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Review article

Sulphur -a general overview and interaction with nitrogen

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Abstract

To minimize the gap between the demand and supply of cereals, oilseeds and pulses, intensive efforts are being made to increase their production. As ever-increasing population and urbanization cannot allow increase in the land area under the cultivation of cereals, oilseeds and pulses anymore due to the pressure on land, hence, yield per unit area needs to be improved further. To achieve this objective, agricultural scientists have laid more emphasis on improving production of oilseeds and pulses through proper nutrition of the crops by evolving high yielding varieties and adopting improved agronomic practices as well as plant protection measures, etc. The most important constraints to crop growth are those caused by the shortage of plant nutrients. Sulphur (S) requirement of plants has become increasingly importance in India as well as world agriculture. However, to achieve high yields and rates of S fertilizer should be recommended on the basis of available soil S and crop requirement.

Keywords: Nitrogen, Sulphur, Fertilizer, Quality, Yield

Introduction

With the improvement of crop productivity through the adoption of high-yielding varieties and multiple cropping systems, fertilizer use has become more and more important to increase crops yield and quality. S is an essential plant nutrient for crop production. For oil crop producers, S fertilizer is especially important because oil crops require more S than cereal grains. For example, the amount of S required to produce one ton of seed is about 3-4 kg S for cereals (range 1-6); 8 kg S for legume crops (range 5-13); and 12 kg S for oil crops (range 5-20). In general, oil crops require about the same amount of S as, or more than, phosphorus for high yield and product quality. In intensive crop rotations including oil crops, S uptake can be very high, especially when the crop residue is removed from the field along with the product. This leads to considerable S depletion in soil if the corresponding amount of S is not applied through fertilizer. S is increasingly being recognized as the fourth major plant nutrient after nitrogen, phosphorus and potassium. The importance of S in agriculture is being increasingly emphasized and its role in crop production is well recognized (Jamal *et al.,* 2005, 2006a; 2006b; 2006c; 2009; 2010; Scherer, 2009). S is best known for its role in the formation of amino acids methionine (21% S) and cysteine (27% S); synthesis of proteins and chlorophyll; oil content of the seeds and nutritive quality of forages (Tandon, 1986; Jamal *et al.,* 2005, 2006a; 2009). Although S is one of the essential nutrients for plant growth with crop requirement similar to phosphorus, this element received little attention for many years, because fertilizers and atmospheric inputs supplied the soil with adequate amounts of S. Now, areas of S deficiency are becoming widespread throughout the world due to the use of high-analysis low S fertilizers, low S returns with farmyard manure, high yielding varieties and intensive agriculture, declining use of S containing fungicides and reduced atmospheric input caused by stricter emission regulation. An insufficient S supply can affect yield and quality of the crops, caused by the S requirement for protein and enzyme synthesis as well it is a constituent of the amino acids, methionine and cysteine. To overcome the problems associated with S deficiency a number of S-containing fertilizers as well as other S containing by-products from industrial processes are available. The information on impact of S-fertilization and S in general has been reviewed and presented under the following heads: The function of S, Soil organic S, Soil inorganic S, S deficiency in soil, Sulphur and nitrogen interaction in soil, Sulphur and nitrogen interaction in plant , Sulphur and nitrogen interaction in relation to yield and quality of crop, Sulphur and nitrogen interaction in relation to uptake and assimilation of sulphur and nitrogen, N:S ratio in relation to sulphur and nitrogen interaction.

The functions of S

The range of biological compounds that contain sulfur is vast. S is found in vitamins viz, biotin and thiamine; cofactors S-adenosyl-L-methionine, coenzyme A, molybdenum cofactor (MoCo), and lipoic acid; the chloroplast lipid sufloquinovosyl diacylglycerol; and many secondary compounds (Leustek, 2002, Leustek and Saito, 1999). It also serves important structural, regulatory and catalytic functions in the context of proteins, and as a major cellular redox buffer in the form of the tripeptide glutathione and certain proteins such as thioredoxin, glutaredoxin and protein disulfide isomerase. A feature of many sulfur-containing compounds is that the S moiety is often directly involved in the catalytic or chemical reactiveness of the compound. A superb example is the way in which cysteine residues in proteins sometimes form covalent disulfide bonds. Disulfides can, in turn, be reduced to the thiol form by glutathione or redox proteins like thioredoxin (Leustek and Saito, 1999; Saito, 2000). For some enzymes, disulfide bond formation serves to regulate activity. Many enzymes of carbon dioxide fixation are regulated in this way as a means to coordinate their activity with the light reactions of photosynthesis. The regulatory molecule in this case is thioredoxin, which reduces target enzymes using electrons from ferredoxin (Leustek and Saito, 1999; Saito, 2000; Scherer, 2001; Matsubayashi *et al.,* 2002).

