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Sulphur: A boon in agriculture

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Abstract

Sulphur is an essential plant nutrient falling in category of secondary nutrient, which we don't need to apply plants but they are received by plant advertently along with application of fertilizer of secondary nutrients. It is the 4th major nutrient after NPK and rank 13 in abundance with estimated concentration of 0.06-0.10%. Since sulphur is an essential nutrient it is required to all crops but its requirement is highest to Brassica crop and least to cereals. Formation of glucosides and glucosinolates, pungency in onion, synthesis different amino acid (methionine, cysteine, cystine), being a component of ferredoxin are some of the vital function performed by sulphur. Although sulphur is taken up by plants as SO_4^{2-} but in order to metabolize different compound from sulphur it is reduced to different forms. S in soils occurs in many more or less distinct forms, organic and inorganic, which can be characterised by appropriate chemical and mineralogical techniques. In nature sulphur is found in several oxidation states which readily undergo transformation by chemical and microbiological processes. Here in this article, facts related to sulphur like its importance, distribution, forms in soil, sources and chemistry of transformation in soil, synthesis and function of sulphur compounds and deficiency symptoms along with its spread is going to be discussed.

Keywords: Sulphur, secondary nutrient, amino acid, oilseed crops

Introduction

Plant nutrition: Supply, absorption and utilisation of chemical compounds to the plants for growth and metabolism is popularly known as plant nutrition. These nutrients are converted to cellular materials or used for energetic purposes. Plant nutrition is not specifically related to photosynthesis but closely inter-related to metabolism.

Essential elements: Presence or absence of certain elements in plants does not signify that they are essential for the growth of the plants. Arnon and Stout (1939) ^[1] proposed the criteria of essentiality to justify whether an element is essential for plant growth or not. These criteria are as follows:

- Plant can't complete its life cycle in the absence or deficiency of the element.
- It should be irreplaceable i.e. the deficiency is specific to the element and can't be corrected by other elements.
- Must be directly involved in plant metabolism or may be required for the activation of an enzyme system.

Based on these criteria 17th nutrients recognised essential for the plant growth which can be divided into macronutrients and micronutrients depending upon their concentration in plant materials as given in following figure.

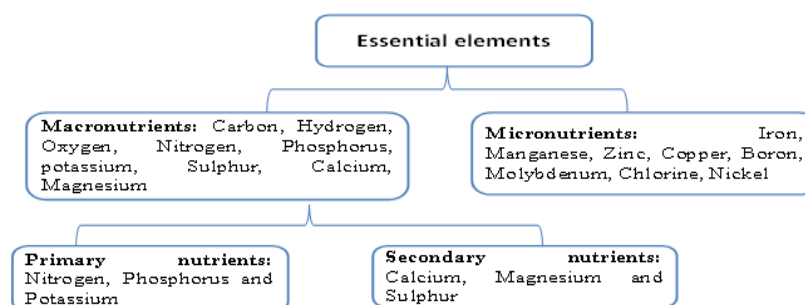


Fig 1: Classification of essential elements

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Peculiar features of Sulphur are

- An important secondary plant nutrient called as synthesizer element.
- Recognized as the fourth major plant nutrient after nitrogen, phosphorus and potassium and taken up by plants in the same rate to that of phosphorus (Meena *et al.*, 2019) ^[24].
- Ranks thirteenth in abundance (in Earth crust composition), with an estimated concentration of 0.06 - 0.10%.
- Sulphur requirement is higher in *Brassica* species (1.10-2.0%) followed by legumes (0.24-0.5%) and cereals have the least requirement (0.15-0.20%). Critical limits of sulphur in plants is 0.20%-0.25%, below which crops generally show sulphur deficiency and/or respond to applied fertilizer sulphur.
- Its importance in agriculture and role in crop production is well recognized (Jamal *et al.*, 2010) ^[15].

Importance of sulphur in Indian Agriculture: Kanwar and Mudahar (1986) ^[16] have enlisted the following four uses of sulphur in agriculture:

1. As soil amendment in sodic soils and for improving the quality of irrigation waters.
2. Plant nutrient: for correcting sulphur deficiency, increasing crop yield and improving the quality of crop produce. Used as pesticides including fungicides.
3. Chemical agent to acidulate phosphate rock and to manufacture phosphoric acid, phosphate fertilisers, ammonium sulphate and other sulphur containing fertilizers.
4. Sulphur is also involved in the formation of chlorophyll, glucosides and glucosinolates (mustard oils), activation of enzymes and sulphhydryl (SH-) linkages that are the source of pungency in onion, oils, etc (Mengel and Krikby, 1987) ^[25].
5. Sulphur is required for the synthesis of sulphur containing amino acids methionine (21%), cysteine (26%) and cysteine (27%). Approximately 90% of plant sulphur is present in these amino acids (Tandon and Messick, 2002) ^[36].
6. Plants absorb S mainly in the form of inorganic sulphate (SO_4^{2-}) ions through the roots, thus sulphate S must be present in soils in sufficient amount in order to meet crop requirements (Brady and Weil, 2008) ^[5].
7. One of the main functions of sulphur in proteins is the formation of disulphide bonds between polypeptide chains. This bridging is achieved through the reaction of two cysteine molecules, forming cysteine. Linking of the two cysteine units within a protein by a disulphide bond (-S-S-) will cause the protein to fold. Disulphide linkages are therefore important in stabilising and determining the configuration of proteins.
8. Needed for the synthesis of other metabolites including coenzyme A, biotin, thiamin or vitamin B₁ and glutathione.
9. Component of other sulphur containing substances including S-adenosyl methionine, formyl methionine, lipoic acid and sulpholipid.
10. Sulphur is a vital part of ferredoxins, a type of non heme

Fe-S protein occurring in the chloroplast. Ferredoxin participates in oxidoreduction process by transferring electrons and has a significant role in nitrite reduction, sulphate reduction, the assimilation of N₂ root nodule bacteria and free living N-fixing soil bacteria.

