Sulphur fertilization and food quality—A review

RAJENDRA PRASAD1 AND Y.S. SHIVAY2

ICAR-Indian Agricultural Research Institute, New Delhi 110 012

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ABSTRACT

About 42% of Indian soils are deficient in sulphur(s) and good yield responses to S fertilization are reported in cereals, pulses and oilseeds. However, little information is available in the country on the effect of S fertilization on quality of grain, seed or oil. Soil or fertilizer S is the main source of S for the plants, which in part being the main source of S-containing essential amino acid methionine and essential vitamin thiamine for the humans. In addition, plants also synthesize a number of metabolites, such as alliin/ allicin, glucosinolates (GSLs) and methylsulfonylmethane (MSM), which have great medicinal value. Studies on the effect of S fertilization on the content of essential amino acids and vitamins and some of the discussed metabolites in grain or seed of food crops will go a long way in enhancing their commercial value and in improving human health. Effects of S fertilization on the composition of fatty acids are also suggested. Development of such analytical facilities at agricultural institutes/ universities will also help in developing varieties with higher contents of desired S compounds.

Key words : Alliin, Cysteine, Biotin, Erucic acid, Essential amino acids, Essential vitamins, Fatty acids, Glucosinolates, Methionine, Methylsulfonylmethane, Thiamin

In the last 25 years or so, sulphur has received considerable attention in India and competes well with zinc for the fourth position as an important plant nutrient after N, P and K. Based on the analysis of about 135,000 soil samples it was concluded that about 42% of Indian soils are deficient in S (Singh, 2001). The number of districts suffering from varying degree of S deficiency has increased from 70 in 1991 to over 300 in 2011 (Tandon, 2011). The main reasons are continued high harvests of crops, substitution of sulphur-containing fertilizers, such as ammonium sulphate and single superphosphate by urea and diammonium phosphate (DAP) and almost nil use of organic manures. A number of field experiments were therefore conducted in India under All-India Coordinated Research Project on Micro and Secondary Nutrients of the Indian Council of Agricultural Research and The Sulphur Institute, Washington, DC-Fertilizer Association of India, New Delhi-International Fertilizer Industry Association, Paris (TSI-FAI-IFA) Project on Sulphur in Balanced Fertilization (Tewatia et al., 2006). The average increase in grain/ seed yield owing to an application of 20–40 kg S/ha was 750 kg/ha (22 kg grain/kg S) in cereals, 403 kg/ha (7 kg seed/kg S) in oilseeds and 252 kg/ha (7 kg seed/kg S) in pulses (Tandon, 2011). More information on yield response to S fertilization, kinds of S fertilizers and rate, method and time of their publication can be obtained from the review on this subject by Tewatia et al. (2014). Most information is, however, restricted to yield of grains or seeds of the crops and oil content in seed and oil yield in the case of oilseed crops and S uptake by different crops. Presently, very little information is available on the effect of S fertilization on grain/ seed/ oil quality or the content of any other S compounds in the Indian literature. This review, therefore, presents the information available on the subject mostly from foreign countries for the benefit of Indian researchers and hopes to initiate some research in India on this important topic.

The main reason for this is that we have not been able to pay much attention to the quality of farm food products, because these are still preoccupied with the shortage of one or the other food commodity in the country. For example, the shortage of cereals in 1960s (Paddock and Paddock, 1967), of edible oils in 1990s and later (Sharma, 2013) and of late of pulses (Knight, 2000; Verma, 2016). Even the temporary shortage of onions (Allium cepa L.) has created problems for the Government of India (Kazmin, 2010; Bhowmick, 2013). On the contrary, the consumer in the advanced countries is very much concerned about the quality of food products and each packet

1Corresponding author’s Email: rajuma36@gmail.com
2Ex-National Professor (ICAR), 3Professor and Principal Scientist, Division of Agronomy, ICAR-Indian Agricultural Research Institute, New Delhi 110 012
in the market contains detailed analysis of the contents.

