Chapter 10

The Role of Sulfur in Plant Abiotic Stress Tolerance: Molecular Interactions and Defense Mechanisms

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Abstract Sulfur (S) is an essential macronutrient in plants that serves numerous plant functions and is vital for the metabolic processes. Moreover, it is the constituent of some essential amino acids and metabolites. Recent studies have provided the notion that S not only improves the productivity of plants under normal condition but also protects them from abiotic stresses like salinity, drought, and toxic metals/metalloids. Different S compounds directly act as antioxidants or modulate antioxidant defense system. Among them, glutathione (GSH) is regarded as one of the powerful antioxidants and stress protectors. Interactions of S with other biological molecules afford stress signaling to provide defense against environmental stresses. However, the S uptake, translocation, and mechanisms of action in plants under stressful conditions are still under research. The recent progress on the roles of S in conferring abiotic stresses and related literature is presented in this chapter.

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Abbreviations

ABA	Abscisic acid
ACS	1-Aminocyclopropane carboxylic acid (ACC) synthase (ACS)
APK	APS kinase
APR	Adenosine-5′-phosphosulfate reductase
APS	Adenosine-5′-phosphosulfate
APX	Ascorbate peroxidase
AsA	Ascorbate
ATP	Adenosine triphosphate
ATPS	ATP sulfurylase
CAT	Catalase
CBL	Cystathionine β-lyase
CGS	Cystathionine γ-synthase
CSC	Cysteine synthase complex
Cys	Cysteine
Cyst	Cystathionine
DHA	Dehydroascorbate
DHAR	Dehydroascorbate reductase
EF-TU	Elongation factor-thermo unstable
GAPDH	Glyceraldehyde-3-P-dehydrogenase
GB	Glycine betaine
GCL	Glutamate-cysteine ligase
Gly I	Glyoxalase I
Gly II	Glyoxalase II
GPX	Glutathione peroxidase
GR	Glutathione reductase
GRX	Glutaredoxins
GSH	Glutathione
GSHS	Glutathione synthetase
GSSG	Oxidized glutathione
GST	Glutathione S-transferase
h-GSH	Homo-GSH
JA	Jasmonates
LOX	Lipoxygenase
MDA	Malondialdehyde
MDHAR	Monodehydroascorbate reductase
Met	Methionine

MG	Methylglyoxal
MRNA	Messenger ribonucleic acid
MS	Methionine synthase
NaHS	Sodium hydrosulfide
NPT	Nonprotein thiol
OAS	O-Acetylserine
OASS	O-Acetylserine sulfhydrylase
OAS-TL	OAS(thiol)lyase
OPH	O-Phosphohomoserine
PAPS	3-Phosphoadenosine-5-phosphosulfate
PCs	Phytochelatins
PEG	Polyethylene glycol
POD	Peroxidase
POX	Peroxidases
ROS	Reactive oxygen species
RT-PCR	Reverse transcription polymerase chain reaction
RuBisCO	Ribulose-1,5-bisphosphate carboxylase/oxygenase
SAT	Serine acetyltransferase
Ser	Serine
SiR	Sulfite reductase
SLG	*S*-D-Lactoylglutathione
SOD	Superoxide dismutase
SULTR	Proton/SO_4^{2-}cotransporter in plants
SURE	Sulfur-responsive element
TBARS	Thiobarbituric acid reactive substances
TRX	Thioredoxins
γ-ECS	γ-Glutamylcysteine synthetase
γ-GluCys	γ-Glutamylcysteine

10.1 Introduction

Water stress, temperature stress, salinity stress, metal stress, nutrient deficiency, UV radiation, and ozone stress are being the most common abiotic stresses throughout the world. Growth and phenological pattern and reproductive development are hampered due to obstruction in water and nutrient uptake, photosynthetic activity, mitochondrial reaction, and plasma membrane transportation of cell organelles in plants grown under abiotic stress condition (Hasanuzzaman et al. 2012, 2017a). The intensity of these stresses is increasing day by day at an alarming rate, and because of that, the abiotic stresses become a matter of immense anxiety to plant productivity. That is why research on abiotic stress effects and how to decrease abiotic stress effects on plants have been increased noticeably previously. Inherent struggling capacity for survival in the era of abiotic/biotic stresses determines the healthy growth of any organisms including plants. Naturally, like any other organisms, plants' genetic potential determines the ability to struggle and survive against abiotic stresses.

Keen observation of plant processes and biomolecules within plants has recognized sulfur (S) as one of the most abundant elements in organic structures. Sulfur is the fourth most important plant nutrient after N, P, and K. Sulfur after taken up by the root in the form of sulfate (SO_4^{2-}) integrated into cysteine (Cys). Cysteine acts as a precursor or donor of key S compounds such as methionine (Met), *S*-adenosylmethionine, glutathione (GSH), homo-GSH (h-GSH), phytochelatins (PCs), sulfolipids, iron-sulfur clusters, allyl Cys, and glucosinolates, which play role in plant developmental processes and/or stress adaptation processes (Rausch and Wachter 2005; Khan et al. 2014; Anjum et al. 2015). Glutathione and h-GSH are involved in stress signal transmission. Several key stress metabolites such as ethylene (C_2H_2) are controlled by *S*-adenosylmethionine. Sulfur compound-mediated function of ATP-S has been reported for stress tolerance response (Anjum et al. 2015). Cysteine improved growth and lessened oxidative stress by modulating cellular redox status and antioxidant defense in barley (Genisel et al. 2014). Sulfur-induced GSH synthesis decreased reactive oxygen species (ROS) and improved photosynthetic efficiency and growth in salt-affected barley (Astolfi and Zuchi 2013). Higher content of S uptake increased accumulation of proteinogenic and non-proteinogenic thiols which improved cadmium (Cd) tolerance (Sun et al. 2007; Lancilli et al. 2014). The S deficiency reduces chl (chl) content, photosystem (PS) II efficiency, and performance of ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCo) (Lunde et al. 2008). Sulfur moiety of Cys can regulate disulfide bond of proteins, which affect the structure of the Fe-S cluster and function of photosynthetic apparatus and electron transport chain (Rochaix 2011). Glyceraldehyde-3-P-dehydrogenase (GAPDH), malate dehydrogenase (MDH), and elongation factor-thermo unstable (EF-TU) are some Cys-bearing protein having oxidative thiol modification functions (Leichert et al. 2008). Ethephon and N jointly augmented S-mediated ethylene and diminished glucose sensitivity, thus improving photosynthesis and growth (Iqbal et al. 2011).

Sulfur has been reported to improve antioxidant defense and metal chelation under Cd stress. In the presence of S, the GSH content, ratio of GSH and glutathione disulfide, GSSG (GSH/GSSG), nonprotein thiols (NPTs) and PCs, ascorbate (AsA) content, ratio of AsA and dehydroascorbate, DHA (AsA/DHA), activities of ascorbate peroxidase (APX), glutathione reductase (GR), and catalase (CAT) improved in Cd-affected Indian mustard plant. Moreover, superoxide dismutase (SOD) expression was upregulated that decreased $O_2^{\bullet-}$ (Bashir et al. 2015). Sulfur addition decreased the As uptake and content in the shoot and modulated thiol metabolism, glycolysis, and amino acid in rice (Dixit et al. 2015a). Thus, S is proved as a potent plant nutrient for plant developmental processes.

There are some sporadic researches on the effect of S on abiotic stress alleviation in plants. Few research findings said about signaling function of S and its derivatives. Based on available research findings, it is obvious that S is a potent molecule that functions in plant developmental and abiotic stress adaptation processes. It is necessary to extend research with S to exploit its function thoroughly. So, a comprehensive review presenting available information and research updates of S will be a base for filling up gaps of previous or existing researchers and exploring new research areas. Therefore, this review concentrates and gathers information on various aspects of S in plants including S metabolism, biological roles and roles in abiotic stress condition of S and its derivatives in plants, and molecular approaches in regulating S status.