Soil organic S

Up to 98% of the total soil S may be present as organic S compounds and is associated with a heterogeneous mixture of plant residues, animals and soil microorganisms (Bloem 1998). The profile of organic S concentration generally follows the pattern of organic matter concentration in soils with depth (Probert, 1980). Soil organic S is divided in two main groups: the first group contains S atom in the oxidized state and the other group contains S atom in the reduced state. According to results of Stevenson (1986) between 1 and 3% of the soil organic S can be accounted for the part of microbiological biomass, while more recent investigations suggest that the soil microbiological biomass S generally accounts for 1.5 -5% of total soil organic S (Banerjee *et al.,* 1993; Wu *et al.,* 1993). Proteins and amino acids are the major form of S in microbial cells (Banerjee and Chapman, 1996). Based on dry weight, the S concentration of most soil microorganisms is ranges between 1 and 10µg/g, the C:S ratio between 57:1 and 85:1 and the N:S ratio is about 10:1. However, there is evidence that the C:S ratio in the biomass is not fixed, but may vary quite rapidly, depending on the supply of S. When S becomes a limiting factor, either because of low S concentrations in the substrate or where plant uptake is competing, the C:S ratio of the biomass may reach values between 80 and 100 (Banerjee *et al.,* 1993). The microbiological biomass is relatively labile and thought to be the most active pool for S turnover in soil (Stevenson, 1986). Generally, the application of organic matter to soil increases the microbiological biomass including microbial S. Further microbial S seems to increase with temperature and to decrease at low soil moisture content (Gupta and Germida, 1989; Ghani *et al.,* 1990). In incubation studies of Wu *et al.,* (1993), 20% of the S in barley straw and about 30% of the S from leaves of oilseed rape incorporated into the soil were converted to microbial S after 5 days at 25^0C.

Soil inorganic S

Inorganic S is usually much less abundant in most of the agricultural soils than is organically bound S (Bohn *et al.,* 1986). Sulphate is the most common form of inorganic S and can be divided into SO_4^{2-} in soil, adsorbed SO_4^{2-} and mineral S (Barber, 1995). Sulphur may precipitate in form of SO_4^{2-} as calcium, magnesium or sodium sulphate. In tidal marshlands large amounts of sulphide metals like pyrite (FeS_2) accumulate. After draining these areas, the S compounds are oxidized to SO_4^{2-} accompanied by a decrease in pH. If adsorbed SO_4^{2-} in soil is not readily available to plants, any treatment causing a decrease in retention and a corresponding increase of SO_4^{2-} in soil solution should increase SO_4^{2-}availability to plants (Elkins and Ensminger, 1971). Mehlich (1964) found that the release of adsorbed SO_4^{2-} was in relation to the addition of successive increments of Ca $(OH)_2$, which is assumed to be the result of increased pH. Therefore, little SO_4^{2-} adsorption is to be expected in surface soils which are adequately limed (Evans, 1986) and consequently the joint application of limestone and gypsum results in an increased availability of SO_4^{2-} (Serrano *et al.,* 1999). The higher concentration of SO_4^{2-} in the soil solution of the uppermost soil layer (Eriksen, 1996) may also be caused by the application of S containing fertilizers and other S inputs. Further, it may be assumed that surface soil material adsorbs less SO_4^{2-} than does subsoil material, because organic matter and phosphate accumulations are thought to be major factors, which block SO_4^{2-} adsorption sites. Barton *et al.,* (1999) found that deeper profile layers showed less capacity for SO_4^{2-} -adsorption. Couto *et al.,* (1979) detected that the adsorption of SO_4^{2-} is increased with the depth in the soil profile. According to their results, this difference between the horizons is assumed to be caused by the higher organic matter content in the topsoil. Johnson and Todd (1983) found that SO_4^{2-} - adsorption is negatively correlated with the soil organic matter content as the adsorption sites of Fe and Al hydroxides can be blocked by anionic groups of organic matter. Further, organic anions in soils, which are derived from decomposition of organic materials, may affect SO_4^{2-} -adsorption by occupying adsorption sites (Martinez *et al.,* 1998) by their preferential adsorption based on the number of oxygen containing functional groups (Inskeep, 1989).

