

REVIEW

# Sulphur in Soil, Plant and Human Nutrition

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Abstract Sulphur is now recognized as the fourth major plant nutrient after N, P and K globally. Sulphur in soils comes from the sulphur containing minerals present in parent materials from which the soils are derived and from the plants and animals residues or from the external addition of elemental S or its minerals. Sulphur enters the biological systems from soil through microbial activities involving mineralization of organic matter, immobilization, oxidation and reduction. Plants take up sulphur only as  $SO_4^=$  and reduce it to form S containing amino acids and other compounds. Amino acid cysteine is the source of sulphur for most other S-compounds in plants. Sulphur containing vitamin thiamine (Vitamin  $B_1$ ) is also synthesized only in plants and not in humans or other animals. Plants also produce vitamin biotin and a number of S-containing metabolites including glutathione, glucosinolates and alliin/allicin. Sulphur deficiency in wheat can lead to poor baking quality and in oilseeds it can lead to reduced oil content and yield. Sulphur is taken in as sulphur containing amino acids (SAAs) cysteine and methionine by human beings. The recommended dietary allowance for SAAs for humans is  $14 \text{ mg kg}^{-1}$  body

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weight. Lack of sulphur can lead to arthritis, muscle and joint stiffness, spondylitis, etc. Dietary supplements containing (chondroitin sulphate, glucosamine sulphate, methylsulfonylmethane etc.) can be beneficial in the treatment of joint diseases.

Keywords Arthritis - Bentonite glutathione -

Glucosinolates · Muscle and joint stiffness · Spondylitis · S-deficiency

## Introduction

Sulphur (S) with an atomic number 16 and an average atomic mass 32.06 occurs in group 16 and period 3 of the periodic table. It has an atomic configuration [Ne]  $3s^23p^4$ . It expresses oxidation states of  $+4$  in SO<sub>2</sub>,  $+6$  in H<sub>2</sub>SO<sub>4</sub>, and  $-2$  in H<sub>2</sub>S [\[1](#page-4-0)]. Sulphur is an essential macronutrient for microorganisms, plants, animals and humans. Proteins store most S. As regards to its abundance, in both plants and humans, S comes after K, Ca and P. In plants, K is present in the largest amount, while in humans, Ca is present in the largest amount.

Sulphur enters the biological systems from the S present in earth crust and soil. Soil is the top layer of earth crust, which has undergone weathering. It contains organic matter and is teeming with living organisms. All these three factors affect the availability of plant nutrients in soil [\[2](#page-4-0)]. S enters the plants as  $SO<sub>4</sub><sup>+</sup>$ , which has the capacity to reduce it to  $SH^-$ or sulfide  $(S^=)$ . Amino acid cysteine is being the main organic molecule. The S containing amino acids (SAAs) as cysteine and methionine are the major forms in which S enters human beings either directly as plant food or indirectly as animal foods. Both cysteine and methionine are essential amino acids although human

Disclaimer The observations made on nutritional supplements and other sulphur compounds are for the general information of the reader and before using these they are advised to consult the nutrition and medical experts.

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beings can synthesize some cysteine. From the biological system, S goes back to soil as crop residues, animal and human excreta completing the S nutrition cycle.

## Sulphur in the Earth Crust

In the earth's crust, S is present in very small amount as compared to iron  $(5.0 \%)$ , calcium  $(3.6 \%)$ , potassium  $(2.6\%)$  and magnesium  $(2.1\%)$  [\[3](#page-4-0)]. Sulphur in the earth crust occurs as elemental sulphur, sulphide and sulphate minerals. The sulphate minerals include anhydrite  $(CaSO<sub>4</sub>)$ , gypsum ( $CaSO_4$ ·2H<sub>2</sub>O), barite (BaSO<sub>4</sub>), Kieserite (MgSO<sub>4</sub>.  $H_2O$ ) and epsonite (MgSO<sub>4</sub>.2H<sub>2</sub>O), while the sulfide minerals include pyrites  $(F \in S_2)$ , chalcocite  $(Cu_2S)$ , bornite  $(Cu_5FeS_4)$ , digenite  $(Cu_9S_5)$ , tetrahydrite  $(Cu_{12}Sb_4S_{13})$ , molybdenite  $(MoS<sub>2</sub>)$ , sphalerite  $(ZnS)$ , galena (PbS) etc. [[4](#page-4-0)].