11. Activates number of proteolytic enzymes e.g. papainases, increases root growth, stimulates seed formation, and promotes nodule formation on leguminous plants.
12. Involved in the metabolism of carbohydrates and formation of cell wall. Many enzymes of carbon dioxide fixation are regulated by thioredoxin which reduces target enzymes using electrons from ferredoxin (Matsubayashi *et al.*, 2002) ^[22].

Oilseeds have been the backbone of agricultural economy of India since long. Indian vegetable oil economy is the fourth largest in the world next to USA, China and Brazil. Oilseed crops play the second important role in the Indian agricultural economy next to food grains in terms of area and production. The major oilseeds cultivated in our country are groundnut, rapeseed and mustard, castor seed, sesamum, nigerseed, linseed, safflower, sunflower and soybean. The area under total nine oilseed crops registered growth of 4.3 per cent and production registered growth of around 8 per cent, which is highest since, independence, both area expansion and technology improvement contributed almost equally to attain this growth in oilseed crops. Oilseed production has registered many fold increase over time. Globally, India account for 19.29% and 11.127% of the total acreage and production.

Sulphur requirement by crops

Sulphur uptake by several crops is equivalent to that of phosphorus but for legumes and crucifers its requirement is more than that of phosphorus (Verma *et al.*, 2020) ^[38]. Highest sulphur requirement (12 kg/t of yield) has been attributed to oil seeds followed by pulses (8 kg/t), millets (5-8 kg/t) and cereals (3-4 kg/t) as per Kanwar and Mudahar (1986) ^[16]. Sulphur uptake by crops can range 5- 80 kg S/ha/year depending upon the type of crop, yield and cropping intensity. Sulphur uptake is generally 9-15% of N uptake and similar to P uptake. Aulakh (2003) ^[2] reported that the quantity of S removal from soil highest by oilseed crops followed by pulses. It has been reported that removal of sulphur per tonne of grain is 3 kg in cereals against 12 kg in oil seeds (Sharma *et al.*, 2009) ^[32]. Among different crops, sulphur requirements of oilseeds are higher as compared to cereals and pulses because of the critical role played by the sulphur in synthesis of oil and production of bold grains essential for oil production (Khalid *et al.*, 2011) ^[18].

Sources of sulphur in soil

Sulphur is mostly present as sulphides, sulphates and organic. The primary source of sulphur is sulphide bearing plutonic rocks where on weathering these sulphides convert into sulphates. >95% of total sulphur in soil is present in organic matter under temperate conditions and arable soils (particularly top soils), as indicated by close relationships between organic-C, total-N, and total-S (Tabatabai and Bremner, 1972) ^[35]. Besides this atmosphere is another source of sulphur in soils where sulphur dioxide is produced which finds its way to soil through rain.

Table 1: The important sulphur bearing minerals in rocks and soils are given below:

Name	Chemical formulae
Gypsum	CaSO ₄ ·2H ₂ O
Gypsum (Anhydrite)	CaSO ₄
Iron pyrite	FeS ₂
Chalcopyrite	CuFeS ₂
Galena	PbS
Sphalerite	ZnS
Cobaltite	CoAsS

Fertilizer sources of Sulphur: There are many excellent sources of S that can be used to supplement the soil supply as given in table 2.

Table 2: Fertilizer sources to supplement S in soil:

S. no	Name of the fertilizer	Description of the fertilizer
1.	Elemental Sulphur (99% S)	Insoluble and requires microbial oxidation to form sulphate before plants can take it up. Elemental S is oxidized by various soil microorganisms, especially by the genus <i>Thiobacilli</i> (<i>Acidithiobacillus</i>). Rate of oxidation is largely governed by the properties of the elemental S and various soil environmental conditions. The surface area per unit mass of S granules is inversely proportional to the particle size. Maximizing the particle surface area speeds the conversion of elemental S to sulphate, so mixing S with the soil is generally preferred over a band application. Very small particles are oxidized more rapidly by soil bacteria than large particles since there is more surface area. Fine S particles are difficult to uniformly apply and air-borne S dust can present a fire hazard and a respiratory irritant, making it impractical as a common fertilizer. When conditions of soil temperature, moisture, pH, and aeration are favorable for microbial growth, S oxidation will be much more rapid than in cool and dry conditions. $2S^{\circ} + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$ (Elemental S) (Sulphuric acid)
2.	Clay-amended Sulphur (90% S):	Molten S is mixed with approximately 10% bentonite clay to form a pellet (or pastille). On getting wet clay swells and breaks the pellet into small pieces with large reactive surface area. Many clay-amended S products are amended with various micronutrients (e.g. Zn, Fe and Mn) that may benefit from the acidity produced during S oxidation.
3.	Gypsum (16 to 18% S)	Slightly soluble in water (0.2 g/L) and provides sulphate and calcium for plant nutrition as dissolve slowly.
4.	Single Superphosphate (11 to 12% S)	Made by reacting sulphuric acid with rock phosphate to produce a mixture of monocalcium phosphate and gypsum. The popularity of this fertilizer has declined because less concentrated forms of P fertilizers are more expensive to transport and handle.
5.	Ammonium Sulphate (24% S)	(NH ₄) ₂ SO ₄ is a commonly used fertilizer to supply both N and S. This is product of various industrial processes, sometimes made by the reaction of ammonia and sulphuric acid. (NH ₄) ₂ SO ₄ is very soluble and frequently used in fluid fertilizers. The soil acidification that occurs following application of (NH ₄) ₂ SO ₄ arises during the nitrification of ammonium (to nitric acid) rather than from the sulphate that is applied.
6.	Potassium Sulphate (17 to 18% S):	K ₂ SO ₄ can be recovered directly from saltwater brines or produced by reaction of various minerals and acids. Soluble and makes an excellent source of sulphate for plants.
7.	Potassium Magnesium Sulphate (20 -22% S)	The langbeinite mineral (K ₂ SO ₄ ·2MgSO ₄) is extracted from geologic sources and provides a soluble source of three essential plant nutrients. It is highly soluble.
8.	Ammonium Nitrate Sulphate (6 to 14% S):	This material is formed by reaction of nitric and sulphuric acid neutralized with ammonia. S content vary depending on the reaction products. More recently, a new fertilizer is available that results from fusing ammonium nitrate and ammonium sulphate into a single granule (14% S).
9.	Sulphur-enriched Fertilizer	Common fertilizers (such as monoammonium phosphate or diammonium phosphate) are sometimes amended with a mixture of fine particles of elemental S and soluble sulphate to provide an immediate and extended release of S. The acidity that develops surrounding the elemental S can be beneficial in maintaining the solubility of nutrients such as P and Zn.
10.	Thiosulphate (10 to 26% S):	Clear liquid fertilizer that contain S in the form of S ₂ O ₃ ²⁻ . These fluids are commonly mixed with other fertilizer solutions. In the soil, thiosulphate is converted to sulphate within a week or two in warm conditions.
11.	Magnesium Sulphate (14 to 22% S):	Two common sources of this material include the minerals kieserite (MgSO ₄ ·H ₂ O) and Epsom salt (MgSO ₄ ·7H ₂ O). These materials are quite soluble and provide a readily available source of sulphate.
12.	Manure and Compost	The S content of manures and composts is quite variable depending on the animal species, diet and handling. On a dry weight basis, the S content of manures and composts generally ranges between 0.3 and 1%. A period of mineralization is required to convert organic S containing compounds to sulphate prior to plant uptake.