10.2 Biological Role of Sulfur in Plants

Plants require a right combination of nutrients to survive, grow up, and reproduce. Sulfur is considered as an indispensable plant macronutrient required by all crops for their normal growth and development (Fig. 10.1). Sulfur is uptaken from the soil solution by the plant principally in the form of SO_4^{2-} (Davidian and Kopriva 2010; Capaldi et al. 2015). Moreover, different S-containing amino acids provide S to the plants. Very little amount of S is supplied from the atmospheric SO_2 and hydrogen sulfide (H_2S) where SO_2 is absorbed by leaf and fruit of plant (Mazid et al. 2011), and H_2S is absorbed through stomata of the leaf (Riemenschneider et al. 2005). Sulfur has an immense function in fundamental processes of plants such as electron transport, cellular structure, and regulation of different metabolic pathways (Capaldi et al. 2015). Sufficient S nourishment to the plants improves photosynthesis by increasing chl formation and contributes to growth and development of plants (Scherer 2008). Furthermore, it has insightful relation with N assimilation. Carciochi et al. (2017) reported that optimum S in the growing media of wheat (Z51) increased nitrogen uptake and improved the root growth, which played a central role in improving yield (Salvagiotti et al. 2009). Sulfur is also a component of various amino acids (Cys, Met etc.), antioxidants, sulfolipids, proteins, and enzymes that

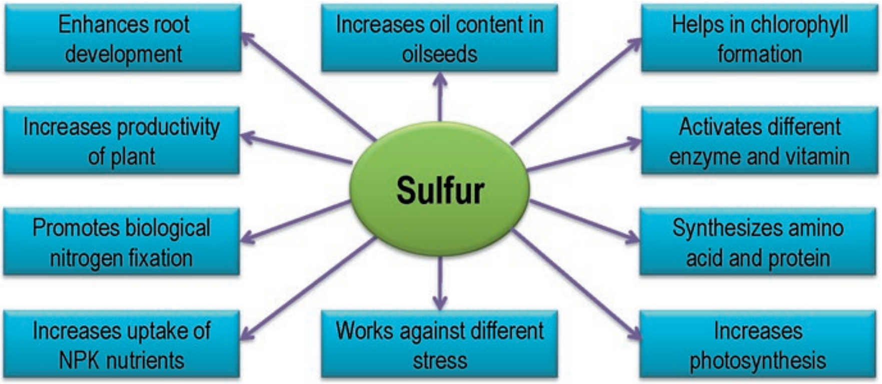

Fig. 10.1 Different biological functions of S in plants

regulate photosynthesis and biological nitrogen fixation and assimilation by the plant (Abdallah et al. 2010; Capaldi et al. 2015). Also, S is an important constituent of Fe-S clusters, lipids, polysaccharides, and a wide range of biomolecules, for instance, vitamins, cofactors, peptides, and different secondary products (allyl cysteine sulfoxides, glucosinolates, etc.) (Nocito et al. 2007; Iqbal et al. 2012). Sulfur is essential for the vegetative development and production of oil and proteins of the plant especially in oilseed crops (D'Hooghe et al. 2013; Mária et al. 2017). Many reports demonstrated the influential effect of S on the yield and total oil content of oilseed crops (Jankowski et al. 2008; Egesel et al. 2009). Sulfur is also responsible for the production of glucosinolates in both the vegetative parts and the seed of oilseed crops, which determine the pungency of plants (Walker and Booth 2003). Sulfur is known to interact with almost all essential macro- and micronutrients by influencing their uptake and utilization (Abdin et al. 2003).

Besides playing an imperative role in growth, development, and productivity of higher plants, S has an immense role to develop stress tolerance in plants (Nazar et al. 2011; Osman and Rady 2012). Elemental sulfur, H_2S, GSH, PC, S-rich proteins, and various secondary metabolites are important S-containing defense compounds that are very important for plant survival during biotic and abiotic stresses. The development of these compounds in the plant is intimately linked to the supply, demand, uptake, and assimilation of S (Capaldi et al. 2015).

10.3 Sulfur Metabolism in Plants

Plants produce many S-containing metabolites of diverse groups: amino acids (Cys, Met), antioxidants (GSH), vitamins (biotin, thiamine), and secondary metabolites (glucosinolates, alliinase). Although these metabolites contain S, their roles in a biological system are functionally distinct. Thus, S metabolism in plants is a topic of interest to explain how S is assimilated into a living system from the environment (Fig. 10.2). Like other macronutrients, S is taken up by the plant through the root as sulfate (SO_4^{2-}). To be incorporated in the metabolic pathways, sulfate is first activated by ATP sulfurylase to yield adenosine-5′-phosphosulfate (APS) which is then reduced to sulfite (SO_3^{2-}) by APS reductase. Finally, sulfite reductase converts the sulfite into sulfide that reacts with O-acetylserine in the presence of O-acetylserine lyase (OAS-TL) to produce Cys (Fig. 10.2). From Cys, GSH is produced by two-step ATP-dependent reactions, where Cys is converted to γ-glutamylcysteine by γ-glutamylcysteine synthetase (also known as glutamate-cysteine ligase, GCL), and the subsequent reaction is catalyzed by glutathione synthetase. Cysteine also serves as a precursor of Met. Homocysteine is produced from cysteine and O-phosphohomoserine by the action of cystathionine γ-synthase (CGS) and cystathionine β-lyase (CBL) (Fig. 10.2). Homocysteine is then converted into Met by methionine synthase (MS). Methionine is considered as the main precursor of glucosinolate synthesis pathway by initiating the side chain elongation reaction to Met (Hirani et al. 2012). Cysteine conjugated with the tryptophan-derived complex is

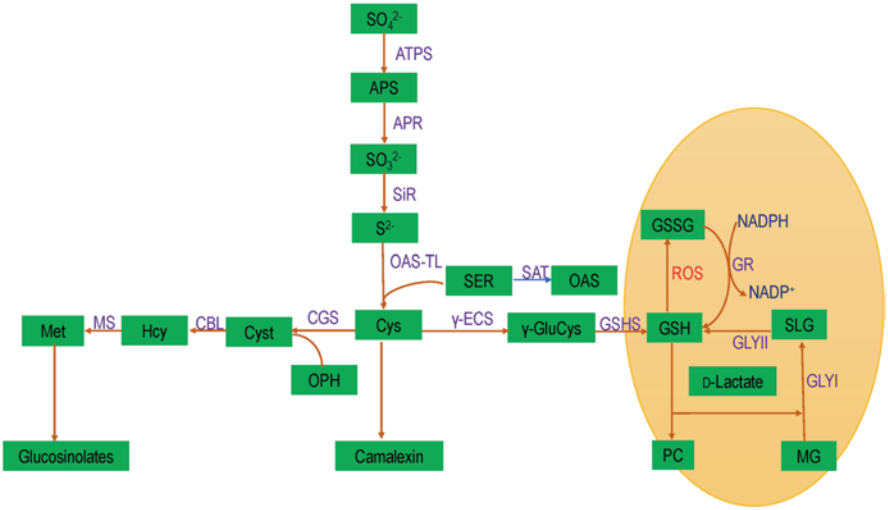

Fig. 10.2 Sulfate metabolism in plant. *APS*, adenosine-5′-phosphosulfate, *Cys* cysteine, *Cyst* cystathionine, *γ-GluCys* γ-glutamylcysteine, *GSH* glutathione, *GSSG* oxidized glutathione, *Hcy* homocysteine, *MG* methylglyoxal, *OAS* O-acetylserine, *OPH* O-phosphohomoserine, *PAPS* 3-phosphoadenosine-5-phosphosulfate, *SLG* S-D-lactoylglutathione, *Ser* serine, *APK* APS kinase, *APR* APS reductase, *ATPS* ATP sulfurylase, *CBL* cystathionine β-lyase, *CGS* cystathionine γ-synthase, *γ -ECS* γ-glutamylcysteine synthetase, *Gly I* glyoxalase I, *Gly II* glyoxalase II, *GR* glutathione reductase, *GSHS* glutathione synthetase, *MS* methionine synthase, *OAS-TL* OAS(thiol) lyase, *SAT* serine acetyltransferase, *SiR* sulfite reductase

involved in camalexin biosynthesis (Bottcher et al. 2009; Romero et al. 2014). Glutathione is a key regulator of redox signaling pathway and the antioxidant required for abiotic stress tolerance (Noctor et al. 2012). Glutathione is oxidized by reactive oxygen species (Noctor et al. 2012). The oxidized glutathione, GSSG, can be regenerated into GSH by GR. In addition, GSH is involved in two-step methylglyoxal (MG) detoxification: in the first step, MG is converted in S-D-lactoylglutathione (SLG) by glyoxalase I (Gly I) using GSH, and in the second step, D-lactate is produced from SLG by glyoxalase II (Gly II) releasing GSH (Hasanuzzaman et al. 2017b). The red circle marked in Fig. 10.2 is very responsive to different abiotic stresses.

