5). In granitic soil, Samosir (1981) reported that the application of S (80 kg S ha^{-1}) resulted in a higher grain yield (45.4 g pot^{-1}) when rice was grown under flooded compared to that under non-flooded (22.5 g pot^{-1}) conditions. A similar result was reported by Ismunadji (1985) who found a higher straw yield under non-flooded than under flooded conditions. This was most likely because of better availability of some nutrients and no water stress (Nearpass and Clark, 1960; Patrick and Mikkelsen, 1971; Sanchez, 1976; Ponamperuma, 1985; Amer *et al.*, 1991).

When no S was applied, the plant growth under flooded conditions (Table 3.5) was poorer than that under non-flooded conditions (Table 3.21). This is most likely due to lower mineralization of organic sulfur under flooded than under non-flooded conditions (Blair and Lefroy, 1987) and to the reduction of sulfate and other inorganic S compounds to sulfide (Freney and Boonjawat, 1983). Sachdev and Chhabra (1974) reported that 37.8 % of S which was applied as inorganic sulfate was transformed into organic forms under flooded conditions.

The previous S application up to 10 kg S ha^{-1} had no significant effect on grain yield or total dry-matter yield in the second crop both under flooded and non-flooded conditions (Tables 3.14 and 3.30 respectively), although the G_3 treatment resulted in a higher grain yield than did C. The lack of strong response to S in the second crop, which was grown on residual S from the first crop, is largely due to the high S uptake by the plant in the first crop. As shown in Figure 3.11, over 50 % of the S applied in the G_2 treatment in the first crop was recovered by that crop leaving little S for the second crop. A poor residual effect of gypsum has also been reported by Chien *et al.*, 1988.

The use of the reverse-dilution technique in this experiment allowed the calculation of fertiliser release rate from different S sources which had not been attempted previously. The results of this study show that the S release rate at different growth stages was affected by S source and that the pattern of release was generally similar in flooded and non-flooded conditions. The data clearly show that oxidation of elemental S took place rapidly under flooded conditions. Figure 3.11 shows that a higher amount of elemental S remained in the soil under flooded than under non-flooded conditions after the first crop. Many studies have demonstrated that the oxidation of elemental S is restricted when the soil water content was above the field capacity (Janzen and Bettany, 1987b, Nevel and Wainwright, 1987). At harvesting it was observed that the rice roots occupied a large part of the soil volume under both flooded and non-flooded conditions. The oxidation of elemental S under flooded conditions occurs within the oxygenated rhizosphere of the rice root (Freney and Boonjawat, 1983). The diffusion of oxygen from the rice root varies between the rice varieties (Blair, 1984) and this can affect S oxidation rates.

In the first crop, both non-flooded (Table 3.21) and flooded (Table 3.5) yields and S uptake, were influenced by S source. The highest total dry matter yield and S content of the whole plant at each harvest, as well as S content (Tables 3.22 and 3.6) of the whole plant at each harvest, as well as grain yield and S content of grains at M, were recorded in the gypsum treatment. The whole plant yield of this treatment was similar to that of PVA and LS treatments and the S content was similar to that of PVA at MT and M. The differences in the growth and yield of the crop were most likely because of different amounts of S provided by the different S sources. The percentage of S derived from the fertiliser and the recovery of fertiliser-S data show that in the first crop a higher amount of S was derived from the gypsum than from the elemental S treatments particularly at AT stage. Under flooded conditions, 41.7 % of S in plant at AT was derived from gypsum compared to 24.3 % from elemental S (Table 3.10). Under non-flooded conditions 42.2 % of S in plant was derived from the gypsum compared to 25.1 % from elemental S (Table 3.26).

The difference in grain yield among the treatments was strongly influenced by the number of tillers produced in the early growth stages. As in the gypsum treatment, a significantly higher number of tillers was produced at AT compared to all other treatments; this was related to the percentage of S derived from the fertiliser. In contrast, the SB treatment resulted in the lowest number of tillers both under non-flooded and flooded conditions, although these results were similar to those of SCU under flooded and to C under non-flooded and flooded conditions. This is most likely because of a lower oxidation of elemental S from this product. Blair *et al.* (1979) and Fox and Blair (1986) stated that S deficiency causes a reduction in number of tillers which leads to a reduction in grain yields.