The selection of the appropriate source of S will depend on the soil properties such as leaching potential, pH and OM content. The need for additional nutrients present in the S fertilizer is also a consideration. The requirement for an immediately soluble source of S will also influence the selection of a specific fertilizer source.

Forms of sulphur in soils

In nature sulphur is found in several oxidation states which readily undergo transformation by chemical and microbiological processes (Zhao *et al.*, 1996). S in soils occurs in many more or less distinct forms, organic and inorganic, which can be characterised by appropriate chemical and mineralogical techniques. Inorganic soil S includes

chiefly primary mineral-S, elemental-S, sulphide S, occluded (co-precipitated-S, insoluble (precipitated) -S, adsorbed sulphate-S, and soluble sulphate-S. Organic soil S comprises chiefly carbon bonded-S, and HI reducible-S, with smaller amounts of more soluble or labile forms (Freney *et al.*, 1969)^[11]. As pointed out by Freney and Swaby (1975)^[10] many of the transformations of sulphur in soils are cyclic because of the relative ease with which S is changed from organic to inorganic and from reduced to oxidised forms, and vice versa.

(a) Inorganic sulphur

i. Primary mineral-S: Sulphur as sulphide or sulphate may persist in the primary minerals of some parent materials. Silicate minerals contain generally <100 ppm S, although higher values occur in some layer-type minerals e.g. biotites and chlorites. Igneous rocks generally have greater total-S content, with a preponderance of sulphide-S (Metson, A. J., 1979)^[26]. In the weathering process mineral-S (chiefly sulphide) is oxidised to soluble sulphate-S which may be lost by leaching.

ii. Easily soluble sulphate: Soils of low-rainfall regions and affected by sea water, reclaimed tidal flats, may contain appreciable soluble sulphates and salts. Most soils of humid regions, contain only trace amounts (upto few ppm) of soluble sulphate-S. The relative absence of soluble sulphate in these soils may be explained by various possible reactions of soluble sulphate with soil colloids as below:

- a. Retained on soil colloids as adsorbed sulphate-S in anion retentive soils;
- b. Leached downwards, laterally, out of the soil profile lacking anion-retention sites;
- c. Utilised for the S nutrition of plants or soil micro-organisms;
- d. May be precipitated as insoluble jarosites; or
- e. Remain as soluble sulphate ions.

Thus, on 'normal' sites, humid conditions generally favour the removal of soluble sulphate ions from the soil profile or their transformation to insoluble forms.

iii. Adsorbed sulphate: S in the form of sulphate (SO_4^{2-}), or possibly the bisulphate (HSO_4^{2-}) ion, is retained by various soil colloids in forms resistant to leaching by water. Sulphate so retained is referred to as 'adsorbed' (Ensminger, 1954)^[9], and is replaceable by other strongly adsorbed anions such as phosphate, hydroxyl, fluoride, and acetate. Since adsorbed sulphate is normally determined by extraction (desorption) with a salt solution or dilute acid, it usually includes small amounts of water soluble-S and labile organic-S. In some lower rainfall regions where the soils contain predominantly 2: 1 lattice (micaceous) clays with very weakly developed anion-retention properties, most of the sulphate present may in fact be in a water soluble form, or extractable by dilute solutions of chloride salts or hydrochloric acid (Williams, 1975)^[40].

iv. Sulphate co-precipitated with calcium carbonate and other precipitated forms: Hu *et al.*, (2005)^[12] observed in calcareous soils a significant fraction of the total-S is present as insoluble calcium sulphate, co-precipitated with deposits of calcium carbonate, and is therefore

virtually unavailable to plants. Sulphates may also precipitate as calcium, magnesium or sodium sulphate and occurs as co-crystallized or co-precipitated impurity with CaCO_3 (Chahal *et al.*, 2020)^[7]. Apart from occluded (co-precipitated) sulphate, Williams (1975)^[40] has listed several kinds of insoluble sulphate that may be present in soils. They include barium and strontium sulphates, and basic iron and aluminium sulphates such as jarosite, basaluminite (basalunite), and alunite. (Metson, A. J., 1979)^[26] observed that in the presence of sulphate or phosphate, Al does not exist in true solution above a pH of approximately 4.7, even when NO_3^- or Cl^- is also present. They showed that the higher the valence of the accompanying anion the lower the pH at which Al precipitated. It is also well known that basic sulphates of the jarosite family are characteristic of acid sulphate soils. These have the general formula $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ in which some substitution of Na for K and Al for Fe may occur. It is therefore possible that some of the insoluble-S in soils ascribed to primary mineral sulphide or mineral-sulphate may in fact consist of secondary precipitated basic sulphates.