Sulfur metabolism in the plant is greatly affected by environmental factors including biotic and abiotic factor. ATP sulfurylase activity or expression increases under sulfate starvation, salt stress, and light, Cd, and cold stress condition, and it contributes to abiotic stress tolerance (Khan et al. 2014; Anjum et al. 2015; Dixit et al. 2015b). Drought-induced alteration in S metabolic pathway in the plant is organ dependent. For example, drought stress decreased the Cys and GSH generation due to the lower assimilation of S in maize leaf. However, Cys, total glutathione, and SO_4^{2-} content were higher in the root (Ahmad et al. 2016). Salinity induced threefold higher expression of APS reductase (APR) in *Arabidopsis* roots (Koprivova and Kopriva 2008). However, salt stress induced by Na_2SO_4 decreases the expression of APR in roots of *Brassica rapa* but not affected by NaCl, indicating APR expression depends on sulfate availability (Reich et al. 2017). Cadmium stress (10 mg kg^{-1}) enhanced the activity of enzymes (ATPS, OASTAL, γ-ECS) of S assimilatory pathway in both root and shoot of *Brassica chinensis* L. (Lou et al. 2017). Above mentioned reports suggest that environmental stresses can alter the metabolic pathway of S. Therefore, this pathway could be the potential target for enhancing abiotic stress tolerance since there are few reports on this topic.

10.4 Sulfur Transporters in S Metabolism

As an inorganic molecule, S first needs to get into the cell. There are many membrane-bound transport proteins that facilitate the entry of nutrient inside the root from the outer environment. A motive force generated due to proton gradient mediates the sulfate influx using H^+/SO_4^{2-} cotransport system. To be metabolized into different metabolites, both inorganic forms of S and an organic molecule containing S must pass the membrane of cellular compartments through transport proteins. Smith et al. (1995) isolated three cDNAs from *Stylosanthes hamata* encoding sulfate transporters, which were highly conserved in other biological organisms: fungi, yeast, plants, and mammals. The two high-affinity H^+/SO_4^{2-} cotransporters, *shst1* and *shst2*, facilitate sulfate uptake from sulfur-deficient media, whereas the low-affinity H^+/SO_4^{2-} cotransporter, *shst3*, transports sulfate to the cellular compartments. All the above mentioned sulfate transporters (SULTRs) contain characteristic 12 putative membrane-spanning domains and STAS (sulfate transporter and anti-sigma factor antagonist) domain playing a role in protein folding and regulating protein activity, respectively (Takahashi 2010; Takahashi et al. 2011). With time some sulfate transporter has been reported in *Brassica oleracea*, potato, and tomato (Buchner et al. 2004; Hopkins et al. 2005; Howarth et al. 2003). Also, 12 sulfate transporters gene were identified in *Arabidopsis* using modern genomic tools and techniques. These transporter proteins are classified into four groups, which have distinct functions; group 1 includes high-affinity SULTRs, while group 2 consists of low-affinity transporters. Both group 1 and group 2 SULTRs mediate SO_4^{2-} uptake from nutrient media. Unlike groups 1 and 2, group 3 includes the transporter localized in plastid and symbiosome membrane playing specific function, sometimes unknown function, whereas group 4 mediates the SO_4^{2-} transport from the vacuole to other cell organelles (Takahashi 2010; Gigolashvili and Kopriva 2014). Localization and expression of sulfate transporters indicate their function in the sulfate metabolism (Table 10.1).

High-affinity sulfate transporters (SULTR1;1, SULTR1;2) categorized in group 1 play a role in the initial uptake of sulfate from the growing media (Takahashi 2010; Takahashi et al. 2011). Yeast mutant lacking *Sultr1;1* showed lower sulfate uptake, while mutant containing overexpressed *Sultr1;1* vector improved sulfate uptake confirming SULTR1;1 is a sulfate transporter (Takahashi et al. 2000). Based on phylogenetic tree relationship and sequence information, it was predicted that other sulfate transporters might be present in the root having similarity in functions

Table 10.1 Sulfate transporters in plants and their function and localization in cell

Group	Transporter gene	Expression organs and tissue localization	Functions	References
1	SULTR1;1	Localized in root hairs, epidermis and cortex, expressed in cell layers	Initial uptake of sulfate from nutrient media	Takahashi et al. (2000)
	SULTR1;2	Localized in root hairs, epidermis and cortex, expressed in cell layers	Initial uptake of sulfate from nutrient media	Shibagaki et al. (2002)
	SULTR1;3	Localized in companion cell of phloem, expressed in both shoot and root	Transport of sulfur from source to sink and uptake of sulfur in phloem companion cell when other transporters are repressed	Yoshimoto et al. (2003) and Takahashi et al. (2000)
2	SULTR2;1	Expressed in root pericycle and xylem parenchyma, as well as in xylem and phloem parenchyma of shoots	Facilitate distribution of sulfate to leaf tissue	Takahashi et al. (2000)
	SULTR2;2	Expressed in companion cell of phloem	Transport of sulfate through root phloem and transfer it to the site of sulfur assimilation	Takahashi et al. (2000)
3	SULTR3;1	Localized in chloroplast, expressed in leaves	Facilitate sulfate uptake in the chloroplast	Cao et al. (2013)
	SULTR3;2	Expressed in leaf	Facilitate sulfate uptake in the chloroplast	Cao et al. (2013)
	SULTR3;3	Expressed in leaf	Facilitate sulfate uptake in the chloroplast	Cao et al. (2013)
	SULTR3;4	–	Facilitate sulfate uptake in the chloroplast	Cao et al. (2013)
	SULTR3;5	Colocalized in root, expressed in root pericycle and xylem parenchyma	Play a role in root to shoot transport	Kataoka et al. (2004b)
4	SULTR4;1	Localized in tonoplast, expressed in root and shoot	Remobilize sulfate from vacuole and regulate transport of sulfate from root to shoot	Kataoka et al. (2004a)
	SULTR4;2	Localized in tonoplast, expressed in root and shoot	Remobilize sulfate from vacuole and regulate transport of sulfate from root to shoot	Kataoka et al. (2004a)

and affinity to sulfate (Takahashi et al. 2000). Selenate-resistant mutant showed lower uptake of sulfate both in sulfur-sufficient and sulfur-deficient medium. By yeast complementation technique, it is proved that the mutant was lacking *Sultr1;2* gene, which is responsible for sulfate uptake in the root (Shibagaki et al. 2002). Interestingly, either SULTR1;1 or SULTR1;2 is not involved in root to shoot transport which indicates the involvement of other sulfate transporters to facilitate sulfate transport from the root to shoot. Getting entry through root hairs, sulfate reaches the endodermis to epidermis and cortex followed by xylem parenchyma through the symplastic pathway. However, sulfate can get entry to xylem parenchyma from the apoplast by SULTR2;1 (Maruyama-Nakashita et al. 2003). Mutant in *Sultr3;5* restricted the transport of sulfate root to shoot. However, *Sultr2;1* coexpressed with *Sultr3;5* increased the root to shoot transport compared to *Sultr2;1* expressed alone (Kataoka et al. 2004b; Takahashi et al. 2011). Furthermore, *Sultr2;1* is found to be expressed in the leaf phloem suggesting its role in the reduction of excess sulfate from above ground part (Takahashi et al. 2000). SULTR2;2 transports sulfate to the mesophyll and palisade cell of leaf unloading from the xylem vessel (Takahashi et al. 2000). Under sulfate-deprived condition, overexpressed *Sultr1;3* facilitates sulfate uptake in the phloem companion cell as *Sultr2;1* repressed under sulfate-deficient condition (Yoshimoto et al. 2003; Takahashi 2010). When excess in supply, sulfate is reserved in the vacuole, but sulfate influx mechanism into the vacuole has not been well studied. However, the efflux of sulfate from the vacuole into the cytoplasm is mediated by SULTR4;1 and SULTR4;2 transporter protein, categorized in group 4 (Kataoka et al. 2004a). With these transporters, sulfur is taken up by roots and subsequently transported to different organs. Finally, sulfate gets into chloroplast where sulfur assimilatory pathway takes place. Using green fluorescent protein (GFP), SULTR3;1 transporter localization in the chloroplast was confirmed. Furthermore, mutant that lack this transporter showed lower sulfate uptake in the chloroplast, indicating SULTR3;1 is associated with sulfate transport in the chloroplast (Cao et al. 2013). Like SULTR3;1, other sulfate transporters like SULTR3;2, SULTR3;3, and SULTR3;4 are also involved in sulfate transport in the chloroplast (Cao et al. 2013). Among the four groups of sulfate transporters, transporters categorized in group 3 are less investigated compared to the others. For example, SULTR3;2-, SULTR3;3-, and SULTR3;4-mediated sulfate uptake mechanisms are still not clear.