In the present study, fertiliser was applied by mixing thoroughly with the soil. Total elemental S which was oxidized after the first crop was 78.3 % under flooded (Table 3.13) and 95.6 % under non-flooded conditions (Table 3.29). Blair *et al.*, 1979 reported that surface application of elemental S was as effective as gypsum. Chien *et al.* (1987, 1988) found that surface application of elemental S was as effective as incorporation and these were more effective than deep placement.

At each harvest in the first crop and under flooded conditions, SCU resulted in significantly lower total dry matter and grain yields than did other treatments except SB (Table 3.8). This result supports the finding of Samosir and Blair (1983) who reported that S-coated urea was not an effective fertiliser in supplying S for flooded rice. A similar result was reported by Janzen and Bettany (1986) who found that S-coated urea was an ineffective S source when rapeseed was used as a test plant. The small response from SCU is most likely due to the sealant (petroleum wax) used in the manufacturing of this product which is used to control the release of nitrogen. This process inhibits the direct contact between the fertiliser material and soil or water. The addition of a small amount of microbiocide in this coating reduces microbial activity (Beaton and Fox, 1971). A second reason is that the application of the S coat as a molten spray results in a substantial reduction in the specific surface area of the elemental S which decreases the oxidation rate. Although S-coated urea has been reported as an ineffective source of S, this material has been promoted to control the release of nitrogen fertiliser under rice-field conditions (Wells and Shockley, 1975 and Hamdallah *et al.*, 1988) and greater grain yields have been reported due to the more effective nitrogen application (Sanchez *et al.*, 1973).

In general, under non-flooded and flooded conditions and at each harvest time, SB resulted in significantly lower total dry matter and grain yields than all other treatments. This is probably due to the low dispersion of this material in the soil. This result supports the finding of Mamaril and Gonzalez (1987) who found that in the first crop, S bentonite was not an effective fertiliser for rice; however, a significant residual effect from this product was observed. Noellemeyer *et al.* (1981) also reported that prilled elemental S and Agri-sul (elemental S combined with bentonite) produced little response in rapeseed dry matter yields and suggested that the lower oxidation from these materials resulted from the slow disintegration of elemental S from the granules and lack of distribution of elemental S in the soil (Boswell *et al.*, 1988b), caused difficulties for microorganisms in oxidizing elemental S. Gupta and MacLeod (1984) also reported that Agri-sul was ineffective in increasing the S concentration of forages and cereals. Extraction of the soil with acetone at harvest showed significantly higher unoxidized elemental S content in the soil from the SB treatment than from all other treatments, except under flooded conditions where the SB and SCU treatments did not differ (Figure 3.11).

In general, among the elemental S treatments, TSP-S (particularly PVA and LS) was more effective than other sources. This is probably due to the higher dispersion of elemental S in the soil. The use of water-soluble adhesive to bind elemental S to the TSP granules is believed to support these findings. In addition the coating process and adhesive materials used in making the coated fertilisers are believed to affect the oxidation of elemental S. The oxidation of elemental S may also have been stimulated by the presence of TSP. Bloomfield (1967) concluded that the oxidation of elemental S was enhanced when this material was combined with diammonium phosphate or TSP. In the present study, it was observed that the HF resulted in a poorer S response than PVA and LS. This is most likely related to the different techniques employed in the production of the products, resulting in a different coat strengths.

In general, greater oxidation rate of elemental S was recorded under non-flooded than under flooded conditions. This finding supports the results of previous investigators (Janzen and Bettany, 1987b; Charoenchamratcheep *et al.*, 1987). Under flooded conditions elemental S should be applied on the surface of the flooded soil in order to achieve the maximum oxidation rate (Blair *et al.*, 1979 and Chien *et al.*, 1987). Under flooded rice, Chien *et al.* (1988) also found that incorporation of elemental S as well as gypsum was as effective in increasing grain and straw yield under flooded conditions.