v. Reduced inorganic sulphur

▪ **Elemental S:** Seldom detectable in soils unless it has recently been applied as such, although it may have a brief existence as an intermediate form during the microbiological transformations of S compounds (Vidyalakshmi, 2009)^[39].

▪ **Sulphide S:** A common constituent of soils under reducing conditions e.g. waterlogging. Black iron mono-sulphides are the products of the microbiological reduction of sulphate to H_2S in the presence of OM as a source of energy for the micro-organisms, followed by precipitation of ferrous sulphide (FeS) (Roberts M, 2018)^[31]. Under permanent flooding, with a continuing supply of OM and sulphate, as in tidal marshes or sea sediments, the iron mono-sulphides are converted to the more stable disulphide pyrite (FeS_2). Subsequently, when drainage is initiated, the pyrite is oxidised to sulphuric acid followed by the precipitation of yellow streaks of basic iron potassium sulphate (jarosite), the process responsible for the formation of acid sulphate soils (Ivarson *et al.* 1982)^[13]. In non-saline soils, Black iron mono-sulphide is often observed in freshly exposed waterlogged profiles and the odour of H_2S may be detectable, but quantitative determination of this unstable sulphide is hardly practicable. However, there may be little or no accumulation of sulphide at E_h value > -150 mv and pH between 6.5 - 8.5.

vi. Organic sulphur: Exists mainly in three forms in soil:

- S not directly bonded to C and reduced to H_2S by treatment with HI (HI reducible-S);
- S directly bonded to C and not reducible by HI (C bonded-S);
- Residual form.

Although various reagent (e.g., pyrophosphate, bicarbonate-carbonate, chelating resins) could be used to extract part of the organic-S in relatively unmodified form, none of the reagents tried was capable of extracting organic-S without some degeneration of the humic acids and some conversion of

organic- to inorganic-S. Mineralisation of soil organic-S is considered to be carried out mainly by micro-organisms. The reverse reaction *i.e.* immobilisation also occurs in the soil (Freney and Swaby, 1975) ^[10]. When added radioactively labelled S was incorporated into both forms of organic-S but (preferentially into HI reducible fraction), McLachlan and Marco, 1975) ^[23] found an increase in C bonded-S with increasing S applications, although this don't appear a permanent sink for the added S. The breakdown of cellulosic plant residues into soil organic matter has been shown to have a high S requirement (Freney and Swaby, 1975) ^[10], and the decomposition of low-S straws depress crop yields by immobilising soil S (Chapman, S.J., 1997) ^[8].

Chemistry of sulphur and its transformations in soils

Transformations of both inorganic and organic sulphur in soils have some practical significance in plant nutrition. Sulphur typically occurs as water soluble sulphate sulphur, adsorbed sulphate sulphur, and elemental and sulphide sulphur as shown in the fig. 6.

Mineralisation of organic sulphur

When the critical C:S ratio in carbonaceous materials of 200:1 to 400:1, immobilisation dominant to mineralisation which is equivalent to 0.1% to 0.2% sulphur (No, T. C. S. (training course series), 2003). Temperature, moisture content, pH and

other environmental factors affect the rate of mineralisation of organic sulphur in soils.

Sulphate reduction and assimilation in plants

Sulphur is an essential element for growth and physiological functioning of plants. However, its content strongly varies between plant species and it ranges from 0.1 to 6% of the plants' dry weight. Sulphates taken up by the roots are the major sulphur source for growth, though it has to be reduced to sulphide before it is further metabolized. Root plastids contain all sulphate reduction enzymes, but the reduction of sulphate to sulphide and its subsequent incorporation into cysteine predominantly takes place in the shoot, in the chloroplasts.

Sulphate uptake by plants

Sulphate is actively taken up across the plasma membrane of the root cells, subsequently loaded into the xylem vessels and transported to the shoot by the transpiration stream. The uptake and transport of sulphate is energy dependent (driven by a proton gradient generated by ATPases) through a proton/sulphate co-transport. In the shoot the sulphate is unloaded and transported to the chloroplasts where it is reduced. The remaining sulphate in plant tissue is predominantly present in the vacuole.