10.5 Sulfate Transporter and Abiotic Stress

Different environmental factors including soil salinity, drought, waterlogging, high temperature, chilling, and heavy metal (HM) stresses affect nutrient metabolism from transport to assimilation. Under such extreme conditions, transporter proteins fail to function properly. As a result, ion homeostasis or nutrient balance is disrupted. Glutathione, a sulfur derivative compound, plays a diverse role under abiotic stress condition. In the presence of selenium (Se), reduction in endogenous GSH has a regulatory role in the expression of primary sulfate uptake transporter *Sultr1;1* (Takahashi et al. 2000; Fig. 10.3). Abscisic acid is a key factor to regulate abiotic stress tolerance. Surprisingly, a mutant lacking sulfate transporter *Sultr3;1* showed lower abscisic acid (ABA) content both in control and salt stress (200 mM NaCl) condition compared to wild type (Cao et al. 2014). This result indicates the

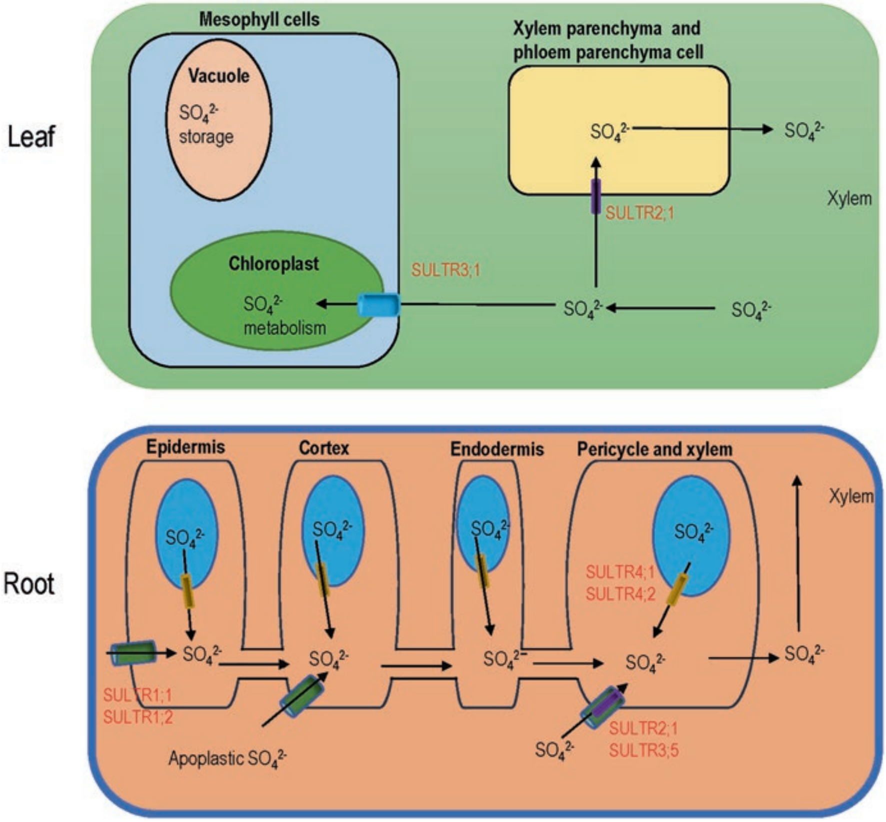

Fig. 10.3 Role of sulfate transporters in sulfate uptake and distribution (Adapted from Takahashi et al. (2011))

possibility of sulfate transporters to be involved in abiotic stress tolerance. In *Medicago truncatula*, almost all sulfate transporters are affected by either drought or salinity (Gallardo et al. 2014). Under HM stresses in particular Cd stress, sulfate uptake increases due to the expression of *ZmST1;1*, very similar to high-affinity sulfate transporter which belongs to group 1 (Table 10.1). Higher sulfate uptake is associated with higher production of PC to detoxify toxic Cd (Nocito et al. 2006). Another high-affinity sulfate transporter *Sultr1;2* is proved to be associated with As stress tolerance as *Arabidopsis* mutant lacking *Sultr1;2* showed sensitivity to As in response to growth parameters (Nishida et al. 2016). The expression of sulfate transporters may vary from the shoot to root under unfavorable condition. For example, under prolonged drought for 10 and 12 days, *Sultr1;2* expression reduced in the leaf and not affected in the root. However, *Sultr4;1* overexpressed in leaf but repressed in roots. This result suggests that with the help of this transporter maize seedling maintained S homeostasis in the root. As a result root growth increased in search of water (Ahmad et al. 2016). As SULTRs are distinguishable in function, their responses also vary depending on the type of stresses, indicating a particular transporter may play a role in tolerance of a particular type of stress. Though there are many indirect pieces of evidence that explain the involvement of sulfate transporter in abiotic stress tolerance, still this hypothesis needs further confirmation with rigorous experimental evidence.

10.6 Exogenous Use of Sulfur in Improving Plant Performances Under Abiotic Stress

Environmental stressors affect cell homeostasis inside plant tissue, and increasing ROS production leads to oxidative damage (Boaretto et al. 2014; Hasanuzzaman et al. 2017). Sulfur is an indispensable macronutrient for plant growth, development, and survival, and at the same time, many S-containing compounds play defensive roles in abiotic stress response, as well as cellular acclimation and adaptation in adverse condition (Cao et al. 2014). Plants respond to abiotic stresses in many ways, but the S assimilation pathway, the important source of reduced S for a variety of cellular mechanisms including Cys synthesis, which further used for Met biosynthesis or GSH production (Siddiqui et al. 2012). Thus the exogenous supply of S helps plants to survive in stress condition by maintaining their usual metabolic process (Table 10.2).

It seems that the HM/metalloid stress increases the demand of reduced S, hence activating the expression of SO_4^{2-} transporters and enzymes in the S assimilatory pathway (Takahashi et al. 2011; Hawkesford 2012). Therefore, many research reports have shown the effect of exogenous S in mitigating various abiotic stresses. Sulfur has a vital role in nutrient homeostasis; thus, it can decrease the uptake of the HMs/metalloids and at the same time increase the absorption of essential plant nutrients. On the other hand, exogenous S may increase the uptake of few HMs/metalloids, thus may be further useful for phytoremediation. In As-stressed plants increased S supply increases thiol metabolism and antioxidant activity, As accumulation, as well as tolerance of plants (Srivastava and D'Souza 2010). Sulfate nutrition plays an important role in regulating As translocation from roots to shoots, possibly through the complexation of AsIII-PCs in rice (Zhang et al. 2011). Conclusively S supplementation reduced the As accumulation in a shoot by increasing thiol metabolism and glycolysis toward amino acid accumulation under AsIII stress in rice (Dixit et al. 2015a). Sheng et al. (2016) found a moderate level of S application, beneficial to wheat against Mn toxicity, via upregulating the antioxidant defense, and the translocation and distribution of Mn from roots to shoots, excess Mn sequestering in vacuoles in the form of PCs, and increased production of GSH, where GSH played a very important role. Applying S in guinea grass may be a vital tool for phytoremediation of Cu under Cu toxicity in Cu-polluted areas, by increasing Cu uptake as well as increasing (30–40% higher) shoot and root dry mass and decreasing of lipid peroxidation (Gilabel et al. 2014).