Major sulphur compounds in plant products include S-containing amino acids cysteine, cystine and methionine, vitamins, such as thiamine and biotin and metabolites alliin, allicin, diallyl-disulfide (DAACDS) and glucosinolates (Prasad, 2014). The available information on the effects of S fertilization of crops on the amounts of these compounds is briefly reviewed.

**Sulphur-containing amino acids (SAAs)**

About 70% of sulphur in plants is present as amino acids. Of the 2 sulphur-containing amino acids (SAAs) making up different proteins, methionine is considered essential, while cysteine is considered semi-essential for humans (Furst and Stehle 2004; Prasad and Shivay, 2016). Bulk of the SAAs must be obtained through diet. The Recommended Dietary Allowance (RDA) (mg/kg/day) for SAAs (methionine + cysteine) is 58 for 3–4 month infants, 27 for 2-year-old children, 22 for 10-12 year old and 13 for adults (Parcell, 2002).

Sulphur fertilization is reported to increase the content of cysteine and methionine in wheat (*Triticum aestivum* L.), spinach (*Spinacea oleracea* L.) and pepper (*Capsicum* sp.) (Table 1); however, Losak et al. (2010) reported that S fertilization increased methionine content by 18-40% in onion, but there was no increase in cysteine content. Losak et al. (2008) also reported that S fertilization reduced the cysteine and methionine content in the tubers of kohlrabi (*Brassica oleracea* var. gongylodes L.).

In addition to its role in human nutrition, methionine is the precursor of ethylene, which is responsible for fruit ripening, an important physiological process in plant from the viewpoint of human nutrition. The fruits which ripen due to ethylene are known as climacteric and include the viewpoint of human nutrition. The fruits which ripen due to ethylene are known as climacteric and include the various *Actinidia* L., apricot (*Prunus armeniaca* L.), avocado (*Persea americana* Mill.), cantaloupe or muskmelon (*Cucumis melo* var. cantalupo Ser.), fig (*Ficus carica* L.), kiwi fruit (*Actinidia* sp.) and tomato (*Solanum lycopersicum* L.), etc (Kader, 1999). The bulk of the fruit industry handles (harvest, transport and storage) climacteric fruits, in which ripening can be controlled by concentration and exposure to ethylene (Dang et al., 2006). In India, a plastic cover is placed over unripe fruits and calcium carbide is placed in open containers in strategic positions. Moisture from the air reacts with calcium carbide and produces ethylene.

**Nitrogen: sulphur ratio in grains**

One of the major effects of S deficiency is the reduction in N : S ratio in grain. Coyle and McAleese (1970) reported that N: S ratio declined from 11–28 to 10–17 in wheat (*Triticum aestivum* L.) and from 26–28 to 8–10 in barley (*Hordeum vulgare* L.) grain due to sulphur fertilization. Lerner et al. (2006) also observed that S fertilization caused significant changes in N : S ratio in wheat. Zhao et al. (1999) reported that when S is deficient, it reduces S-containing amino acids in wheat, which creates an imbalance between high molecular weight (HMW) and low molecular weight (LMW) glutenin sub-units (Gupta et al., 1993) reducing bread-making quality of wheat. Randall et al. (1981) reported that when S concentration in wheat grain is below 1.2 mg/g and N : S ratio is above 17:1, the grain is deficient in S and both yield and quality are affected. Unger et al. (2002) also observed that a high N : S in wheat grain was associated with low loaf height and volume in bread. In baking higher cysteine residues in wheat flour produce a more extensible and pliable dough due to disulphide bonds leading to better-quality bread (Alary and Kobrechel, 1987; Flaten, 2004). In rice also, Shivay et al. (2014) found that application of 45 kg S/ha reduced the N : S ratio in grain from 9.77 in check (no S) to 7.79.

**Sulphur-containing vitamins**

Thiamine (or thiamin or vitamin B1) and biotin (or B7 or vitamin H or coenzyme R) are two sulphur-containing amino acids. Thiamin is one of the components of vitamin B complex. It is water-soluble. Thiamine pyrophosphate or thiamin diphosphate is a coenzyme involved in the catabolism of sugars and amino acids (Fattal-Valevski, 2011).