Elemental S is found near hot springs and volcanic regions in Indonesia, Chile, Japan and Italy [\[5](#page-4-0)]. The anaerobic bacteria acting on sulphate minerals, such as, gypsum in salt domes produce S. Such deposits in salt domes occur along the coast of Gulf of Mexico and evaporate in Europe. Fossil based S deposits from salt domes which have been recently the basis of commercial S production in USA, Russia, Turkmenistan and Ukraine [\[6](#page-4-0)]. However, today most elemental S is produced as a byproduct of natural gas and petroleum industry [[7\]](#page-4-0).

#### Role of Microbes

Microbes play an important role in releasing S from elemental S and sulfide minerals in the earth surface to soil. Only from sulphate minerals, S becomes readily available in soil and to plants, since plants take up sulphur only as  $SO<sub>4</sub>$ . Elemental S, sulfide S and thiosulfate S have to be first oxidized. Microorganisms from all the three domains, bacteria, arachaea and eukaryotes (fungi) are involved in the oxidation of sulphur; however, the major role is played by the bacteria, Thiobacillus sp. In the domain Archaea, aerobic oxidation of sulphur is restricted to the members of the Sulfolobales [[8\]](#page-4-0). The fungi reported to be involved in the oxidation of elemental-S and thiosulphate are Alternari atenui, Aureobasidium pullulans and Epicoccum nigrum, and a range of Penicillium sp. Selecobasidium constrictum, Myrothesium circutum and Aspergillus sp. [[9,](#page-4-0) [10\]](#page-4-0). The bacteria involved in the oxidation of sulphur can be clas-sified into three groups as under [[11,](#page-4-0) [12\]](#page-4-0).

#### Chemolithoautotrophs

These bacteria obtain energy from oxidation of sulphur and carbon from carbon-dioxide for their growth and development. The examples are Thiobacillus thioparus, T. neapolitanus, T. denitificans, T. thiooxidans, T. ferrooxidans, T. halophilus and some species of Thiomicrospira.

### Chemolithoheterotrophs

These bacteria obtain energy from oxidation of sulphur and carbon from organic molecules for their growth and development. The examples are Thiobacillus novellus, T. acidophilus, T. aquaesulis, Paracoccus dentrificans, P. versutus, Xanthobacter tagetidis, Thiospaera pantotroph and Thiomicrospira thasirae.

#### Chemolithomesoptrophs

These bacteria obtain energy from oxidation of sulphur and carbon from inorganic as well as organic molecules for their growth and development. The examples include Thiobacillus denitrificans and T. ferrooxidans.

There are a number of enzymes involved in sulphur oxidation. These include thiosulphate dehydrogenase, tetrathionate hydrolase, trithionate hydrolase and sulphur oxygenase [[13,](#page-4-0) [14\]](#page-4-0).

On the contrary, sulphates are reduced to  $H_2S$  by S reducing organisms under anaerobic conditions such as those obtained in low-land rice paddies.  $H_2S$  is responsible for the bad odour from paddy fields. Sulphate reducing bacteria reduce sulphate to obtain energy. Sixty genera containing 220 species of sulphate reducing bacteria are known [\[15](#page-4-0)]. The largest group (about 23 genera) includes Desulfpbacteriales, Desulfovibrionales and Syntrophobacterales [\[16](#page-4-0)]. The second largest group includes genera Desulfotomaculum, Desulfosporomusa and Desulfosporosium.

## Sulphur in Soil and Crop Responses to S Fertilization

Sulphur in soil comes from the sulphur containing minerals present in parent materials in rocks from which the soils are derived and from the plant and animal residues or from the external addition of elemental S or its minerals. Total S content in soils is reported in the range of 30–400 mg  $kg^{-1}$ and about 50–90 % of it is bound to soil organic matter [\[17](#page-4-0)]. The C:N:S ratio in soil organic matter is about 100:8.9:1 [\[18](#page-4-0)]. Only a small fraction of total S present in soil is available to crops in a growing season and there are a number of soil tests for available S, such as  $0.15\%$  CaCl<sub>2</sub> extractable S [\[19](#page-4-0)]. For this procedure, the critical deficiency level is 10 mg S  $kg^{-1}$  soil [[20\]](#page-4-0).