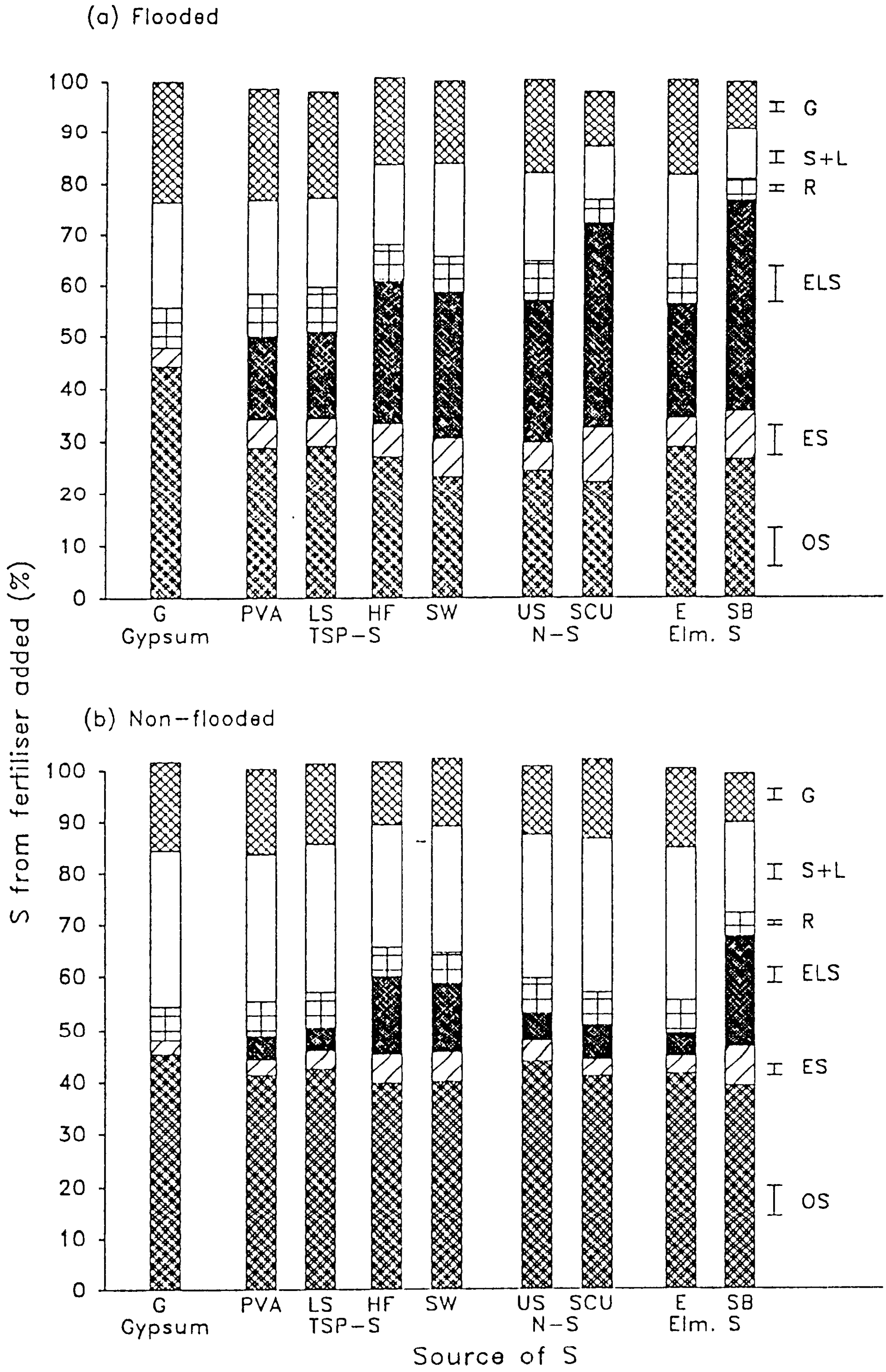


Figure 3.11 The percentage of fertiliser S incorporated into the grain (G), stem+leaf (S+L), root (R), unoxidized elemental S (ELS), extractable S (ES) and organic S (OS) after the first crop under flooded and non-flooded conditions. Vertical bars indicate LSD (P = 0.05).

In many rice-growing areas, cultivation of rice as a second crop is a common practice. Drying the soil before harvesting as well as soil preparation between crops could increase the oxidation of elemental S remaining in the soil. This will supply available S for the second crop. In this study the effectiveness of residual S fertilisers from the first crop was investigated.