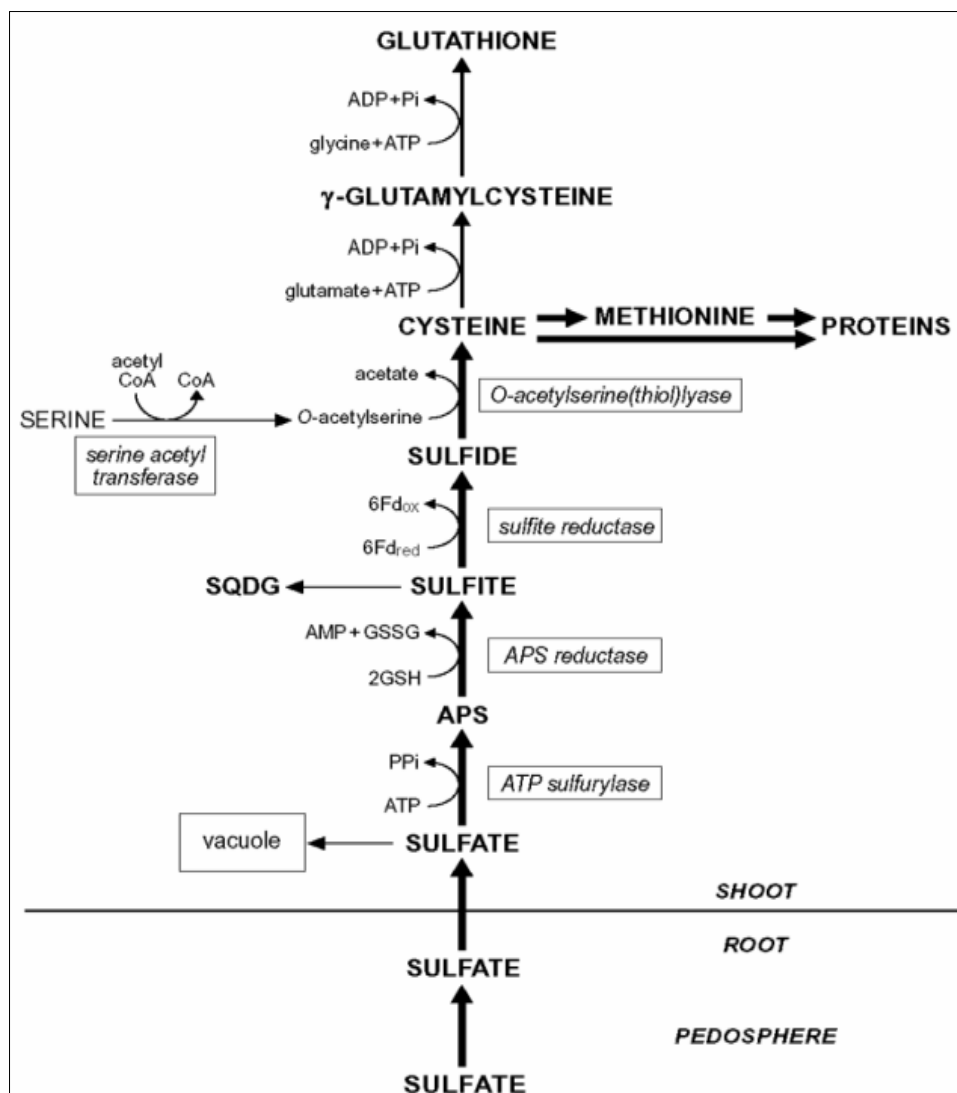


Fig 2: Sulphate reduction and assimilation in plant (Hawkesford, 2012).