<table>
<thead>
<tr>
<th>Crop</th>
<th>S conc. (unit)</th>
<th>Cysteine</th>
<th>Methionine</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>−S</td>
<td>+S</td>
<td>−S</td>
</tr>
<tr>
<td>Winter wheat</td>
<td>g/kg grain</td>
<td>1.74–2.75</td>
<td>1.76–3.10</td>
<td>1.26–2.11</td>
</tr>
<tr>
<td>Spring wheat</td>
<td>g/kg grain</td>
<td>4.14</td>
<td>4.39</td>
<td>2.90</td>
</tr>
<tr>
<td>Spinach</td>
<td>g/kg grain</td>
<td>0.32</td>
<td>0.45</td>
<td>0.41</td>
</tr>
<tr>
<td>Pepper</td>
<td>g/kg DM</td>
<td>0.11</td>
<td>0.35</td>
<td>0.11</td>
</tr>
</tbody>
</table>

DM, Dry matter
Thiamin is involved in the biosynthesis of DNA and RNA and neuro-transmitters acetylcholine and γ-aminobutyric acid (GABA). It is on the list of World Health Organization (WHO) as essential medicines needed in the basic health system (WHO, 2013). Just like methionine, only plants, bacteria and fungi can synthesize thiamine and humans must obtain it from the food that they eat. Cereal grains are the most important source of thiamine. In cereal grains, thiamine is concentrated in the outer layer and germ, which are generally removed in the refining process. Yeast and yeast extract are the most highly concentrated source of thiamine. Leavened (bakery made) wheat bread is, therefore, richer in thiamine than unleavened bread (Indian chapati). The RDA or thiamine is 1.4 mg.

Human nervous system is particularly sensitive to thiamine deficiency and well-known diseases caused by this deficiency include beriberi (Shils et al., 2006; Spinazzi et al., 2010), Wernicke-Korsakof syndrome (alcohol abuse syndrome) (Krill, 1996) and optic neuropathy (bilateral visual loss, impaired colour perception) (Spinazzi et al., 2010). Nitrogen fertilization is reported to increase thiamine content in plants (Mozafar, 1993); this of course is possible only when adequate S is available in soil. Biotin is a coenzyme involved in the synthesis of fatty acids, isoleucine and valine and in gluconeogenesis. In humans, intestinal bacteria produce enough biotin and therefore there is no RDA for it, although pregnant females may need biotin supplement. Leafy green vegetables are a good source of biotin. Biotin is considered to be involved in strengthening of hair and nails.

Oil content and quality in oilseeds

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 (Malhi and Leed, 2000; Kumar et al., 2001; Subhani et al., 2003; Gupta and Jain, 2006; Sen et al., 2006; Jankowski et al., 2008), groundnut (Reddy and Requeeba, 2000; Maity and Giri, 2003), sunflower, (Helianthus annuus L.) (Sarkar and Mallick, 2009) and soybean (Glycine max) (Aulakh and Pasricha, 1997). Information on the influence of S fertilization on the quality of oil in Indian mustard (Brassica juncea (L.) Czernj. & Cosson]) is available only from Ray et al. (2015). They reported that the content of fatty acids in oil of Indian mustard was not significantly influenced by S fertilization (30 to 60 kg S/ha); the values for different fatty acids were: oleic (C18 : 1) 14.8–15.8%; linoleic (C18 : 2) 12.5–13.0%; linolenic (C18 : 3) 9.1–9.4% and erucic (C22 : 1) 48.6–50.2%. El-Beltagi and Mohammed (2010) reported that fatty acid content in 5 cultivars (‘Pactol’, ‘Silvo’, ‘Topas’, ‘Serw 4’ and ‘Serw 6’) of oilseed rape or canola (Brassica napus L.) was: oleic 56.31–58.67%; linoleic 10.52–13.74%; α-linolenic 8.83–10.32% and erucic 0.51–0.91%. High value of erucic acid in Indian mustard may be compared to less than 1% in canola. Safe limits for canola [‘Can’ for Canada, ‘o’ for oil, ‘l’ for low and ‘a’ for acid] are 2% of erucic acid in oil and 30 µmol/g for glucosinolates in oil-free meal (Grombacher and Nelson, 1992). Canola has also the lowest saturated fat content (Grombacher and Nelson, 1992). Both erucic acid and glucosinolates are responsible for pungency and bitterness in oil and meal and are harmful for human and animal health (Dupont et al., 1989; Muhammed et al., 1991).