Table 10.2 Studies showing beneficial response of exogenous sulfur and its derivatives in plants conferring various abiotic stresses

Plant species	S treatment	Abiotic stressors	Protective effects	References
Brassica napus var. Xiangnongyou 5710	Elemental S, 60 kg ha^{-1}	Se (Se 60 g ha^{-1} applied as $Na_2SeO_4.10H_2O$)	Reduced Se and erucic acid content in seed Increased seed yield and seed oil content	Liu et al. (2017)
Hydrilla verticillata	2.0 mM as $MgSO_4$	As (50 mM Na_2HAsO_4)	Increased total thiols and antioxidant content, except CAT Improved redox status	Srivastava and D'Souza (2010)
Oryza sativa cv. IR-36	5.0 mM S as SO_4^{2-}	As ($NaAsO_2$ 25 μM and (Na_2HAsO_4 50 μM)	Increased root As accumulation and restricted As translocation to the shoots Enhanced synthesis of NPTs and PCs Counterbalanced redox state and reduce H_2O_2 content Improved activity of APR, CS, SAT, γ-ECS, GR and SOD, APX, GPX, CAT, AR, and AO except γ-glutamyl transpeptidase (γ-GT), GST	Dixit et al. (2015b)
O. sativa cv Jiahua 1	0.7 mM SO_4^{2-}	As (10 μM arsenite/10 μM arsenate)	Reduced As in root and translocation to shoot Increased NPT and PCs and GSH content	Zhang et al. (2011)
O. sativa cv IR-36	5.0 mM SO_4^{2-}	As (25 μM $NaAsO_2$)	Reduced As accumulation in shoot Improved glycolysis, thiol metabolism, and antioxidant enzyme activity	Dixit et al. (2015a)
B. juncea cv. Pusa Jai Kisan (ethylene-sensitive) and SS2 (ethylene-insensitive)	1.0 mM SO_4^{-2} as $MgSO_4$	Cd (0.50 mM Cd as $CdCl_2$)	Reduced thiobarbituric acid reactive substances (TBARS) and H_2O_2 and ethylene content Upregulated SOD, APX, GR, SAT, ATPS, ACS, and RuBisCO activity Increased Cys and GSH content Promoted photosynthesis and dry mass accumulation	Asgher et al. (2014)

(continued)

Table 10.2 (continued)

Plant species	S treatment	Abiotic stressors	Protective effects	References
B. chinensis cv. Aikangqing and Qibaoqing	4 mM Na_2SO_4	Cd (0.1 mM $CdCl_2$)	Decreased Cd content, MDA, and $O^{2\bullet-}$ in both root and shoot; increased NPT, PCs, GSH, AsA, and redox state in both root and shoot	Liang et al. (2016)
B. chinensis cv. Aikangqing and Qibaoqing	50 mg Na_2SO_4 kg^{-1} soil	Cd (1 mg and 10 mg $CdCl_2.5H_2O$ kg^{-1} soil)	Increased growth	Lou et al. (2017)
			Stimulated antioxidant enzymes	
			Upregulated ASA-GSH cycle and S assimilation	
			Boosted PC and NPT production	
B. juncea cv. Pusa Jaikisan	300mMSO_4^{2-}	Cd (100 mM $CdCl_2$)	Reduced TBARS content while increased AsA and GSH, PCs, NPT, and chl contents and balanced redox state	Bashir et al. (2015)
			Upregulated SOD, CAT, APX, and GR activity	
Triticum aestivum cv. Yan Long 19	1.5 mM Na_2SO_3/ $NaHSO_3$ (3:1)	Cd (1.0 mM $CdCl_2$)	Increased H_2S content; amylase and esterase activity thus elevated reducing sugars and soluble protein levels in germinating seeds	Hu et al. (2014)
			Reduced MDA, H_2O_2, and $O_2^{\bullet-}$ generation and retained plasma membrane integrity of the radical tips	
			Boosted the activity of POX, APX, SOD, and CAT and reduced LOX activity	
T. polonicum	10mMSasSO_4^{2-}	Mn (3.0 mM Mn)	Improved GSH production and sequestering surplus Mn in vacuoles	Sheng et al. (2016)
			Inhibited translocation of Mn from roots to shoots	
			Stimulated antioxidant enzymes	

(continued)

Table 10.2 (continued)

Plant species	S treatment	Abiotic stressors	Protective effects	References
Panicum maximum cv. Tanzânia	2mMSasSO$_4^{2-}$	Cu (1000 μM Cu)	Increased Cu uptake and translocation Osmotic adjustment via Pro Nonsignificant but reduced MDA and H_2O_2 content	Gilabel et al. (2014)
T. aestivum	1.2 mM SO_2 as $NaHSO_3$/Na_2SO_3	Al	Reduced the accumulation of $O_2^{\bullet-}$, H_2O_2, and MDA Enhanced the activities of POX, CAT, and APX and decreased the LOX activity	Zhu et al. (2015)
Arabidopsis thaliana (ecotype Columbia, Col-0)	1500 μM S as SO_4^{2-}	Salinity (200 mM NaCl)	Upregulated some antioxidant enzyme and kept steady-state ABA level	Cao et al. (2014)
B. juncea var. Varuna	Elemental S 200 mg kg^{-1} soil	Salinity (100 mM NaCl)	Reduced Na^+ and Cl^- content of leaf Increased ATP-S activity, RuBisCo activity, Cys content, GSH content, and redox state Amplified chl content, stomatal conductance, PSII activity, and net photosynthesis Increased leaf area and dry mass	Fatma et al. (2014)
Fragaria × *ananassa* cv. Camarosa	100 μM NaHS	Salinity (100 mM NaCl) and drought (10% PEG 6000)	Increased leaf chl fluorescence, stomatal conductance and leaf relative water content, and NO levels Lowered MDA and H_2O_2 levels and balanced redox state	Christou et al. (2013)
Capsicum annum	S (5 and 10 g L^{-1} of nutrient solution)	Salinity (5 dS m^{-1} EC using NaCl)	Enhanced growth, leaf number, fruit number and weight, photosynthesis rate, and stomatal conductance Reduced Na^+ content in leaf and increased Pro and glycine betaine (GB) production in both root and shoot	Mukhtar et al. (2016)

(continued)

Table 10.2 (continued)

Plant species	S treatment	Abiotic stressors	Protective effects	References
A. thaliana (ecotype Columbia-0)	100 mM NaHS	Salinity (150 mM NaCl)	Increased seedling survival rate Decreased generation of $O_2^{\bullet -}$ and H_2O_2 and balanced GSH redox state Upregulated SOD, CAT, POD, and GR activity	Shi et al. (2015)
A. thaliana (ecotype Columbia-0)	S as 100 mM NaHS	Drought	Increased seedling survival rate Decreased generation of $O_2^{\bullet -}$ and H_2O_2 and balanced GSH redox state Upregulated SOD, CAT, POD, and GR activity	Shi et al. (2015)
B. juncea cv. Red Giant	Elemental S as 3 mM $CaSO_4$	Drought (50% of well-watered)	Increased levels of aliphatic glucosinolates in leaves and roots followed by decrease in ABA content	Tong et al. (2014)
T. aestivum cv. Luyuan 502 and Jimai 22	0.15 mM NaHS	Heat stress (38/28 °C day/night temperature, respectively)	Increased activities of SOD, CAT (decreased in Jimai 22), and APX; higher H_2S and soluble sugar contents but lower H_2O_2 and MDA contents	Min et al. (2016)
Nicotiana tabacum	50 µM NaHS	Heat stress (43 °C)	Increased sulfhydryl compounds (H_2S, Cys, GSH), upregulated antioxidant enzymes SOD, CAT, POX, and GR	Li et al. (2015)
A. thaliana (ecotype Columbia-0)	100 mM NaHS	Freezing (4 °C)	Increased seedling survival rate Decreased generation of $O_2^{\bullet -}$ and H_2O_2 and balanced GSH redox state Upregulated SOD, CAT, POD, and GR activity	Shi et al. (2015)