Sulphur is now recognized as the fourth major plant nutrient after N, P and K globally [[21\]](#page-4-0) and crop responses to S fertilization have been reported from Asia [[22,](#page-4-0) [23](#page-4-0)], Africa [[24\]](#page-4-0), Europe [[25\]](#page-4-0), north America [[21\]](#page-4-0), south America [[26\]](#page-4-0) and Oceania [[27\]](#page-4-0). Sulphur is now considered as an important component of balanced fertilization of crops [\[28](#page-4-0), [29](#page-4-0)]. Crop response to sulphur in India is the highest for oilseeds (rapeseed/mustard, sunflower, safflower, groundnut, soybean etc.). Average S uptake (kg per metric ton of grain/seed) by crops is reported to be 9.9 for oilseeds, 7.6 for pulses or beans and 4.1 for the cereals [\[29](#page-4-0)]. Sulphur fertilization increases protein content in the grains of cereals [[30\]](#page-4-0) and oil content in seeds of oilseeds [\[31](#page-4-0), [32](#page-4-0)]. The recent increase in S deficiency in soils of India and other Asian countries is due to use of high analysis fertilizers such as urea and diammonium phosphate (DAP) in place of sulphur containing ammonium sulphate and single superphosphate, use of high yielding varieties and hybrids of cereals and practicing intensive cropping systems such as rice–wheat [\[33](#page-4-0)]. Sulphur fertilizers in India include elemental S, gypsum, pyrites and bentonite S [\[30](#page-4-0), [34](#page-4-0)]. In addition, S is also present in a number of nitrogen (ammonium sulphate, ammonium phosphate sulphate), phosphorus (single/ordinary super phosphate, triple/concentrated super phosphate), potassium fertilizers (potassium sulphate, potassium magnesium sulphate) and micronutrient fertilizers (zinc sulphate, copper sulphate, manganese sulphate) [\[18](#page-4-0)]. Application of nitrogen, phosphorus and potash increases the availability of applied S to the crops [[35](#page-4-0)]. Also when elemental S or pyrites are used as a source of S, they should be applied on soil surface to permit their oxidation to sulphate [[12,](#page-4-0) [36](#page-4-0)].

#### Sulphur in Plants

#### Important Components

Assimilation of sulphur by the plants is very important, because only through plants it enters the human beings. Sulphur is taken up by plants as  $SO_4^=$  and is present as aqueous solutions in xylem tissue and in vacuoles of plant cells. In plant tissue, it occurs as  $SH^-$  (thiol orsulfhydryl) group) or  $S^=$  (Sulfide) in various organic molecules including proteins. Many thiols have strong odors resembling that of garlic. Most S in plants is stored as proteins.

Sulphate in plants is changed to adenosine 5'phosphate (APS) catalyzed by ATP sulfurylase and later to 3'adenosine 5'phosphosulphate (PAPS), which is reduced to sulphite  $(SO_3<sup>=</sup>)$  catalyzed by PAPS reductase and later to sulfide  $(S^+)$  catalyzed by sulfide reductase. Sulphide so produced is then exchanged with acetyl group of Oacetylserine produced from serine with the help of serine acid transferase and produces cysteine [[37\]](#page-4-0). Amino acid cysteine is the source of sulphur for most other S-compounds in plants. In the synthesis of another amino acid methionine, the main backbone is derived from aspartic acid and sulphur from cysteine or methanethiol or hydrogen sulfide and the three steps involved in the biosynthesis of methionine from homoserine are acylation, sulfurylation and methylation [[36\]](#page-4-0). Methionine is the only amino acid with a thio-ether group (i.e. C–S–C) and in addition to structural role in proteins, methionine is best known for its role in the initiation of translation [\[38](#page-4-0)].