Important Metabolites

Alliin/ Allicin

Alliin, a sulfoxide, is a derivative of cysteine and is a natural constituent of fresh garlic and a precursor of alliin (Iberi, 1990). Allicin is produced from alliin when fresh garlic is chopped or crushed with the help of enzyme allinase. Alliin and allinase are present in separate compartments of the cell and react only when the compartments are broken. It is responsible for the pungency in onion, which can lead to tears in eyes in some people, when onion is chopped. Allicin is responsible for the fresh aroma of fresh garlic, Allium sativum (Kourounakis and Rekka, 1991) and is fairly unstable and soon changes into a series of sulfur compounds including diallyldisulfide. Allicin provides protection to the garlic plants from insect pests. Allicin has anti-bacterial (Cutler and Wilson, 2004), anti-viral (Block, 2010) and anti-protozoal (Salama et al., 2014) properties. It reduces fat deposition (Abramovitz et al., 1999), cholesterol absorption (Nijjar et al., 2010) and blood pressure (Silagy and Neil, 2003; Elkayam et al., 2003). It has also anti-inflammatory and anti-oxidant properties (Banerjee et al., 2001; Bautista et al., 2005). Raw garlic, powdered garlic supplements are equally efficacious in curing human health problems (Choudhary and Tomer, 2013).

Diallyl-disulfide (DADS) is derived from garlic and few other genera of Alliaceae and some of the benefits of garlic, such as prevention of colorectal cancer (Jo et al., 2008) are due to it. It is used as a flavouring agent and improves the taste of meat, vegetables and fruits. It is also an environmentally benign nematicide (Block, 2010). Sulphur fertilization increased alliin content in leaves and bulbs of onion and garlic (Bloe, 2005). Bloe et al. (2011) also reported that alliin content in peeled garlic cloves increased 2.3 fold from 11.4 mg/g DM to 26.8 mg/g DM after 83 days of storage when the crop received an application of 45 kg S/ha. Imen et al. (2013) reported that in a solution culture study alliin content in rosy garlic, an edible endemic species in Northern Africa (Allium
roseum), increased from 0.859 g/kg fresh weight with 0.01 mmol/L sulphate solution to 2.285 g/kg fresh weight with 1.5 mmol/L sulphate solution.

Glucosinolates

Glucosinolates (GSLs) are natural pungent metabolites in plants of family Brassicaceae (rapeseed/mustard, cabbage, broccoli, horse radish etc.). These metabolites contain glucose and amino acids and are water soluble. About 132 GSLs have been reported so far. When the plant material is cut, chewed or crushed, the enzyme myrocinase cleaves off glucose from GSLs in the presence of water and releases isothiocynates (commonly known as mustard oil) (Glawisching et al., 2003), which are responsible for pungency and defense mechanism against insect-pests (Wolfsen, 1982; Wittstock et al., 2004) and increased resistance to some diseases (Rosa et al., 1997). In the plants, the enzyme myrocinase and GSLs are kept in separate compartments but come in contact when the plant tissue is cut or crushed. Some GSLs are toxic (mainly as goitrogens) to humans and animals at high doses (Dupont et al., 1989; Muhammed et al., 1991). However, recently GSLs have been reported to be involved in mitigating cancer (Beecher, 1994; Williamson et al., 1998; Das et al., 2000; Hayes et al., 2008) and consumption of large amounts of vegetables especially broccoli (Brassica oleracea var. italic Plenck), Brussels sprout (Brassica oleracea var. gemmifera DC.) and cabbage (Brassica oleracea var. capitata L.) is being encouraged (Fahey and Stephenson, 1999). Zhao et al. (1993a) observed that nitrogen application decreased GSL content in seeds of double low (Brassica napus L.) in the absence of S but increased it when adequate S was applied along with nitrogen. They (Zhao et al., 1993b) also reported that the pod walls were the major site for the biosynthesis of GSL and a metabolic block in the pathway of GSL biosynthesis is responsible for low GSL content in the seeds of double low varieties of Brassica napus L. Josefsson (1970) and Schung (1989) also reported that the S fertilization increased GSLs in rapeseed (Brassica napus L.). A number of other researchers have also reported that S fertilization increases GSL content in rapeseed by 20–30% (Fismes et al., 2000; Chen et al., 2006).