S deficiencies in soil

S deficiency in crops has only recently become widespread (Scherer, 2001). Previously, sufficient S to meet crop requirements was obtained from the frequent incidental additions of S to soils when N and P fertilizers, such as ammonium sulphate and single superphosphate, were applied. Industrial pollution as a result of coal combustion also contributed substantial amounts of S for plant needs by aerial deposition. Over the last two decades, however, there has been a fundamental shift in the S balance toward deficit in agricultural systems for several reasons. High analysis N and P fertilizers have gradually replaced traditional ones that contain S. In addition, yields of agricultural crops have increased markedly, and in some cases more than doubled, during the last two decades, resulting in increased removal of nutrients, including S from soils (Scherer, 2001). In intensive crop rotations including oil crops, S uptake can be very high, especially when the crop residue is removed from the field along with the product. This leads to considerable S depletion in soil if the corresponding amount of S is not applied through fertilizer. It is now well established that S deficiency is wide spread in Indian soils, and in all probability is on the increase. S deficiency which was noticed many years ago only in localized areas has engulfed much larger area in its fold (Takkar, 1987). In 1986, ninety districts had been identified to have S-deficiency problem of varying degree and intensity (Tandon, 1986). In 1991, the number of S-deficient districts increased to about 120 (Tandon, 1991). It has been reported that in India more than 41% of soil are deficient in S (Singh, 2001). When a soil is deficient in S and the deficiency is not rectified, then full potential of a crop variety can not be realized, regardless of top husbandry practices (Eppendorfer, 1971).

Sulphur and nitrogen interaction in soil

An intensive agriculture with use of improved cultivars and high analysis fertilization offers conditions of nutrients exhaustion resulting in nutrient imbalance in soils. Fazili *et al.,* (2008) reported that lack of S limits the efficiency of added N, therefore, S addition becomes necessary to achieve maximum efficiency of applied nitrogenous fertilizer. Kowalenko and Lowe (1975) noticed that a high N:S ratio (produced by addition of N) resulted in a decrease in mineralization of S in the soil sample during incubation. Janzen and Bettany (1984) indicated the optimum ratio of available N to available S to be 7:1. Ratios below 7 gave the reduced seed yields. A rapeseed and mustard crop under field conditions recovered 27-31% of added S without N, but 37-38% with 60 kg N ha^{-1} (Sachdev and Deb, 1990).

Sulphur and nitrogen interaction in plant

Because of central role of S and N in the synthesis of proteins, the supplies of these nutrients in plants are highly inter-related. Sulphur and nitrogen relationships were established in many studies (Zhao *et al.,* 1993; McGrath and Zhao 1996; Ahmad *et al.,* 1998; and Jamal *et al.,* 2005; 2006a; 2010) in terms of dry matter and yield in several crops. Barney and Bush (1985), while working on tobacco plant concluded that there was apparent accumulation of one nutrient when the other nutrient was limited and that accumulated nutrient was used in protein synthesis when the treatment were reversed. A shortage in the S supply to the crops lowers the utilization of the available soil nitrogen, thereby increasing nitrate leaching (Likkineni and Abrol, 1994). O'Connor and Vartha (1969) observed that large dose of gypsum reduced the yield of hay when N status in soil was unsatisfactory. Likewise, large dose of N created S deficiency (Eppendorfer, 1971). It has been established that for every 15 parts of N in protein there is 1 part of S which implies that the N:S ratio is fixed within a narrow range of 15:1. The N:S ratio in the whole plant in general is 20:1 (Cram, 1990). Clarkson *et al.,* (1989), while working on barley plants, demonstrated that at the whole plant level the apparent matching of supply to demand is accompanied by an apparent linkage of SO_4^{2-} to NO_3^- uptake. Sulfur and nitrogen both are required for the synthesis of protein, therefore, the ratio of total N to total S in plant tissue can reflect the ability of N and S in protein synthesis (Brunold and Suter, 1984). Thus, a change in the ratio of reduced-N to reduced-S (N_R/S_R), which is a reflection of the amount of S amino acids, suggests that protein metabolism has been significantly altered and has important implications for protein quality (Friedrich and Schrader, 1978).