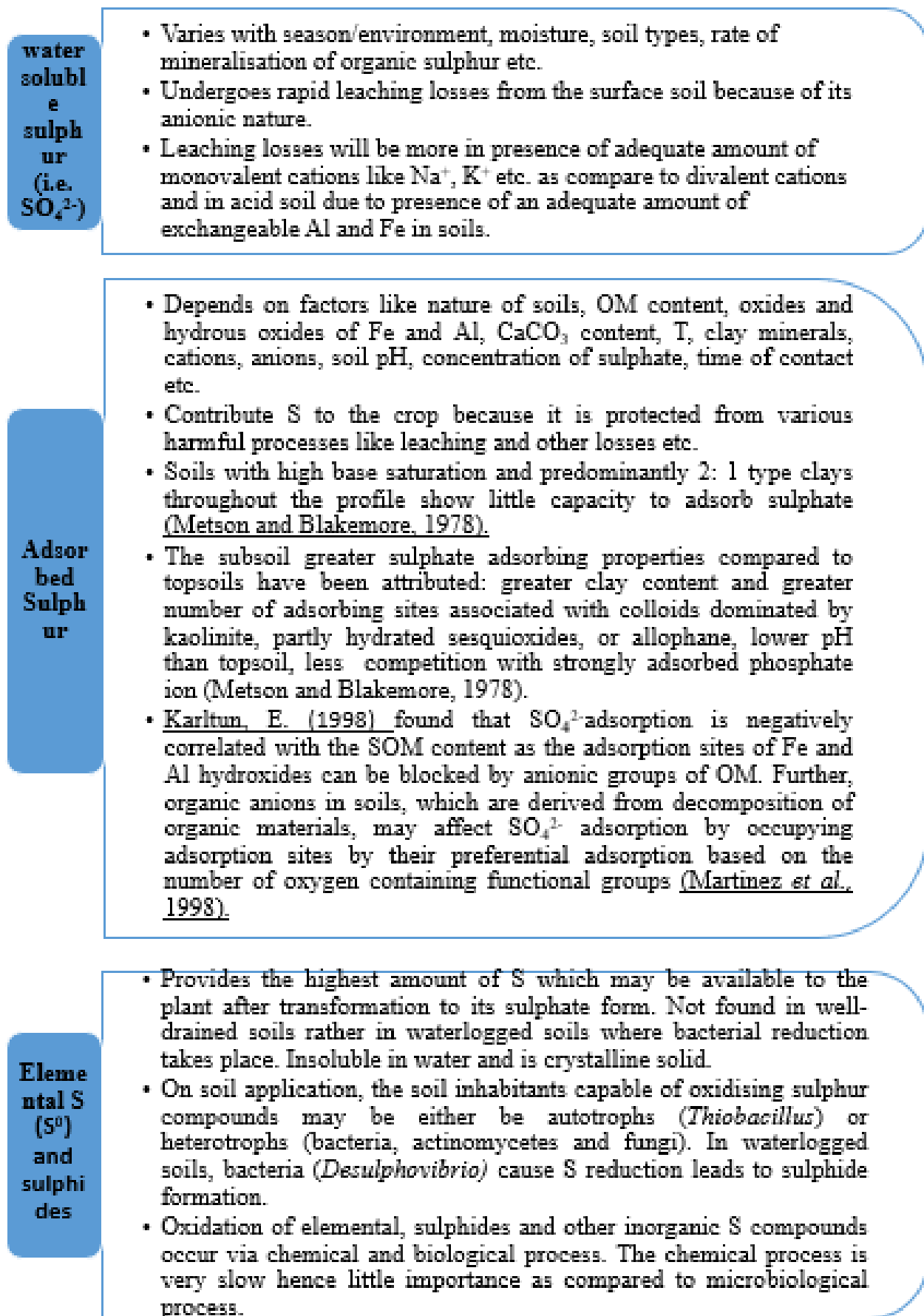


Fig 3: Forms of sulphur and their transformation in soil

Sulphate reduction in plants

Sulphate reduction enzymes are present in root plastids

mostly though sulphate reduction predominantly takes place in the leaf chloroplasts and the process occurs in three steps:

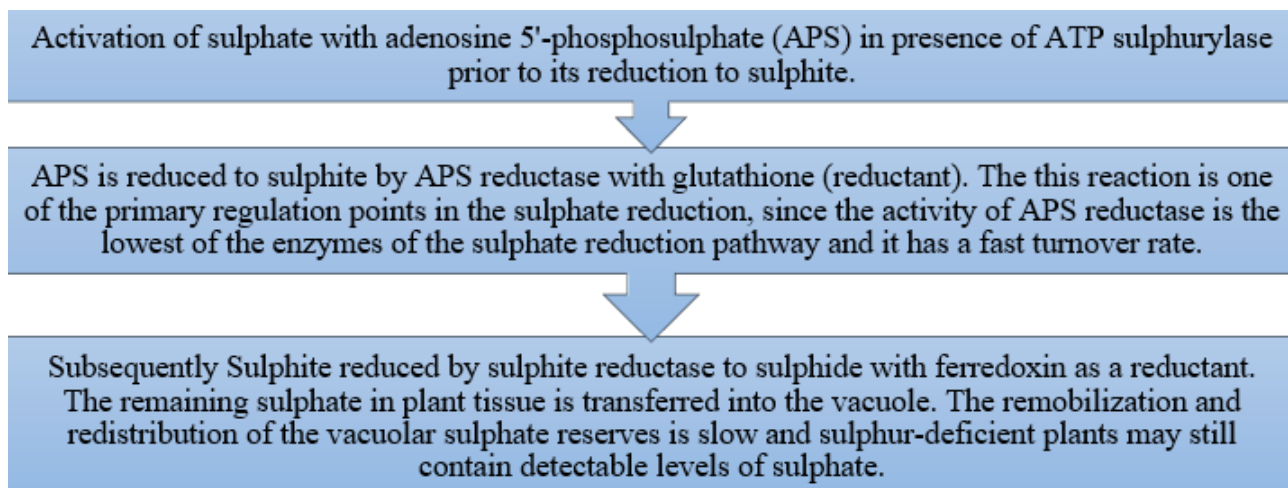


Fig 4: Sulphate reduction in plant tissue

Synthesis and function of sulphur compounds in plants

Cysteine: Sulphide is incorporated into cysteine, catalysed by O-acetylserine (thiol)lyase, with O-acetylserine as substrate. The synthesis of O-acetylserine is catalyzed by serineacetyltransferase and together with O-acetylserine (thiol)lyase it is associated as enzyme complex named cysteine synthase. The formation of cysteine is the direct coupling step between sulphur (sulphur metabolism) and nitrogen assimilation in plants. Cysteine is sulphur donor for the synthesis of methionine, the major other sulphur-containing amino acid present in plants. This happens through the trans-sulphuration pathway and the methylation of homocysteine. Both cysteine and methionine are sulphur-containing amino acids and are of great significance in the structure, conformation and function of proteins and enzymes, but high levels of these amino acids may also be present in seed storage proteins. The thiol groups of the cysteine residues in proteins can be oxidized resulting in disulfide bridges with other cysteine side chains (and form cystine) and/or linkage of polypeptides. Disulfide bridges (disulfide bonds) make an important contribution to the structure of proteins. The thiol groups are also of great importance in the synthesis of sulfolipids. Sulfolipids are still under investigation. From recent studies it is evident that sulphite is the likely sulphur precursor for the formation of the sulfolipid group of this lipid.

Glutathione: Cysteine is the direct precursor for the synthesis of glutathione (and its homologues). First, γ -glutamylcysteine is synthesized from cysteine and glutamate catalysed by gamma-glutamylcysteine synthetase. Second, glutathione is synthesized from γ -glutamylcysteine and glycine (in glutathione homologues, β -alanine or serine) catalysed by glutathione synthetase. Both steps of the synthesis of glutathione are ATP dependent reactions. Glutathione is maintained in the reduced form by an NADPH-dependent glutathione reductase.

Secondary sulphur compounds: Brassica species contain glucosinolates, which are sulphur-containing secondary compounds. Glucosinolates are responsible for the flavor and anti-carcinogenic properties to Brassicaceae species. Allium species contain γ -glutamylpeptides and alliin (S-alk(en)yl cysteine sulfoxides). The content of these sulphur-containing secondary compounds strongly depends on stage of development of the plant, temperature, water availability and

the level of nitrogen and sulphur nutrition. The alliin and their breakdown products (e.g. allicin) are the flavor precursors for the odor and taste of species. Flavor is only released when plant cells are disrupted and the enzyme alliinase from the vacuole is able to degrade the alliin, yielding a wide variety of volatile and non-volatile sulphur-containing compounds.

Why deficiency of sulphur occurs?