As regards vegetable turnip rape (Brassica rapa L.), Kim et al. (2001) observed that application of lower doses of N with adequate S fertilization increased GSL concentration in edible portion; total GSL content varied from 28 to 80 µ moles/g DM and gluconapin and glucobrassicanapin were the main GSLs, which were also responsible for the bitterness. Some data on the effect of S fertilization on GSL content in rapeseed-mustard from the Indian sub-continent are in Table 2. The GSL content in Brassica juncea (Indian mustard) was not affected by S fertilization but was much higher than that in Brassica napus (canola) in which S fertilization increased GSL content significantly. Higher GSL content in Indian mustard is partly responsible for its higher pungency and bitterness. As regards vegetables, Rosen et al. (2005) reported that in cabbage (Brassica oleracea var. capitata), an application of 110 kg S/ha increased GSL content to 284.5 µmol/100 g from 225.7 µmol/100 g in check (no S). On the other hand, it decreased from 283.7 µmol/100 g to 226.8 µmol/100 g, when N application was increased from 125 to 250 kg/ha. Perez-Ballibrea et al. (2010) found that sulphur fertilization increased GSLs in broccoli (Brassica oleracea var. italica) sprouts during germination.

Methylsulfonylmethane (MSM)

Methylsulfonylmethane (MSM) (an oxidation product of dimethylsulfone) is found in fruits, corn, tomatoes, tea (Camellia sinensis), coffee (Coffea arabica L.), alfalfa (Medicago sativa L.), human, bovine milk and in human urine (Richmond, 1986). It is being used for treating arthritis, hyperacidity, parasites, constipation, and allergies.

Table 2. Oil content and GSL content in brassicas as influenced by sulphur fertilization

<table>
<thead>
<tr>
<th>S applied (kg/ha)</th>
<th>Oil content (%)</th>
<th>GSL content (µmol/100 g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brassica napus</td>
<td></td>
<td></td>
<td>Ahmed et al. (2007)</td>
</tr>
<tr>
<td>0</td>
<td>41.9 c</td>
<td>13.6 c</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>42.5 b</td>
<td>16.9 c</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>42.8 a</td>
<td>20.9 b</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>42.6 b</td>
<td>24.6 a</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brassica juncea</td>
<td></td>
<td></td>
<td>Ray et al. (2015)</td>
</tr>
<tr>
<td>0</td>
<td>35.3 a</td>
<td>42.9</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>37.7 b</td>
<td>43.0</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>39.1 b</td>
<td>42.9</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>41.3 a</td>
<td>43.1</td>
<td></td>
</tr>
</tbody>
</table>

Values followed by same letter did not differ significantly.
and for immunomodulation (Parcell, 2002). No information on the effect of S fertilization on MSM is available.

Thus, sulphur fertilization affects the content of S-containing amino acids and vitamins and metabolites alliin/ allicin, glucosinolates and methylsulfonylmethane in seeds/ grains and other plant parts, but this information has not been generated in India and needs to be attended in the interest of human health, higher profits to the farmers and development of crop varieties with better quality.

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