Sulphur containing thiamine (Vitamin  $B_1$ ) is also synthesized only in plants and not in human beings. Cysteine is the S donor in thiamine synthesis, which involves a number of S carrier proteins (ThiO, ThiG, ThiS, ThiF etc.) like cysteine desulfurase and a host of other enzymes. The thiazole [hydroxyethyl thiazole (HET-P)] [\[39](#page-4-0)] and pyrimidine [hydroxymethyl thiamine (HMP-PP)] [\[40\]](#page-4-0) moieties of thiamine are synthesized separately and then are coupled to form thiamine monophosphate, which is further phosphorylated to thiamine pyrophosphate (Vitamin B1) [[41](#page-4-0)]. In plants, thiamine is able to enhance tolerance to oxidation stress during different abiotic stress conditions [\[42](#page-4-0)]. It is also required for shoot meristem maintenance in maize [[43\]](#page-5-0). Biotin (vitamin H or coenzyme R) is another S-containing vitamin. It has two moieties ureido and thiophene. Its precursors are alanine and S-containing pimeloyl-CoA [\[44](#page-5-0)].

Plants also produce a number of S-containing metabolites. One of the important metabolite is glutathione (GSH), a tripeptide (L- $\gamma$ -glutamyl-L-cysteine-glycine) [[45\]](#page-5-0). It is an important anti-oxidant in plants, animals, fungi and some bacteria and prevents damage to important cellular compounds caused by free radicals and peroxide [\[46](#page-5-0)]. Thiol groups in GSH are reducing agents and in the process GSH is oxidized to GSH-disulfide (GSSH) also called  $L-(-)$ GSH. It is later reduced to GSH by GSH-reductase using NADP as an electron donor [\[47](#page-5-0)]. Other secondary metabolites include glucosinolates (GSLs) in the members of the Brassicae family, such as, rapeseed-mustard, cabbage, broccoli, horse radish etc. and alliin/allicin in the members of Alliaceae family, such as, garlic, onion etc. [\[48](#page-5-0)]. These secondary metabolites are part of plant's protection mechanism against diseases and pests, but they have been found to be useful for alleviating several diseases in humans as discussed later.

#### Sulphur Deficiency Symptoms in Plants

Since S and N are components of proteins, therefore their deficiency symptoms in plants are similar, that is, yellowing of leaves. However, since S is less mobile in plants, its deficiency symptoms first appear on the younger leaves as a contrast to N deficiency symptoms which first appear on lower leaves [[49\]](#page-5-0). In rapeseed/mustard, young leaves of S deficient plants become pale and chlorotic and are cupped.

In most other crops interveinal yellowing of young leaves is observed, which under extreme deficiency may get bleached in some crops [\[50](#page-5-0)]. The general critical level for severe deficiency in leaves is 0.15 %, while the sufficiency level is 0.45  $%$  on dry matter basis [[50\]](#page-5-0).

## Sulphur Fertilization and Crop Quality

Sulphur deficiency in plants reduces not only yield but also reduces the quality of the produce. Zhao et al. [\[51\]](#page-5-0) reported that when S is deficient, it reduces S-containing amino acids in wheat, which create an imbalance between high molecular weight (HMW) and low molecular weight (LMW) glutenin sub-units [[52\]](#page-5-0) reducing bread making quality of wheat. Randall et al. [\[53](#page-5-0)] reported that when S concentration in wheat grain is below 1.2 mg  $g^{-1}$  and N:S ratio is above 17:1, the grain is deficient in S and both yield and quality are affected. Unger et al. [\[54](#page-5-0)] also observed that a high N:S in wheat grain was associated with low loaf height and volume in bread. In rice also Shivay et al. [[55\]](#page-5-0) found that application of 45 kg S/ha reduced N:S ratio in grain from 9.77 to 7.79.

Sulphur has received special attention in oilseed crops and a number of reports are available on the increase in seed yield and oil content in rapeseed/mustard [\[56–58](#page-5-0)], groundnut  $[31, 59]$  $[31, 59]$  $[31, 59]$  $[31, 59]$  $[31, 59]$ , sunflower  $[32]$  $[32]$  and soybean  $[60]$  $[60]$ .