Application of S to Cd-stressed pak choi (*Brassica chinensis* L.) plants enhanced Cd tolerance by promoting the AsA-GSH cycle and PC biosynthesis. After application of S exogenously, its assimilation increased by the activity of ATP sulfurylase (ATPS) and O-acetylserine (thiol) lyase (OAS-TL) and decreased Cd translocation from the roots to the shoots (Liang et al. 2016; Lou et al. 2017). Indian mustard (*Brassica juncea*) plant supplemented with S under Cd stress accumulated the higher amount of AsA and GSH content as well as improved AsA/DHA, and GSH/GSSG ratio indicated the role of exogenous S in producing GSH, NPTs and PCs, and tolerance against Cd stress (Bashir et al. 2015). A similar result was also found by other researchers in *B. juncea* which suggested that Cd stress overproduced ethylene, which can be alleviated with S by antioxidant (GSH) metabolism (Asgher et al. 2014). Under Cd stress, seed priming with the SO_2 donor moderately increased the amylase and esterase activities and increased the levels of reducing sugars and soluble protein in germinating wheat seeds. Pretreatment with the SO_2 donor also reduced the MDA and and $O_2^{\bullet-}$ and restrain the plasma membrane integrity of the wheat seedlings radical tips as well as increase the activity of POD, APX, SOD, and CAT while reducing the activity of LOX (Hu et al. 2014). Zhu et al. (2015) reported a higher level of H_2S in wheat seeds primed with the SO_2 donor ($NaHSO_3/Na_2SO_3$). Wheat seed pretreated with 1.2 mM $NaHSO_3/Na_2SO_3$ reduced overaccumulation of $O_2^{\bullet-}$, H_2O_2, and MDA, with lower lipoxygenase (LOX) activity, while the activity of guaiacol peroxidase (POD), CAT, and APX increased to enhance tolerance against Al toxicity (Zhu et al. 2015).

Tobacco cell culture pretreated with the H_2S donor, sodium hydrosulfide (NaHS), $KHSO_3$, and precursor Cys significantly increased the survival percentage of tobacco cells under high heat (Li et al. 2015). They also found an elevated level of sulfhydryl compounds such as H_2S, sulfhydryl proteins, Cys, and GSH as well as higher antioxidant enzyme activity, for instance, SOD, CAT, cell wall peroxidases (POX), and GR, by pretreating with NaHS. Meanwhile, NaHS-pretreated wheat seedlings were found with higher antioxidant defense and H_2S and soluble sugar contents, while lesser H_2O_2 and MDA contents are induced by heat stress. But the little effect was found regarding antioxidant enzyme activities and other soluble substance levels compared to control (Min et al. 2016). In cluster beans under heat stress, S supplementation helps to mitigate the oxidative stress with higher AsA-GSH content and to lower the H_2O_2, MDA, and electrolyte leakage. Sulfur also increased dry weight and chl content under heat stress (Mobin et al. 2016). The study explored that pretreatment of strawberry roots with NaHS (100 μM for 48 h) could induce long-lasting tolerance to salinity (100 mM NaCl) or drought (10% PEG-6000) for 7 days. Furthermore, NaHS pretreatment resulted in lower NO and H_2O_2 content in leaves along with high AsA and GSH content, following salt and drought stresses. Thus, H_2S pretreatment managed the plants to overcome the salt and drought stress through upregulating antioxidant defense mechanisms and the coordination of the salt overly sensitive (SOS) pathway in strawberry (Christou et al. 2013). Salt stress drastically reduces the yield of crops by ionic toxicity and physiological drought. But exogenous S application from a foliar spray can mitigate the salinity stress by increasing photosynthetic rate, stomatal conductance, chl content, Pro, and GB content. The result suggested that S at both 5 and 10 g L^{-1} of spray solution improved the morphophysiological and biochemical traits in chili plants subjected to salinity (Mukhter et al. 2016). While working with mustard, Fatma et al. (2014) reported that excess S in the soil more rapidly alleviated the negative effects of salinity and improved photosynthesis and growth by increased GSH production. To support their statement, they again applied 1 mM GSH exogenously and found similar results of that excess S supplementation and confirmed excess S/GSH as a potential protectant against salt stress. At the time of salt stress, Cys is required to produce ABA to combat stress, while S supplementation increased the Cys production for ABA biosynthesis (Cao et al. 2014).

10.7 Sulfur Derivatives and Their Roles in Abiotic Stress Tolerance

Overproduction of ROS and MG is an inevitable process that occurs in different tissue types, under a diverse adverse environmental conditions including salinity, drought, toxic metal, high temperature, low temperature, waterlogging, etc., which might be regulated by a number of defensive molecules or systems in plants (Hasanuzzaman et al. 2012, 2017a; Sharma et al. 2012). Sulfur-containing compounds, for example, GSH, H_2S, Met, Cys, PC, ATP-S, protein thiols, etc., play an immense role in normal functioning of the plant cell (Fig. 10.4). Also, such S derivatives primarily work in plant stress tolerance (Colville and Kranner 2010; Zagorchev et al. 2013). Under stress condition in most of the cases, the content of endogenous S-containing compounds increased up to a certain extent to protect plants from respective stress (Khan et al. 2013; Zagorchev et al. 2013; Hasanuzzaman et al. 2017b). Recently the exogenous application of different S derivatives (GSH, H_2S, etc.) against a variety of abiotic stresses is receiving attention due to their effectiveness in enhancing stress tolerance.

Sulfur-rich Cys is very important for plants not only as an amino acid but also due to its role as a precursor for a huge number of vital biomolecules (Haag et al. 2012). Cysteine possesses a vital position in plant metabolism because it plays an essential role in the biosynthesis of important S-containing cellular compounds, for example, GSH and different proteins (Romero et al. 2014). These compounds directly or indirectly work in the redox signaling pathway and stress tolerance mechanisms. Moreover, Cys triggers metabolism of nitrogen at the biochemical and molecular level which plays an imperative role in enhancing plant stress tolerance (Zagorchev et al. 2013; Erdala and Turk 2016). On the other hand, Cys is a powerful metal chelator, but Cys-metal ion complexes are capable of activating the most devastating Fenton reaction, which may create toxic $OH^{\bullet}$ radical in a plant cell (Bashir et al. 2012). Though endogenous Cys played a great function in a plant cell, the exogenous application of Cys for alleviating abiotic stress from the plant is very rare. Erdala and Turk (2016) demonstrated that Cys application to maize seedlings

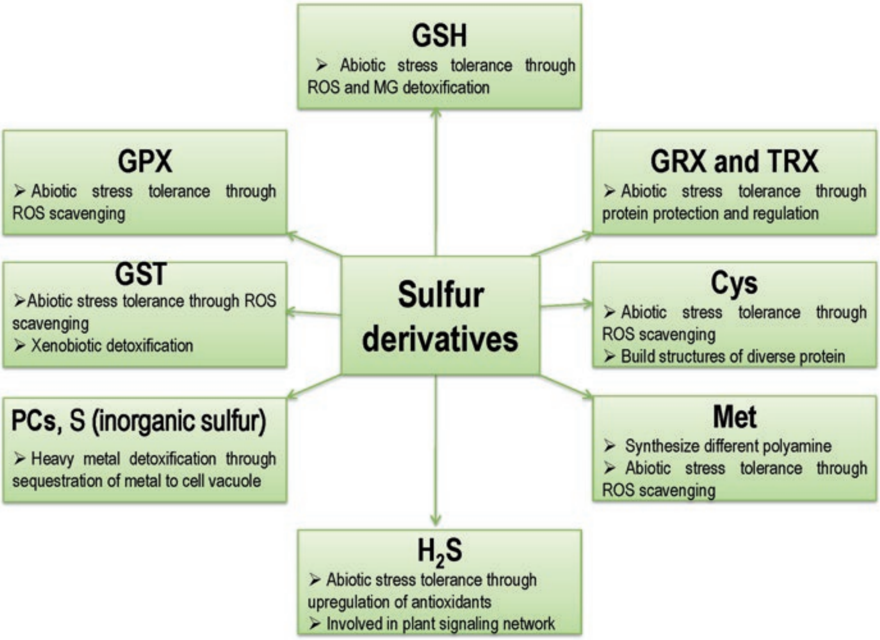

Fig. 10.4 Roles of S derivatives in abiotic stress tolerance of plant

mitigates Cd-induced oxidative stress. Like Cys, Met can undergo ROS-mediated oxidation through a class of cytosolic and plastidic enzymes that are involved in mitigating the oxidative damage of plant (Dos Santos et al. 2005; Cabreiro et al. 2006). Methionine is also a substrate for the synthesis of a range of polyamines (putrescine, spermidine, spermine, etc.), which has important roles in stress tolerance (Alcázar et al. 2010).

