

Importance of Sulfur in Balanced Fertilization for Enhancing Crop Productivity through Sulfur Management in India

Yash Chauhan¹, Sandeep Singh², Shivam Pratap³, **Rajendra Singh Chauhan**⁴✉

¹Dept. of Soil Science & Soil Chemistry, RBS College, Bichpuri, Agra, U.P. 283105

²Subject Matter Specialist, Soil Science,

³Subject Matter Specialist, Agricultural Extension,

⁴Senior Scientist & Head, Krishi Vigyan Kendra, Bichpuri, RBS College, Agra (U.P.)

✉ chauhanyc2002@gmail.com DOI: 10.5281/zenodo.17331616

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Sulphur is now being recognized as the fourth major plant nutrient along with nitrogen (N), phosphorus (P), and potassium (K). It is listed as a secondary nutrient. Sulphur uptake by most crops is 10 to 15% of N uptake. In oilseed crops in general, uptake is about the same for S and P. In cereals, S uptake is about 60 to 75% that of P. It is now well accepted that Sulphur deficiency in Indian soils is widespread and a major constraint in the way of increasing crop productivity, produce quality, and farm income. On the whole, about 42% of soil samples analyzed have been found to be low/deficient in available Sulphur.

Oxidation states

Sulphur falls in the group of elements of the p-block with the atomic number 16 and atomic mass of 32.066. It has an electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^4$. It, therefore, has 6 active electrons and exhibits oxidation states -2, 2, 4, and 6. In soil solution, xylem, and vacuoles, it mainly occurs as SO_4^{2-} , while in organic molecules, it occurs as SH^- or $S=$.

Forms of S in Plants

Sulphur is absorbed by plant roots almost exclusively as sulphate (SO_4^{2-}). Small quantities of SO_2 can be absorbed through plant leaves and utilized within plants, but high concentrations are toxic. Thiosulphate ($S_2O_3^{2-}$) can also be absorbed by roots. When plants absorb thiosulphate ($S_2O_3^{2-}$), less energy may be required by the plant in conversion to S^{2-} and cysteine. SO_4^{2-} uptake is not inhibited by other anions (NO_3^- or $H_2PO_4^-$), but is inhibited by chromate and

selenate. Typical S concentrations in plants range from 0.2 to 0.5%. S content increases in the order *Gramineae* < *Leguminosae* < *Cruciferae*, where the typical S content of their seeds ranges from 0.17 to 0.19%, 0.25 to 0.30%, and 1.0 to 1.7%, respectively. Most SO_4^{2-} is reduced in the plant to $-\text{S}-\text{S}$ and $-\text{SH}$ forms, although SO_4^{2-} occurs in plant tissues and cell sap. Selected volatile S compounds in the mustard and onion families are responsible for their characteristic taste and smell.

Forms of S in Soil

A. Solution SO_4^{2-} : SO_4^{2-} is transported to roots by mass flow and diffusion. In soils containing ≥ 5 ppm SO_4^{2-} , the total S requirement of most crops can be supplied by mass flow. Solution concentrations of 3–5 ppm SO_4^{2-} are sufficient for most crops, although some high-S crops (rapeseed/canola, alfalfa, broccoli, etc.) require higher solutions. Sandy, low OM soils often contain < 5 ppm SO_4^{2-} . Except for soils in dry areas that may have accumulations of SO_4^{2-} salts, most soils contain less than 10% of total S as SO_4^{2-} . Large seasonal and year-to-year fluctuations in SO_4^{2-} can occur due to the influence of environmental conditions on organic S mineralization, downward or upward movement of SO_4^{2-} in soil water, and SO_4^{2-} uptake by plants. SO_4^{2-} content of soils is also affected by the application of S-containing fertilizers and wastes and by SO_4^{2-} deposition in precipitation and irrigation. Like NO_3^- , SO_4^{2-} can be readily leached through the soil profile. Increasing the quantity of percolation water increases potential SO_4^{2-} leaching. Leaching losses are lower in acid soils with appreciable exchangeable Al^{+3} and AEC to adsorb SO_4^{2-} .

B. Adsorbed SO_4^{2-} : Adsorbed SO_4^{2-} is an important fraction in highly weathered, humid regions soils containing large amounts of Al/Fe oxides. Many ultisol (red-yellow podzol) and oxisol (latosol) soils contain up to 100 ppm adsorbed SO_4^{2-} in subsoil and can significantly contribute to S nutrition of plants as root growth progresses. Mechanisms of SO_4^{2-} adsorption include:

- (-) charges on Fe/Al oxides or on clay edges, especially kaolinite, at low pH
- Adsorption to $\text{Al}(\text{OH})_x$ complexes
- (-) charges on soil OM at low pH

Reserves of adsorbed SO_4^{2-} in acid subsoil result from SO_4^{2-} leaching from surface soil, accounting for 30% of total subsoil S compared to 10% in surface soil. Although crops utilize subsoil-adsorbed SO_4^{2-} , S deficiency can occur during early growth stages until root development is sufficient to explore the subsoil. Once established, deep-rooted crops (e.g., alfalfa, clover, and lespedeza) readily access plant-available S in the subsoil.