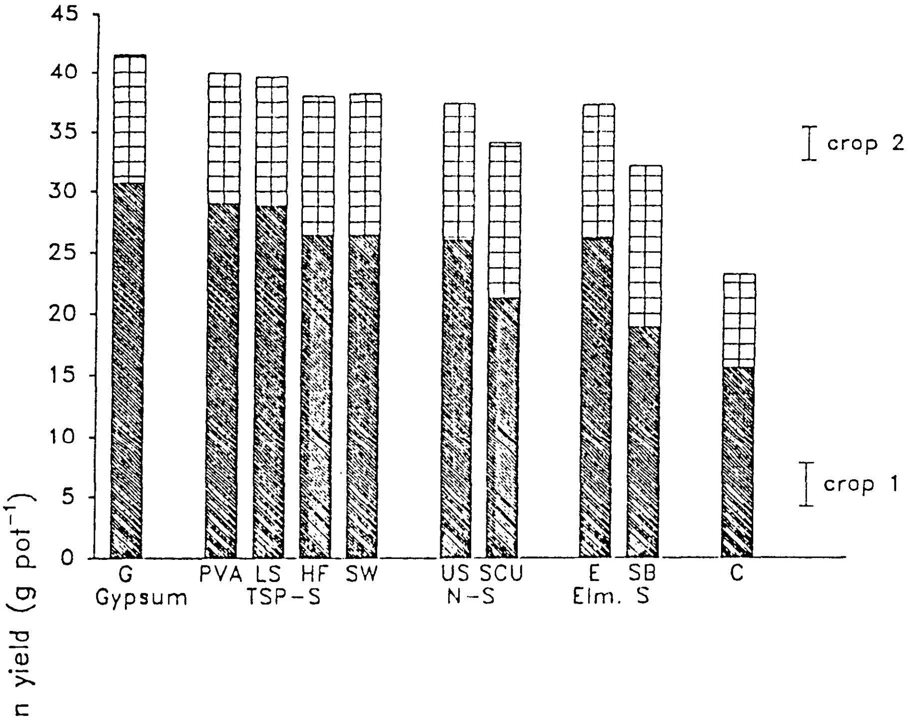
Figure 3.12 summarizes the initial and residual effects of different S sources on grain yield under flooded and non-flooded conditions. In the second crop, the effect of different S sources on the growth and yield of plant was inversely related to the first crop. The fertilised treatment which resulted in the highest grain yield in the first crop produced the lowest grain yield in the second crop. This was most likely because of the greater S uptake by the plant in the first crop (Figure 3.11). In the second crop the SB treatment resulted in the highest grain yield (Figure 3.12) and fertiliser-S recovery in the whole plant (Fig 3.13), although this was similar to that of SCU under flooded conditions. Among the fertilised treatments in the second crop, G resulted in the lowest grain yield (Figure 3.12) as well as the recovery of fertiliser S in the whole plant (Figure 3.13). The lower yield from the TSP-S treatments, as well as G, compared to the SB treatment in the second crop is most likely due to the higher oxidation rate of elemental S from the TSP-S products which leads to the higher S uptake in the first crop (Figure 3.11).

The soil data after the second crop showed a higher recovery of fertiliser S in the organic fraction than in the extractable S fraction (Figure 3.13), suggesting that the mineralization of organic S was very low during crop 2. As suggested by Freney *et al.*, (1971), only a small proportion of organic S pool (3 - 6 %) was involved in mineralization and immobilization. Till and May (1971) and Sachdev and Chhabra (1974) have also reported inorganic sulfate immobilization when this material was incorporated into the soil. Under non-flooded conditions, there was no elemental S detected after crop 2 and only a small amount detected under flooded conditions. This suggests that the oxidation of applied elemental S was complete after the second crop.

Using the S-release model developed by McCaskill and Blair (1989), a higher oxidation rate was predicted in the early stages of plant growth both under flooded and non-flooded conditions compared to observed S oxidation, although significant correlation was observed between predicted S release and oxidation of elemental S (Figure 3.14). This overprediction could have been due to the slow proliferation of S-oxidizing microorganisms in the early stage of the experiment.

In conclusion, PVA and LS were generally as effective as gypsum for flooded and non-flooded rice and therefore, these products are recommended as effective S sources, although further field trials are required to confirm these findings. The higher oxidation rate from PVA and LS compared to SB resulted in poor residual value for the second crop. Therefore PVA and LS needs to be applied at the beginning of each crop.