Sulfate is first activated by ATP-S to yield APS which is then reduced to SO_3^{2-} by APS reductase and then further reduced to S^{2-} and finally incorporated into Cys which helps to produce S-rich GSH. So, enhancement of ATP-S in a plant cell is very urgent for developing plant stress tolerance. Glutathione is one of the most important nonenzymatic antioxidants for living systems which plays a noteworthy role in cellular metabolism and works as a vital component in scavenging of toxic ROS in a plant cell (Gill and Tuteja 2010; Hasanuzzaman et al. 2012; Noctor et al. 2012; Nahar et al. 2016). Also, it works in glyoxalase system to detoxify toxic MG (Hasanuzzaman et al. 2017a). By upholding the reduced status of α-tocopherol and zeaxanthin, GSH protects the membrane of the cell, which contributes to the reduction of protein denaturation under stress condition. Moreover, it functions as a substrate of glutathione peroxidase (GPX) and glutathione *S*-transferase (GST). Both GPX and GST play a direct role in scavenging of toxic ROS and protecting plants from oxidative stress induced by different abiotic stresses (Hasanuzzaman et al. 2012; Asgher et al. 2017). Glutathione *S*-transferase is also involved in detoxification of xenobiotics (Zagorchev et al. 2013). Glutathione, as a precursor of PC, assists in metal chelation, which transfers the toxic metals or metalloids to the cell vacuole as an inactive form (Hasanuzzaman et al. 2017a, b; Sharma and Dietz 2006). Consequently, it acts an imperative function in detoxification of toxic metals/metalloids (Hasanuzzaman et al. 2017b; Srivalli and Khanna-Chopra 2008). In addition to a variety of functions of GSH reported before, there is a confirmation that GSH is highly associated with controlling different genes (Zagorchev et al. 2013). Such abovementioned biochemical characteristics of GSH make it indispensable for plant growth and development under both usual and adverse growing conditions. Many previous reports confirmed that endogenous or exogenous GSH contributes to increase tolerance level of plants to diverse abiotic stresses, including salinity, drought, high temperature (HT), low temperature, and toxic metal stress (Kumar et al. 2010; Mahmood et al. 2010; Wang et al. 2011; Wu et al. 2011; Chen et al. 2012; Hasanuzzaman et al. 2012; Jozefczak et al. 2012). Here, we discussed few recent findings. Cheng et al. (2015) reported that exogenous application of reduced GSH in *Arabidopsis* plant could improve abiotic stress tolerance. They also claimed that endogenously enhanced GSH bestowed tolerance on the same plant under salt and drought stress. Furthermore, senescence and flowering are delayed due to both exogenous and endogenous GSH. Their translatome analysis also uncovered that GSH treatment triggered the biosynthesis process of ABA, auxin and jasmonic acid (JA), as well as signaling genes, which might be helpful for increasing plant stress tolerance. Çevik and Ünyayar (2015) checked the function of exogenously applied AsA and GSH on antioxidant system of *Cicer arietinum* plant under drought stress and observed that both GSH and AsA contribute to enhancing tolerance level against drought stress in chickpea. Nahar et al. (2015a) reported that exogenous GSH enhances the activity of most of the enzymes of antioxidant defense system (APX, MDHAR, DHAR, GR, GPX, GST, SOD and CAT) and glyoxalase system of drought-affected mung bean plant either considerably or slightly. Accordingly, GSH reduced the content of over-generated ROS and MG which finally successfully decreased the oxidative damage. But the performance of GSH was day dependent. With the increasing stress duration, GSH showed lower effectivity to counter stress. A similar trend of positive findings was recorded due to exogenous GSH in the same plant under high temperature (HT) and salt stress (Nahar et al. 2015b, c). Compared to only stress supplementation of GSH in HT-stressed cucumber plants, considerably increased soluble protein content, proline level, activities of different antioxidants and their associated gene expression, as well as exogenous GSH reduced the ROS production and decreased the cell lipid peroxidation (Ding et al. 2016). Their results suggest that exogenously applied GSH improve tolerance level of HT-stressed cucumber plants due to its positive action in water status, photosynthetic process, and antioxidant defense system. Khan et al. (2016) demonstrated that exogenous GSH application decreased MDA and H_2O_2 content of cotton leaves because of increased activity of POD, APX, GR, SOD, and CAT. These findings recommended that exogenous application of GSH decreased the undesirable effects of Pb and enhanced tolerance of cotton plants to oxidative stress. Glutathione enhanced the manufacture of NO and total S-nitrosothiol contents and upheld a reduced cellular redox status and increased antioxidant capacity along with induction of transcripts of transcription factors and antioxidant genes under Cd stress in tomato plants (Hashem et al. 2016). Similarly, Daud et al. (2016) observed the GSH-mediated oxidative stress tolerance in the cotton plant under Cd stress. Therefore, it is very obvious that any source of GSH either endogenous or exogenous develop plant stress tolerance under the adverse growing condition, but success depends on the interaction of it to the stress regarding the proper amount of GSH.

Even though H_2S is considered as a phytotoxin, it is documented that plants can themselves produce and liberate this gas, particularly when uncovered to external Cys, sulfate, sulfite, or SO_2 (Li 2013; Li et al. 2016; Wei et al. 2017). Maybe for the indulgence of excess S, the plant goes through such mechanism. Nevertheless, under few biotic and abiotic stresses, plants release H_2S more than basal, endogenously produced rates (Jin et al. 2011; Wei et al. 2017). Additionally, as a vital sulfur compound, H_2S works in various developmental processes of plant and contributes to enhance plant stress tolerance as it can upregulate the transcripts of multiple abiotic and biotic stress-related genes and hinder accumulation of ROS (Shi et al. 2014; Li and Hey 2015; Chen et al. 2017). Endogenous H_2S accumulation is a widespread feedback of plants to environmental stress, including salt, drought, HM/metalloid, and heat and cold stress which might be intimately connected with the acquisition of plant stress tolerance (Li 2013; Calderwood and Kopriva 2014; Hancock and Whiteman 2014). Hydrogen sulfide is involved in a complex signaling network consisting of many secondary messengers such as Ca^{2+}, ABA, H_2O_2, and NO, which protect the plant from stress-induced damage (Li et al. 2016). In recent time, low concentration of exogenous H_2S is emerging as a novel gaseous signal molecule which confirmed its positive effect in different plants under normal and adverse growing condition. It has numerous positive functions on plant growth and development. The action of supplemented H_2S is also found to enhance plant stress tolerance under environmental difficulties (Li 2013; Li et al. 2016). Interestingly, exogenous application of H_2S confirms considerable positive effects on germination of seed (Li and He 2015; Wojtyla et al. 2016), plant growth and development (Fang et al. 2014), and regulation of senescence (Zhang et al. 2011), with the increasing of plant stress tolerance against salt (Christou et al. 2013; Chen et al. 2015; Deng et al. 2016), drought (Christou et al. 2013; Shen et al. 2013; Chen et al. 2016; Ma et al. 2016), toxic metal (Chen et al. 2013, 2017; Cui et al. 2014), high temperature (Li et al. 2013a,b; Li 2015), and cold stress (Fu et al. 2013; Du et al. 2017). The above functions of H_2S signify that it might be a promising candidate for signal transduction in plant's cross-adaptation. Recently, Chen et al. (2017) observed that H_2S acted as an antioxidant and scavenged ROS through regulating different antioxidant enzymes, thus preventing metal-induced (Hg) oxidative damages. In contrast to stressed plant, exogenous application of H_2S in drought-affected wheat seedlings increased the activity of different antioxidant enzymes and reduced ROS production and lipid peroxidation in both leaves and roots. Moreover, H_2S addition in plants enhanced ABA biosynthesis, which participated in developing drought stress tolerance (Ma et al. 2016). In parallel, Chen et al. (2016) found that H_2S regulates the polyamines and sugar changes in *Spinacia oleracea* seedlings under drought stress condition, which provided stress tolerance for the plants. Exogenously applied H_2S in salt-affected plants maintained the balance between Na^+ and K^+ in growing media and cell along with upregulation of different ROS scavenging enzymes, which maintained the cellular balance and protected plant from the salt-induced damages (Christou et al. 2013; Chen et al. 2015; Deng et al. 2016). A similar type of actions of H_2S in enhancing stress tolerance was observed under other abiotic stresses including heat and cold stress (Li et al. 2013a, b; Fu et al. 2013; Li 2015; Du et al. 2017).