C. Reduced Inorganic S: Sulfides do not exist in well-aerated soils. Under waterlogged, anaerobic conditions, H_2S accumulates as OM decays or from added SO_4^{2-} . S⁻² accumulation is limited primarily to coastal regions

dominated by saturated, submerged soils. The characteristic “rotten egg” scent of H_2S is readily detected. Similar reactions also occur under paddy rice culture. In normal submerged soils well supplied with Fe, H_2S liberated from OM is almost completely removed from solution by reaction with Fe^{+2} to form FeS , which undergoes conversion to pyrite (FeS_2). If H_2S is not subsequently precipitated by Fe and other metals, it escapes to the atmosphere.

D. Organic S: There is a close relationship between organic C, total N, and total S in soil. The C:N:S ratio in most well-drained, non calcareous soil is about 120:10:1. 4. Differences in C:N:S between soils are related to variations in soil-forming factors (parent material, climate, vegetation, and topography). The N:S ratio in most soils falls within the narrow range of 6 to 8:1. The organic S fraction governs the production of plant-available SO_4^{2-} . Three groups of organic S compounds in soil include *HI-reducible S*, *C-bonded*, and *residual S*.

- *HI—reducible S* is soil organic S that is reduced to H_2S by hydriodic acid (HI). The S occurs in ester and ether compounds that have C–O–S linkages (e.g., aryl sulfates, alkyl sulfates, phenolic sulfates, sulfated polysaccharides, and sulfated lipids). HI—reducible S represents 40–60% of total organic S.
- *Carbon-bonded S* occurs as S-containing amino acids (cystine and methionine), accounting for ~ 10-20% of total organic S.
- *Residual S* represents the remaining organic S fraction and generally represents 30–40% of total organic S.

Major causes of increasing S deficiencies

- Progressively greater removal of soil S as a result of higher agricultural production.
- Increase in depletion of soil S not only by the removal of grain, but also by the removal of stover/straw from the field.
- Low level of fertilizer use, in general, in pulses and oilseeds that have a higher requirement of S than cereals per unit of grain production.
- Depletion of soil S due to higher S removals as compared to S additions, resulting in negative S balances in many soils and cropping systems.
- Increased use of high-analysis fertilizers containing little or no S.
- Greater control of industrial emissions of S combined with the decreased use of high-S fuels.
- Declining reserves of soil S.
- Decreased use of pesticides in recent years
- Distinct possibility of leaching losses of soil S with the spread of flood irrigation to large areas and in areas receiving heavy rainfall.

Deficiency symptoms

Sulphur is not as mobile in plants as N, P, and K, and therefore S-deficient plants are generally stunted with short slender stalks. Because of less mobility there is not much translocation of S from older leaves to younger leaves. Sulphur deficiency in plants therefore shows up in younger leaves. As a contrast, N, P, and K deficiencies show up in older leaves. In rice, wheat, maize, sorghum, and cotton, interveinal yellowing of young leaves is observed; in sorghum, reddening of stem and leaf edges may also be observed. In rapeseed mustard, young leaves of S-deficient plants become pale and chlorotic with reddish lower parts and have a cupped appearance. In chickpea (gram), the S deficiency first appears on the middle trifoliate, which spreads to younger and then to lower leaves, finally making the entire foliage chlorotic. In soybean, sunflower, sesame, linseed, green gram (mung bean), black gram, and cowpea, laminae of S-deficient plants become pale and develop chlorosis on younger leaves, which eventually get bleached, while the older leaves remain green. Specific deficiency symptoms in some crops are described in Table 1.