Sulphur (S) deficiency has been recognized as a constraint to sustainable crop production in many parts of the world including Asia (Malav *et al.*, 2018). Sulphur deficiencies in India are widespread (Singh *et al.*, 2014). Major reasons for sulphur deficiencies are: introduction of high yielding crop varieties, application of sulphur free fertilizers, injudicious use of irrigation water, areas of low atmospheric deposition of sulphur and with excessive winter rainfall and calcareous and waterlogged soils. Soil usually prone to sulphur deficiency are: light textured soils with low organic matter, canal irrigated areas, areas where sulphur free fertilizers are used, acid soils are more prone to sulphur deficiency due to stronger adsorption of SO_4^{2-} , wheat is more prone to sulphur deficiency than rice.

Sulphur deficiency in our country

Sulphur deficiency in Indian soil is increasing due to extensive use of sulphur free fertilizers coupled with the increasing area under high sulphur demanding crops such as oilseeds and pulses. Also a high level of cropping intensity in irrigated areas as well as wide gap between the addition and removal of sulphur causes sulphur deficiency. The data generated by the ICAR project and the TSI-FAI project reported that 46 per cent samples were deficient in S and another 30% samples were medium in available S which could be considered as potentially S deficient (Tandon and Messick, 2007) [37]. In West Bengal, six districts *viz.* Birbhum, Burdwan, Murshidabad, Midnapore, Nadia and 24 Parganas have been reported to be sulphur deficient (Mondal *et al.*, 2020) [28]. Both the surface and sub-surface soils of four districts *viz.* Birbhum, Bankura, Burdwan and Purulia under red and lateritic soils of West Bengal has been found to be deficient in sulphur (Patrac *et al.*, 2012) [30].

Deficiency symptoms

- Recognition of characteristic symptoms is often the first step in diagnosis of sulphur deficiency. Under inadequate

sulphur plant first suffer from hidden hunger. When the deficiency is severe, the plants show typical sulphur deficiency symptoms, crop growth suffers at such levels and respond well to sulphur application. The critical level varies with the crop and the stage of development.

- Resembles to those of nitrogen deficiency (pale-yellow or light green colouration of leaves) but first appear on younger leaves unlike N. Plants deficient in sulphur are small and spindly with short and slender stalks, their growth is retarded, maturity in cereals is delayed and fruits often do not mature fully and remain light green in colour.
- Nodulation in legumes may be poor and nitrogen fixation reduced. Forages have undesirably wide N: S ratio they

are of low nutritive value.

- Sulphur deficiency results in discolouration and abnormal growth of plant tissues. Sulphur deficiency may not only lead to decreased yields, but also to poor bread-making quality for wheat.

Effect on yield and quality parameters

Sulphur deficiencies persisting into the seed filling stage will reduce seed sulphur concentration and this may affect seed quality. Nitrogen as well as sulphur supply can affect seed sulphur through interaction on nutrient translocation. Sulphur deficiency affects milling and baking quality of wheat. Grain of sulphur deficient wheat is harder than normal and the dough is tougher and less extensible.

Table 3: Effects of sulphur levels on different quality parameters of mustard

S levels (kg/ha)	Yield (kg/ha)	Seed yield (g/plant)	Oil content (%)	Net returns (Rs/ha)	B:C ratio
10	2226	11.10	18.36	24856	3.39
20	2534	12.28	18.68	29769	3.79
30	2494	12.00	18.35	27716	3.56
40	23760	11.44	18.37	26648	3.52
Mean	2408	11.68	18.44	27247	3.57
Absolute control	2123	10.13	18.33	----	----
CD (P=0.5)	159.83	1.01	0.22	2296	0.19

Source: Singh *et al.*, 1998

Table 4: Effect of sulphur on seed yield and quality parameters of sunflower oil

S level/ha	Seed yield (q/ha)	Free fatty acid (%)	Saponific-ation number	Iodine value	Stea-ric acid (%)	Palmitic acid (%)	Oleic acid (%)	Linoleic acid (%)
0 kg	14.3	1.9	193.7	127.5	2.80	5.5	49.0	40.4
15 kg	14.6	1.7	193.5	128.4	2.75	5.3	48.8	40.8
30 kg	15.0	1.6	193.5	129.7	2.68	5.3	48.5	41.4
45 kg	15.2	1.5	193.4	131.3	2.61	-	48.3	41.7
CD at 5%	0.53	0.03	NS	0.6	0.04	0.1	0.24	0.34

Source: Krishnamurthi and Mathan, 1996

Toxicity symptoms

Excess of sulphur causes interveinal yellowing in sorghum and lemon leaves. The symptoms produced by excessive SO₂ in the environment are divided into:

- Acute injury:** Collapsed marginal or interveinal areas which at first have a dull, water soaked appearance, later drying and bleaching to an ivory colour in most species. These lesions are caused by rather sudden absorption of enough gas to kill the tissue.
- Chlorotic injury:** Yellowing of the leaves which may progress slowly and bleaches completely. This is due to absorption of an amount of gas somewhat insufficient to cause acute injury.

Sulphide injury (H₂S) is common in poorly drained rice soils which is characterised by inhibited root development and browning and death of roots resulting the stunting of shoots. The H₂S toxicity also depresses the uptake and translocation of P and other nutrients.

Improvement in yield, crop response to sulphur fertilization

The response of different oilseed crops, cereals and legumes to application of sulphur has been reported in different state in India. Applied sulphur has been reported to increase 6.2% oil, 6.0-8.4% protein and 21.1% amino acids in groundnut kernel. Also sulphur fertilisation increase oil content in rapeseed mustard and sunflower (Aulakh *et al.* 1980)^[4]. The oil content of mustard varied from 37-40% with the application of different levels of applied S and the maximum oil content of 40.5% was obtained with the application of 60 kg S ha⁻¹. On an average, oil content increased from 37-40.5% with the increase in level of S application from 0 to 60% kg S ha⁻¹. Oil content increased significantly with the application of sulphur it may be attributed to increase in glycosides. Also the mustard seed yield increased significantly by 17.8 to 60% over control with application of different doses of fertilizers (Jaga, 2013)^[14].