Thioredoxins (TRX), glutaredoxins (GRX), and glutathionylation are considered as protein thiols, which contain sulphydryl groups and are considered as protective and regulatory compounds for plant cell (Zagorchev et al. 2013). Different abiotic stresses raise both TRX and GRX in protein or gene level. Proteomics study of rice seedlings demonstrated the upregulation of responsible genes of TRX and GRX under Cu toxicity (Song et al. 2012). However, their function varies from stress to stress. Fatehi et al. (2012) reported that TRX activity increased by manyfold under salt stress in barley plant. On the other hand, amusingly, cold stress seemed to downregulate most TRX genes, but drought stress upregulated them, as a minimum at the earlier stages of the stress treatment (Nuruzzaman et al. 2012). Like TRX and GPX, the function of glutathionylation in a plant cell regarding abiotic stress tolerance is not so clear to date. Colville and Kranner (2010) reported that protein glutathionylation is a probable provider of defense mechanisms that confer desiccation stress tolerance.

10.8 Molecular Approaches in Regulating S Status in Plants

For growth and development, plants require a certain amount of sulfur. Due to the dynamic nature of the environment, plants may not get the exact amount of S as per requirement. Thus, plants have evolved with some strategies to control the S status in plants under diverse situations including S deficiency and unfavorable environmental condition (Table 10.3). From S uptake to assimilation into a metabolite, different regulatory factors tightly control the pathway to ensure proper concentration of S-containing compounds or inorganic SO_4^{2-} in cellular compartments essential for metabolic functions (Table 10.3). Understanding of molecular mechanism involved in S homeostasis allows us to engineer pathway in a way ensuring proper S level in plant even under environmental stress condition. Therefore, the study of transporter proteins, metabolites, and enzymes of the assimilatory pathway under S-deficient condition could be a pertinent approach to find out the regulatory factors of S metabolism. Under S deficiency, *Sultr1;1* expression is greatly enhanced, and *Sultr1;1* is more responsive to S status than *Sultr1;2* (Yoshimoto et al. 2002). To understand how the transporter proteins are controlled, different enzymes inhibitors were used: phosphatase inhibitors, OKA and CalyA, and kinase inhibitors, K252a. Phosphatase inhibitors, OKA and CalyA, inhibited the expression *Sultr1;1* under sulfur deficiency indicating the involvement of protein phosphatase in the

Table 10.3 Regulatory components of S metabolism and their function

Regulatory component in S metabolism	Target in S metabolic pathway	Mode of action	References
Sulfur-responsive element (SURE)	Present in promoter region of *Sultr;1*	Provide binding sequence 5 bp GAGAC for regulatory element	Maruyama-Nakashita et al. (2005)
SLIM1	*Sultr1;2* and Glucosinolates	Activate sulfate uptake and degrade glucosinolates	Maruyama-Nakashita et al. (2006)
Long hypocotyl 5 (HY5)	APS reductase (APR)	Control the APR gene expression	Lee et al. (2011)
MYB	APS reductase (APR)	Control the APR gene expression and regulated by SLIM1	Takahashi et al. (2011), Koprivova and Kopriva (2014)
miRNA395	ATP sulfurylases (APS) and *Sultr2;1*	Regulate APS expression and induced by SLIM1	Kawashima et al. (2009)
Cysteine synthase complex (CSC)	Cys	Modulate Cys biosynthesis	Wirtz et al. (2010)

regulation of *Sultr1;1* expression (Maruyama-Nakashita et al. 2004a). Further investigation revealed that among different phytohormones, only cytokinin could repress the *Sultr1;1* and *Sultr1;2* expressions in *Arabidopsis* indicating a role of cytokinin in S homeostasis in the plant (Maruyama-Nakashita et al. 2004b). Again, a sulfur-responsive element (SURE) was identified in 5′ promoter region of *Sultr1;1*. Furthermore, microarray analysis suggested that SURE is associated with some genes responsive to S deficiency (Maruyama-Nakashita et al. 2005). Another transcription factor, SLIM1, was reported to be involved in regulation of *Sultr1;2* expressions under S-limiting condition. Interestingly, SLIM1 itself was not affected by S concentration in the growing media. Also, there was no SLIM1 binding site in the sulfate transporters except *Sultr4;2* suggesting the presence of another factor that may connect the signaling between transporter genes and SLIM1 (Maruyama-Nakashita et al. 2006). A binding site for EIL group transcription factors was identified in the promoter region of *UP9C* gene in tobacco, a gene responsive to the sulfur limitation (Wawryzynska et al. 2010). Kasajima et al. (2007) suggested that *ASR1*, also known as *BIG* gene, is involved in sulfate metabolism pathway as the mutant *asr1-1* showed upregulation of SULTR2;2 and adenosine-5′-phosphosulfate reductase 1 (APR1) which was not affected by SLIM1. To investigate the transcriptional regulation of sulfate assimilatory genes, long hypocotyl 5 (HY5), a transcription factor, was reported to modulate APR expression. Unlike SURE and SLIM1, HY5 can bind to the promoter region of APR1 and APR2 but not in APR3 (Lee et al. 2011). However, APR expression is also regulated by MYB transcription factors (Yatusevich et al. 2010).

In some cases, gene expression is regulated posttranscriptionally by some RNA, microRNA (miRNA). These miRNAs bind with a protein to form RNA-induced silencing complex (RISC). The RISC then binds with mRNA complementary to miRNA. As a result target mRNA fails to be translated into protein. Sulfur deficiency in growth medium induces miRNA395 which in turn regulates the expression of *Sultr2;1* and *APS1* genes in the sulfur metabolic pathway. Interestingly, transcription factor SLIM1 can induce miRNA under sulfur limitation (Kawashima et al. 2009). The multienzyme complex formed by SAT and OAS-TL, known as cysteine synthase complex (CSC), is involved in sulfur homeostasis (Takahashi et al. 2011; Koprivova and Kopriva 2014). The CSC regulates Cys biosynthesis in different cell organelles and maintains SAT activity. However, S limitation induces accumulation of OAS which dissociates the complex (Droux et al. 1998; Wirtz et al. 2010). Still, there are not enough reports to elucidate the mechanism completely. Furthermore, regulatory networks of S metabolism could be investigated under abiotic stress condition which will allow us to answer the question how S is metabolized under adverse environment.

10.9 Conclusion and Future Perspectives

Although there are several reports on the role of S in plants under abiotic stress, the exact mechanisms and interactions are not revealed yet. Sulfur-associated amino acids (Met, Cys), iron-S-clusters, lipids, vitamins (biotin and thiamine), cofactors (CoA and S-adenosylmethionine), and peptides (such as GSH and PCs) play a significant role in abiotic stress tolerance. Molecular approaches to manipulate enzymes of S assimilation pathway such as ATP sulfurylase (ATP-S), APS kinase, PAPS reductase or APS reductase, sulfite reductase, serine acetyltransferase (SAT), and O-acetylserine/O-acetylhomoserine sulfhydrylase will widen the eyes view to exploit S as a more persuasive molecule in developing stress tolerance of plant (Anjum et al. 2015; Khan et al. 2016). Sulfur deficiency disrupts homeostasis of other essential nutrients, and thus the formation of basic structural components of the cell is hindered. A cross talk among GSH pools, miR395 levels, and ATP-S transcripts/activity regulates S pool and the pool of other essential nutrients within the plant which maintains the nutrient homeostasis for better plant development both under normal growth and abiotic stress condition (Anjum et al. 2015). This aspect should be considered for further studies.

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