Table 1: Specific sulphur deficiency symptoms in some crops

Crops	Deficiency symptoms
Wheat	General and interveinal yellowing of young leaves, older leaves remain green
Maize	Interveinal yellowing, followed by reddening of stems and leaves starting from leaf edges and gradually spreading to midrib; older leaves remain green
Sorghum	Interveinal yellowing, reddening of stems and leaf edges
Rice	General and interveinal yellowing of young leaves, older leaves remain green
Mustard	Leaves cupped inwards and reddening on underside
Sunflower	Pale leaves and inflorescence, shorter internodes, markedly smaller plants
Peanut	New leaves smaller, yellower, stand from petiole more erect, foliate leaves V-shape
Soybean	Pale yellow colour of new leaves at beginning but due to severe deficiency whole plant becomes yellow, smaller leaves and shorter internodes
Tobacco	New leaves uniform pale yellow green, extend with time to all parts of plants, smaller leaves, shorter internodes
Cotton	Yellowing of new leaves, reddening of petioles, stoopty leaves
Potato	General yellowing, reddening of stems, young leaves curl inwards (cupping)
Tomato	Interveinal yellowing of leaves, reddening of petioles & stems, shorter internodes, small leaves
Cabbage	Distorted leaves, in rolling of edges, reddening and purpling of leaves
Lettuce	General yellowing of leaves, leaves and plants of reduced size, thicker and stiffer
Alfalfa	Reduced tillering, new growth pale yellow-green, reddening of stems, leaflets more erect

Sulphur requirement of crops

Crops and cultivar within crops vary considerably in their S requirements (Table 2). The crops have been divided into three broad groups as per their S requirement. Group I includes Crucifers and Brassicas which have high S requirement (20 to 80 kg S ha⁻¹). Group II includes plantation crops, which have moderate S requirements (10 to 50 kg S ha⁻¹). Group III includes cereals forages and other field crops and has low S requirement (5 to 25 kg S ha⁻¹). As a thumb rule, kg S uptake/tonne grain production can be taken as: 3-4 kg for cereals (range 1-6), 5-8 kg for millets (range 3-11), 8 kg for pulses (range 5-13) and 12 kg for oilseeds (range 5-20).

The quantities of S uptake per tonne of economic produce of various crops under field conditions are presented in Table 3. The data indicates that there are large variations in S uptake per tonne of economic produce among different crops.

Table 2: Tentative classification of crops according to their S fertilizer requirement

Groups	Crop	Fertilizer requirement in deficient areas (kg S ha ⁻¹)
Group I (high)	Cruciferous forages	40-80
	Alfalfa	30-70
	Rapeseed	20-60
Group II (moderate)	Coconuts	50
	Sugarcane	20-40
	Clovers and grasses	10-40
	Coffee	20-40
	Cotton	10-30
Group III (low)	Sugarbeet	15-25
	Cereal forages	10-20
	Cereal grains	5-20
	Peanuts	50-10

Table 3: Sulphur removal by crops

Commodities	Crops	Kg Mg ⁻¹ grain/seed
Oilseeds	Groundnut	7.9
	Rapeseed/mustard	17.3
	Soybean	6.7

	Sesame	16.6
	Sunflower	11.7
Pulses	Chickpea	8.7
	Pigeonpea	7.5
	Greengram	12.0
	Blackgram	5.6
Cereals	Rice	3.0
	Wheat	4.7

Crop response to S

Response of crops to S application can be judged based on the nature and severity of deficiency which can be known, either through visual symptoms on plant foliage, plant analysis, soil analysis and/or response of crops to the applied nutrients. Significant yield increases due to S have been recorded in diverse soils for cereals, oilseeds, pulses, fodder crops, commercial crops, plantation crops, vegetables etc. Mean yield increases are in the range of 638-813 kg/ha for cereals, 168-428 kg/ha for pulses and 144-566 kg/ha for oilseeds. Some data on crop responses to S on the farmers fields in India are presented in Table 4.

Table 4: Crop response to S fertilization

Commodities	Crop	No. of trials	Increase in crop yield (%)	Agronomic efficiency kg ¹ /kg S	Relative efficiency (%)
Oilseeds	Sunflower	5	60	11	8
	Rapeseed/mustard	4	29	6	14
	Groundnut	16	23	8	10
	Soybean	9	25	12	13
Pulses	Pea	2	44	6	2
	Cowpea	2	20	9	7
Cereals	Rice	49	22	26	18
	Wheat	3	30	30	27
	Maize	17	19	27	9
	Sorghum	3	16	16	10
	Pearl millet	3	58	26	16

Fertilizers and Management Aspects of Sulfur

The earth's crust contains about 0.06% sulphur. It is mostly present as sulphides, sulphate and organic combinations with C and N. Another source is the industrial emission, which had now reduced due to stringent laws of controlling pollution. Common sulfur-containing fertilizers include ammonium sulfate, single superphosphate, gypsum, and elemental sulfur (Table 5). Sulphur requirements can be met easily through number of sources and methods (Table 6). All of them contain sulphur either in readily available form or in a form that is rendered available by environmental action.