(a) Flooded



(b) Non-flooded

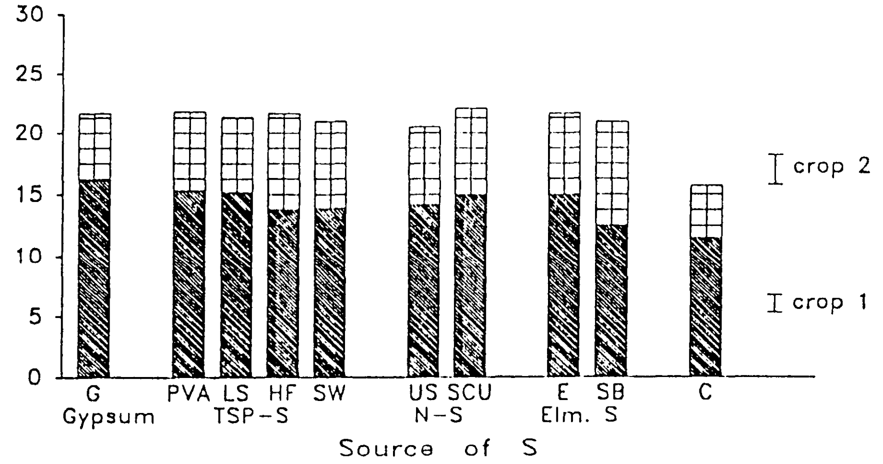
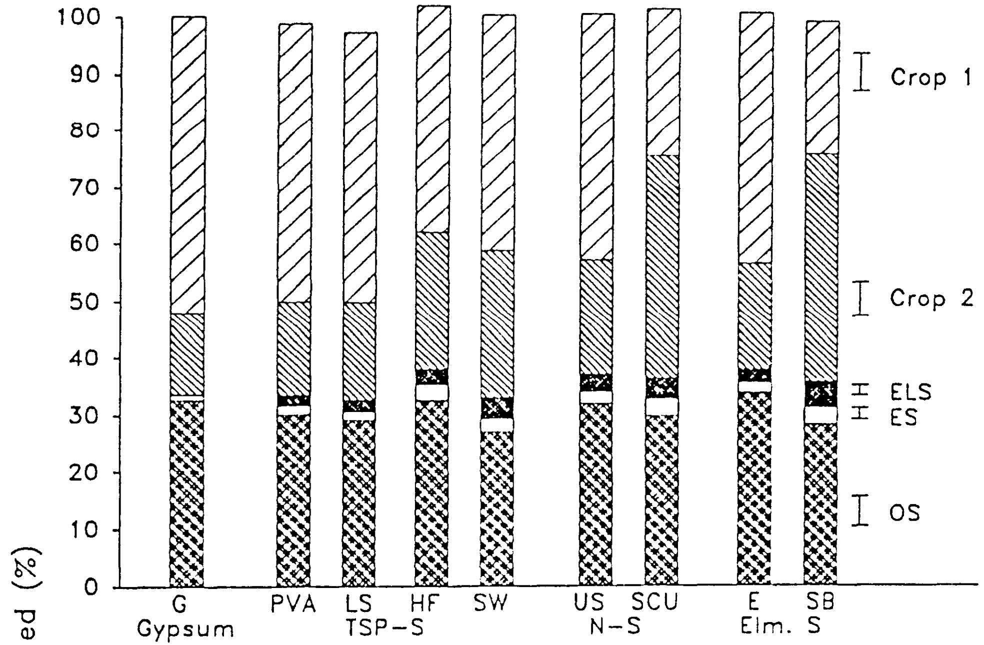


Figure 3.12 The initial and residual effects of different S sources on grain yield at the same rate of S application under flooded and non-flooded conditions. Vertical bars indicate LSD (P = 0.05).