#### Sulphur in Humans

Sulphur is an abundant element in human body and along with nitrogen and phosphorus it forms a triad of elements needed for most of the body tissue. As regards the amounts of minerals, it comes only after calcium and phosphorus. Human proteins contain 3–6 % sulphur containing amino acids (SAAs) [[61\]](#page-5-0). Although some cysteine is synthesized in human body, most sulphur is taken in as SAAs cysteine and methionine. Recommended dietary allowance (RDA) for sulphur containing amino acids (SAAs) (cysteine and methionine) is 14 mg  $kg^{-1}$  body weight. Thus, a person weighing 70 kg would need around 1.1 g SAAs and a safe intake is about 2 g SAAs per day [\[62](#page-5-0)].

Disulfide bonds in S-compounds are involved in the function of connective tissue and provide flexibility in tissue. Lack of sulphur can lead to tendonitis, arthritis, bursitis, muscle and joint stiffness, spondylitis, fibrosis and sclerosis etc. Dietary supplements containing sulphur (chondroitin sulphate, glucosamine sulphate, Methylsulfonylmethane etc.) can be beneficial in the treatment of joint diseases [\[63](#page-5-0)].

Glutathione (GSH) is an important detoxifier in liver and takes care of free oxygen radicals and peroxides [\[64](#page-5-0), [65](#page-5-0)]. GSH is also the way sulphur is stored in liver. GSH has

also a role in biosynthesis of prostglandines (PGS), which are associated with key processes in inflammation.

Cysteine deficiency can lead to a number of disorders in humans and its derivative acetylcystein or N-acetylcystein is used as a nutritional supplement to cure paracetamol toxicity [[66\]](#page-5-0), prevention of acute renal failure [[67\]](#page-5-0) and progressive interstitial lung disease [\[68](#page-5-0), [69\]](#page-5-0) and treatment of psychiatric disorders [\[70](#page-5-0)].

Sulphur is involved in the formation of collagen and keratin. Sulphur deficiency can lead to hair, skin and nail problems. Lack of methionine leads to build up hydrogen peroxide in hair follicles and a gradual loss of hair colour [\[71](#page-5-0)]. An important metabolite of methionine S-adenosylmethionine (SAMe) is involved in many metabolic processes in humans [\[72](#page-5-0)]. SAMe nutritional supplements are used for curing depression [\[73](#page-5-0)] and osteoarthritis [\[74](#page-5-0)]. However, too much methionine can be harmful and methionine restriction without energy restriction may extend life span in rats [\[75](#page-5-0)]. Methionine restriction is also reported to inhibit age related processes in rats [\[76](#page-5-0)].

Thiamine deficiency in humans disturbs the central nervous and circulatory systems and causes beriberi [\[77](#page-5-0)], Wernicke–Korsokof syndrome (alcohol abuse syndrome) [\[78](#page-5-0)] and bilateral visual loss or impaired colour perception [\[79](#page-5-0)]. Excess sulphur from humans and animals is excreted as sulphate. Small amounts of sulphur enter human and animals as a number of sulpha drugs, but discussion on these is beyond the scope of this review.

### Conclusion

Sulphur is an essential element for plants and humans, where most of it is present as sulphur containing amino acids (SAAs) cysteine and methionine. Although humans can synthesize some cysteine (hence semi essential), most of it and all methionine (essential, because humans cannot synthesize it) must be obtained from plant or animal foods. Sulphur deficiency leads to a number of ailments including joint stiffness and arthritis. RDA for SAAs in humans is 14 mg per kg body weight. Plants can synthesize both these SAAs, but should be able to get enough of S as sulphate from the soil. Adequate S fertilization of soils is the key for adequate S nutrition of the plants and humans. Sulphur fertilizers in India include elemental S, gypsum, pyrites and bentonite S. In addition S is also present in a number of nitrogen (ammonium sulphate, ammonium phosphate sulphate), phosphorus (single/ordinary super phosphate, triple/concentrated super phosphate), potassium (Potassium sulphate, potassium magnesium sulphate) and micronutrient fertilizers (zinc sulphate, copper sulphate, manganese sulphate).

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#### Compliance with Ethical Standards

Conflict of interest Both the authors declare that they do not have any conflict of interests for the publication of this review in the Proceedings of the National Academy of Sciences, Biological Sciences.

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