Table 5: Sulphur sources

Fertilizer	S content (%)	Fertilizer	S content (%)
Ammonium nitrate sulphate	5.4	Gypsum	18.6
Ammonium phosphate	4.5	Commercial gypsum	13-14
Ammonium phosphate sulphate	15	Phosphogypsum	13-18
Ammonium sulphate	24	Iron pyrite	18-20
Ammonium sulphate nitrate	15	Potassium sulphate	18
Ammonium thiosulphate	26	Potassium magnesium sulphate	22
Copper sulphate	12.8	Magnesium sulphate	13
Manganese sulphate	14.5	Single superphosphate (SSP)	12
Elemental sulphur	85-100	Zinc sulphate	17
Agriculture grade sulphur	90	Ferrous sulphate	18.8

Table 6: Fertilizers and their management aspects

Fertilizer	Management aspects
Ammonium sulphate	Integrated N+S application, particularly suitable for top dressing to correct S-deficiency.
Single superphosphate	Intergraded P+S application for basal dose. Also for groundnut where Ca is needed for pod formation
Potassium sulphate	Integrated K+S application where crops are sensitive to Cl.
Ammonium P sulphate	Integrated N+P+S application as basal.

Elemental S products	Particularly suitable for fine-textured calcareous soils. Application 3-4 weeks before planting in moist and aerated soil. Smaller particle sized materials will be available to plants sooner.
Iron pyrites	Suitable for alkaline soils. Application on surface 3-4 weeks before planting in moist and aerated soil.
Gypsum	Suitable as S source, particularly for crops which also need high Ca
Zinc sulphate	Need dictated by Zn and to be compensated accordingly.

These sulphur fertilizers can be used to apply recommended rates of S application. Much of the S needs of a cropping system can be met if at least one S-containing fertilizer is included in the fertilizer schedule. Recommended rates of S application for major crops are provided in Table 7.

Table 7: Optimum rates of S fertilization for crops

Crop	S rate kg/ha	Remarks
Cereals	30-40	Rice, wheat, maize, sorghum
Pulses	30-45	Chickpea, Pea, Lentil, Urd bean, Mung bean, Pigeonpea
Oil seeds	30-60	Groundnut, Soybean, Mustard, Linseed, Sunflower, Safflower
Fodder	25-50	Maize, Sorghum, Cowpea, Egyptian clover
Tubers	25-60	Potato, Cassava
Spices	40-50	Onion, Garlic

Sulphur and crop quality

Sulphur has profound effect on crop quality which is mainly due to its involvement in protein synthesis, oil production and in optimizing the N: S ratio of fodders and forages for efficient animal production. Sulphur is important for protein production by virtue of its being a constituent of amino acids methionine, cystine and cysteine, which are the building blocks of proteins. Sulphur is a part of oil compounds, and its application leads to an increase in the oil content of seeds in most oilseeds, thus fetching higher profit for the farmer (Table 8).

Table 8: Effect of applied S on oil content and oil yield of oilseeds

Crop	Treatments applied S kg ha ⁻¹	Oil %	Oil yield kg ha ⁻¹	Protein %	Protein yield kg ha ⁻¹
Mustard	0	35.0	541	18.7	289
	40	37.3	699	19.5	367
Soybean	0	19.7	340	35.2	609
	40	22.1	530	36.4	907
Linseed	0	41.5	397	NA	NA
	60	44.4	579	NA	NA
Groundnut	0	42.7	668	27.8	435
	40	44.5	858	30.3	584

Source: Tiwari and Gupta (2006)

Apart from protein and oil content of crops, S is also responsible for other crop quality characters such as improving starch content of tubers, baking quality of wheat, sugar recovery in sugarcane, enhancing marketability of crops, increasing head size in cauliflower, improving quality of chillies, increasing the morphine, codeine, and the bacine and decreasing narcotine content in opium and improving the quality of tea.

Interaction of S with other nutrients

Nutrient interactions have a great role to play in determining the course of outcome of balanced and efficient fertilizer use which are of high interest in fertilizer management. Balance is the prerequisite of high efficiency and is the backbone of efficient fertilizer use. The effect of S on crop performance also depends on the level of other nutrients. Interaction of S with other nutrients can be synergistic, antagonistic or absent. At the practical level, the interactions involving N, P, B and Zn are of greatest importance. The positive interaction should be fully exploited for maximum gains in terms of yield and quality. The synergistic nature of P and S interaction is equally valuable for farmers as most of them are not using high rates of P application at which antagonism are observed. The interaction between S and B deserves special attention for oilseed production that may be one reason why B applications are recommended for oilseeds in most cases. The Zn-S interaction may turn out to be like P-S interactions that is, dependant on the rates of nutrients involved.