Sulphur and nitrogen interaction in relation to yield and quality of crops

A strong interaction of S and N for seed yield was found in rapeseed and mustard (McGrath and Zhao, 1996; Ahmad et al, 1998; Ahmad et al, 1999; Ahmad and Abdin 2000; Fazli *et al.,* 2005; Fazili *et al.,* 2010a; 2010b), sunflower (Hocking *et al.,* 1987) linseed (Verma and Swarankar, 1986) Groundnut (Jamal *et al.,* 2006a; 2010) and Soybean (Jamal *et al.,* 2005; 2006b). Aulakh *et al.,* (1977) reported the maximum grain yield in mustard was obtained with 30 kg S ha^{-1} supplied as gypsum along with 120 kg N ha^{-1} as urea. Aulakh *et al.,*(1980), based on the results of three years of field experiments on mustard, reported that maximum yields of oil were obtained when both N (75 kg ha^{-1}) and S (60 kg ha^{-1}) rates were high, which indicate significant S and N interaction. The combined application of S and N had the largest effect on the concentration and uptake of S and N and on protein and oil content of grains, and their yield. A field study involving S and N interaction on the yield of turnip rape (*Brassica campestris* L.) was conducted by Janzen and Bettany (1984), and it was demonstrated that seed production is very sensitive to S deficiency. The maximum yield responses of rapeseed to S and N were observed only when the availability of S and N was in approximate balance. Application of nitrogen alone suppressed the seed yields, whereas S alone produced no seed yield response. McGrath and Zhao (1996) observed an increase of 42-267% in seed yield of *Brassica napus* with the application of 40 kg S ha^{-1} with 180 and 230 kg N ha^{-1}. Seed yield was found to decrease, when N was applied at the rate of 180-230 kg ha^{-1} without S. In field trials on a soil testing 5.6 ppm available S, 2.5% increase in mustard oil yield due to S and N application could be attributed to their synergistic effect (Sachdev and Deb, 1990). Shinde *et al.,* (1980) noted the significant S and N interaction in winter wheat. The crop did not respond to S application when N was deficient of optimum, and S applied with excess N increased straw but not grain yield. In wheat crop, the yield increased linearly in the S and N interaction study (Reneau *et al.,* 1986) with increased N application. It was further suggested that S concentration of 0.2% and a N/S ratio of 18 in the flag leaf is sufficient for obtaining higher yields, while Mahler and Maples (1987) noticed that a minimum S concentration and N:S ratio of wheat tissue for maximum yield were 1050 and 16.5 ppm, respectively. Hocking *et al.,* (1987) reported a decrease of 30% in cysteine and methionine concentration in seeds of S deficient but N sufficient sunflower plants. Baily (1986) compared alfalfa, rape and barley in their sulphur response and requirements. Barley was the most responsive to applied S, although it had the lowest concentration of S (0.15 mg S g^{-1} dry herbage) and highest plant N:S ratio (16) at its highest yield. Dev and Kumar (1982) reported N:S ratio of 15.6, 3.1, 14.8 and 7.1 in grain for maximum response to sulphur in maize, mustard, groundnut and wheat, respectively. There is a very narrow range in the N:S ratio that ensures optimum yield and quality of the crop, and unbalanced fertilizer use adversely affects crop production. Sulphur deficiency causes profound changes in N metabolism with reduced protein synthesis and accumulation of soluble organic and inorganic nitrogenous compounds. Lack of S is accompanied by nitrate accumulation and proteolysis resulting in the formation of NH_4^+ and organic-N compound such as amide and amino acids (Charliers and Carpenter, 1956). Amounts of cysteine and methoinine were lower in S-deficient rice plants and occurrence of asparagine and arginine was thought to indicate abnormal S and N metabolism (Beaton, 1966). When NO_3 was limited in the nutrient solution or there was a lack of S in the tissue, repression of NR activity resulted. A positive role of sulphate in regulating nitrate reductase {an enzyme that perform the rate-limiting step of the nitrate assimilation pathway Beevers and Hageman, (1969)}, was reported by Pal *et al.,* (1976), and Friedrich and Schrader (1978). Smith (1975) observed the role of nitrogen in the regulation of sulphate assimilation at the ATP-sulphurylase step. The work of Jamal *et al.,* (2006b) and Ahmad *et al.,* (2007) showed that sulphur availability has a role in regulating nitrate reductase, in addition to its role in regulating ATP-sulphurylase. Moreover, nitrogen availability has a role in regulating ATP-sulphurylase as well as in regulating nitrate reductase. The synthesis of cysteine as a result of the incorporation of sulphide moiety into O-acetylserine appears to be the meeting point between N-and S-metabolism. Naturally occurring thiol compounds viz., cysteine and glutathione were shown to influence nitrate reductase activity in wheat and *Brassica* (Lakkineni and Abrol, 1992; Ahmad *et al.,* 1999). It has also been reported (Lopez-Jurado and Hunnway, 1985; Jamal *et al.,* 2010) that S is specifically involved in nitrogen fixation in legumes and S additions significantly increased N_2 fixation, nodule weight plant^{-1}, nodule weight per unit weight of root and N_2-fixation per unit weight nodule. Friedrich *et al.,* (1977) also observed severe reduction in nitrate reductase activity (NRA) in S-deprived maize seedlings.