Table 5: Effect of applied sulphur on oil content in seeds, content and uptake of S (kg/ha) by seed and straw of mustard crop

S levels (kg ha ⁻¹)	Oil content		S content in seed		S content in straw		S uptake in seed		S uptake in straw	
	Site-I	Site-II	Site-I	Site-II	Site-I	Site-II	Site-I	Site-II	Site-I	Site-II
0	37.5	37.0	0.30	0.29	0.09	0.12	32.3	30.0	28.3	36.0
15	39.5	38.9	0.35	0.35	0.16	0.14	51.1	42.7	58.5	48.1
30	39.6	39.5	0.38	0.38	0.17	0.16	60.9	46.1	68.3	61.5
60	40.5	40.0	.45	0.42	0.19	0.18	77.3	63.0	82.8	70.9
CD (0.05)	0.23	0.28	0.01	0.009	0.02	0.006	1.84	4.2	6.9	3.0
CV	0.48	0.59	2.7	2.1	10.7	3.2	2.7	7.6	9.4	4.4

Source: Jaga, 2013^[14]

Sulphur and nitrogen interaction in relation to yield and quality of crops:-Sulphur 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) [6]. A strong interaction of S and N for seed yield was found in rapeseed and mustard, Groundnut and Soybean (Jamal *et al.*, 2010) [15]. Aulakh *et al.* (1980) [4], 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. There are many examples of how an adequate supply of both S and N are required to achieve desired yields. Aulakh and Malhi (2004) [3] found that Sulphur deficiencies in legumes also decrease proper N utilization, since the number of root nodules and the effectiveness of atmospheric N fixation are reduced with low S.

Factors Affecting Availability

- Soil texture: Sulfur is leachable, plus sandy soils are typically low in OM, therefore these soils are often low in sulfur.
- Soil organic matter: Organic matter is a reservoir for S
- Soil temperature: The conversion of various forms of S to the available sulfate (SO₄) form is a microbial process; therefore low soil temperatures slow this process.
- Drainage: The conversion of various forms of S to the available sulfate (SO₄) form is a microbial process requiring oxygen, therefore saturated soil slow this process.
- Pollution: Soil that, over the years, has been subject to high levels of deposition from industrial sources of S.
- Irrigation water: Irrigation water may contain high levels of S, and excess irrigation of sands can leach S out of the root zone.
- SO₄:NH₄ Applications: Added NH₄ has been shown to appreciably enhance the uptake of SO₄.

Sulphur Management using the 4R Nutrient Stewardship Principles

The 4R Nutrient Stewardship principles (Right Source of nutrient applied at the Right Rate, Right Time, and Right Place) is applicable to all plant nutrients. Since S can be supplied from many different sources, including animal manures, the 4R principles help with efficient nutrient delivery. As an example of these 4R concepts, ammonium sulphate (Source) is commonly used in the seed-row (Place) of small-seeded crops at planting (Time), but fertilizer additions (Rate) must be low to reduce the risk of ammonia (NH₃) damage, especially with wide rows and when grown in dry and sandy soils. Following are considerations of 4R Nutrient Stewardship principles to properly supply S for crop nutrition.

Source: Sulphur fertilizers contain either soluble sulphate or a form of S that will be converted to sulphate. An estimate must be made of the time that will be required for conversion of insoluble S to plant-available sulphate. A variety of excellent dry and fluid fertilizers that contain various forms of S are available for blending or direct application. A combination of soluble sulphate and elemental S may be useful to provide

both an immediate and a prolonged source of plant nutrition. The particle size of elemental S can be a key property for making this estimate, as smaller S particles tend to oxidize to sulphate more quickly than large particles.

Time: Fertilizer application must synchronize crop demand since they are readily available. However elemental S must be applied in advance of the crop need to allow microbial oxidation. In areas with cold winter temperatures, application may need to precede plant uptake by many months. The release of sulphate from SOM and crop residues will proceed more quickly in warm soils and can supply significant amounts of S during the growing season. A constant supply of soluble sulphate is required by most plants.

Place: Band placement near the seed row of annual crops is quite effective. Simultaneously we are to avoid large amounts of sulphate in direct contact with seedlings to avoid osmotic damage to roots. Since sulphate is fairly mobile in soil, it move with water through the root zone. Elemental S is most effective when broadcast onto the soil and tilled into the ground. In flooded soils, elemental S is best left at the surface so it can be converted to sulphate in the thin aerobic zone at the soil-water interface.

Rate: Should be adjusted as per crop demand, soil conditions (texture and OM content), and environmental factors (T and rainfall) and for multi-year crop rotations. For example in a canola-barley-wheat rotation in Western Canada, the high S demand by canola can be met with a single S application to supply nutrition over the three-year cycle. Inadequate S will reduce protein synthesis and will result in poor utilization of applied N and reduced N₂ fixation by legumes.

Conclusion

Sulphur is an important component of various amino acids, vitamins and enzymes and involved in several plant metabolic processes. Soil sulphur is largely in the form of complex organic molecules, with smaller amounts of inorganic sulphur, of which only soluble sulphate is available for plant uptake. Mineralizing biological sulphur to sulphate requires soil microorganisms, and this is likely the rate-determining phase in the soil sulphur cycle. Many factors influence the availability of sulphate to plants, including the availability of other nutrients (such as nitrogen) and the presence of adsorbing minerals. Other inorganic sulphur compounds, aside from sulphate, are normally low in concentration, unless during waterlogging, when sulphides might accumulate. So its application positively influences yield attributes, oil content, protein content and other quality parameters. The oilseed crop should be fertilized @ 30-45 kg S/ha mainly as basal along with recommended dose of N, P and K for boosting production and other desired quality parameters.

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