(a) Flooded



(b) Non-flooded

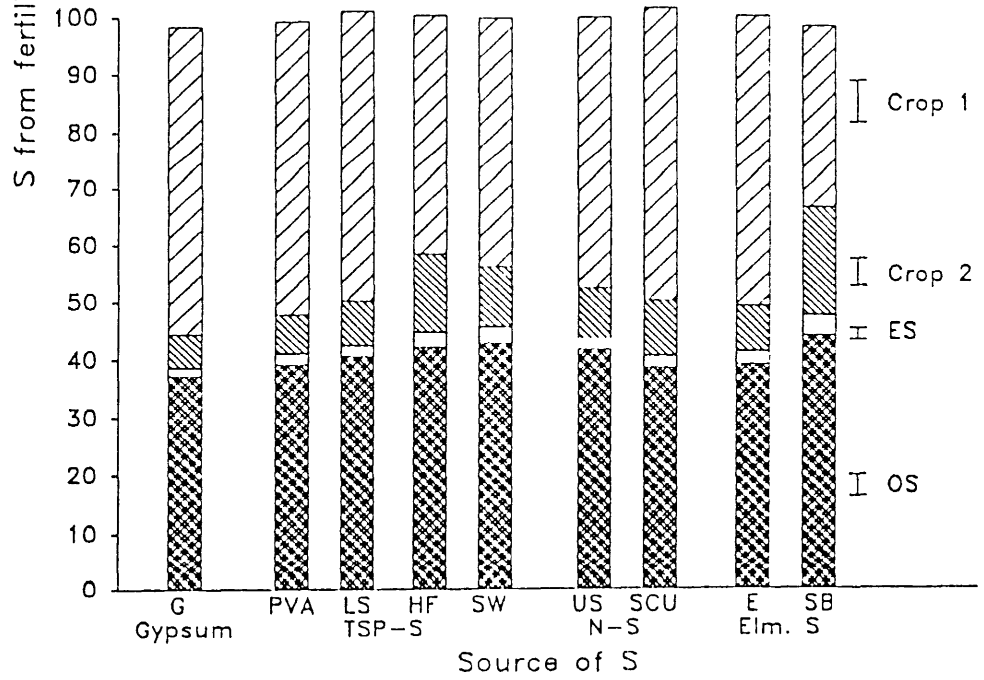
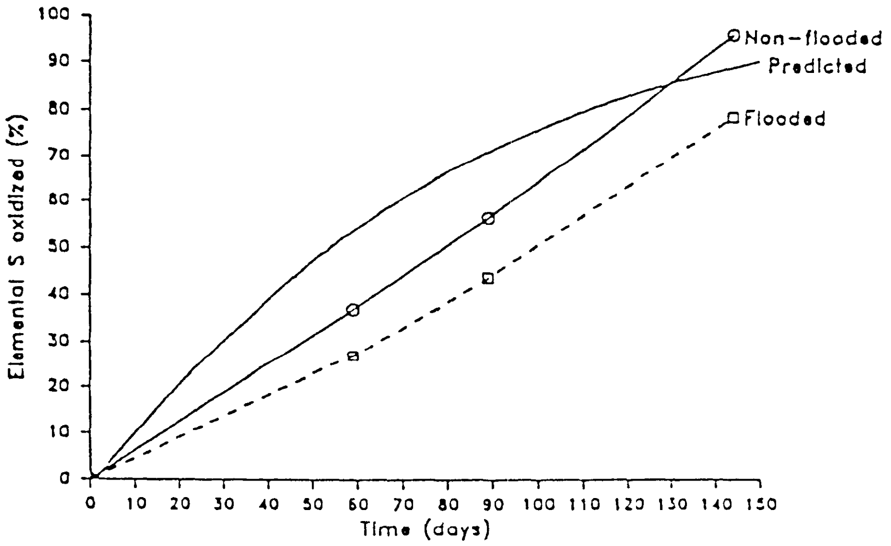


Figure 3.13 Summary diagram showing the fate of fertiliser S applied into the two successive crops under flooded and non-flooded conditions. Vertical bars indicate LSD (P = 0.05).

a)



b)

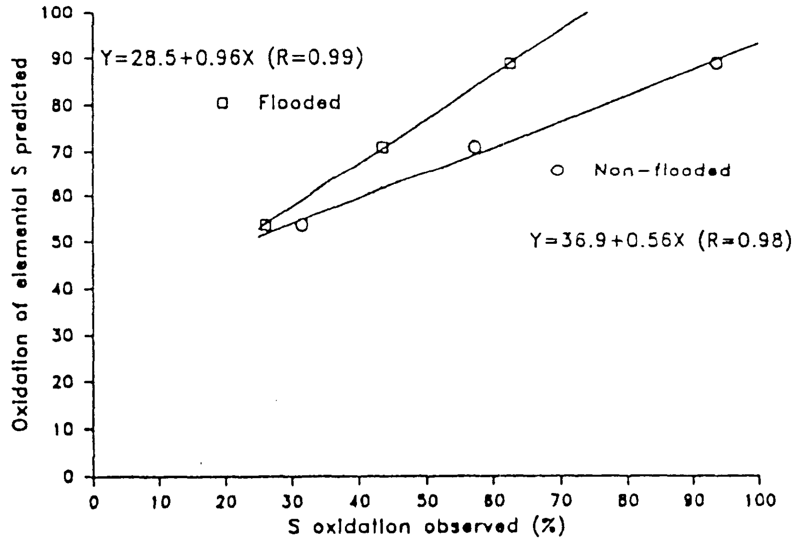


Figure 3.14 a) Prediction of S oxidation of elemental S and b) correlation between predicted S oxidation and observed S oxidation under flooded and non-flooded conditions.