Sulphur and nitrogen interaction in relation to uptake and assimilation of sulphur and nitrogen

Nitrogen increased utilization of fertilizer-S in plants (Dhankar *et al.,* 1995). Eppendorfer (1971) observed that large doses of N created a deficiency of S. Application of S in the absence of N decreased the N concentration in mustard plants, but when N was added, the effect was synergistic (Dev and Kumar, 1982). However, N content in Chinese cabbage was found to increase marginally with sulphur application (Hazra, 1988). Kastori and Jocic (1995) reported high positive correlation between S and N content on wheat. Application of S in the absence of N decreased nitrogen concentration in mustard plants, but when N was added, the effect was synergistic (Dev and Kumar, 1982). Similar results were reported for amide S and N in sunflower by Sharma and Dev (1980). Fazli *et al.,* (2008) found that uptake of N was considerably reduced under S deficiency in *E. sataiva*. Aulakh *et al.,* (1977, 1980) noticed the positive and significant interaction between applied S and N in plant tissues of brown sarson. The concentration of S and N in brown sarson was the highest with combined application of 75 kg N ha^{-1} and 60 kg S ha^{-1}. Janzen and Bettany (1984) reported that application of S and N increased their respective uptake by rapeseed. However, the effect of N rate on S uptake varied with S application rate. Sulphur application had no appreciable effect on N uptake at low N application rates but significantly enhanced dry matter produced. Singh *et al.,* (1980) reported S and N interaction non-significant in rapeseed and noticed a significant decrease in S content with addition of nitrogen. But nitrogen content increased significantly with both S and N application. Such interaction was also observed in other plants. A number of studies indicated synergistic effect of combined application of S and N on the uptake of these nutrients by maize, rapeseed (Dev *et al.,* 1979, Fazli *et al.,* 2008). Rabufetti and Kamprath (1977) reported that S and N fertilization increased the percent total S in corn grain. Sulphur addition, however, significantly increased the percent N in grain at S rate of 112 kg ha^{-1} or above, but slightly depressed the N content when applied @ 50 kg N ha^{-1}. Randall *et al.,* (1981) observed that S application increased the wheat grain S concentration more with low N treatment, but had only small effects on N concentration in grain. However, N application increased the grain S concentration at high but not at low S and increased grain N concentration in all S treatments.

N:S ratio in relation to sulphur and nitrogen interaction

A number of studies on S requirement of the crop in relation to N have been reported (Jamal *et al.,* 2005; 2006a, 2006b, 2009, 2010). There is a significant positive S x N interaction in relation to the oil content and yield. Adequate N: S ratio has been found to be 7.5:1 in grains, above which deficiency of S can be observed (Aulakh *et al.,* 1980). There is a strong relationship between S and N content in plants. The ratio of total N to total S and protein S determine the degree of availability of deficiency of S in protein. The N and S ratio is often preferred over concentration as a diagnostic criterion for S deficiency (Stewart and Whitefield, 1965). The total S content in plant tissues varies among plant species. In greenhouse trails with subterranean clover, N: S ratio was shown to be less variable with plant age and N supply than total S and total sulphate (Freney *et al.,* 1977). Experiments with rapeseed showed that the N:S ratio of rapeseed tops sampled at the rosette stage was very sensitive and changes due to change in sites, year and seed varieties and these changes were sometimes greater than differences between S deficient and S sufficient rapeseed (Maynard *et al.,* 1983). Dev and Saggar (1974) observed that S application lowered total N: total S ratios in soybean. It was also shown that at the S levels where consistency in total N and total S ratios was obtained, one part of S was required for every 14 and 16 parts of N in protein formation in different varieties of soybean. Dev *et al.,* (1981) reported that application of 20 kg S ha^{-1} lowered N: S ratio in mustard seeds from a range of 14:1-16:1 to 11:1- 12:1 and it was further reduced to 10:1, when S was applied at 40 kg ha^{-1}. Aulakh *et al.,* (1977) found N: S ratio of 15.5:1 in plant tissue of mustard to be critical, above which the inadequacy of S may cause drastic reduction in grain yield.

Conclusion

Sulphur is an important nutrient for plant growth and development. Sulphur interactions with nitrogen nutrients are directly related to the alteration of physiological and biochemical responses of crops, and thus required to be studied in depth. This would help to understand nutritional behaviour of sulphur in relation to nitrogen nutrients and provide guidelines for inventing balanced fertilizer recommendations in order to optimise yield and quality of crops.

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