Role of Sulfur for Plant Production in Agricultural and Natural Ecosystems

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Summary

Sulfur is essential for plant growth and functioning. Sulfate taken up by the roots is the primary sulfur source for growth, but additionally plants are able to utilize absorbed sulfur gases by the shoot. Prior to its assimilation sulfur needs to be reduced and cysteine is the primary precursor or sulfur donor for other plant sulfur metabolites. Sulfur is of great significance for the structure of proteins and functioning of enzymes and it plays an important role in the defense of plants against stresses and pests. Sulfur metabolites such as glutathione provide protection of plants against oxidative stress, heavy metals and xenobiotics. Secondary sulfur compounds (viz. glucosinolates, γ-glutamyl peptides and alliins), phyto-alexins, sulfur-rich proteins (thionins), localized deposition of elemental sulfur and the release of volatile sulfur compounds may provide resistance against pathogens and herbivory. Plant species vary largely in sulfur requirement, and an adequate and balanced sulfur nutrition is crucial for their production, quality and health. The assimilation of sulfur and nitrogen are strongly interrelated and sulfur deficiency in plants can be diagnosed by the nitrogen to sulfur ratio of plant tissue. In agricultural ecosystems, the

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occurrence of sulfur deficiency of soils can easily be corrected by the application of sulfur fertilizers, which additionally prevents negative environmental side effects such as leakage of nitrate to drainage water. Plants in natural ecosystems generally have an adequate sulfur supply, which partly originates from atmospheric sulfur inputs. Humans and animals rely on plants for their reduced sulfur, and plant sulfur nutrition has a decisive effect on food quality, e.g., availability of methionine, breadmaking and malting quality, and on health, because some secondary sulfur compounds have significance as phyto-pharmaceuticals. A balanced sulfur diet is essential in animal feeding and deficiency negatively affects sheep wool production, though excessive sulfur may induce copper or selenium deficiency in cattle.

I. Introduction

Sulfur is an essential nutrient for plants and is considered as the fourth major plant nutrient after nitrogen, phosphorous and potassium. Total sulfur content in plants tissue ranges from 0.3% to 7.6%; the latter is found in plants from gypsum soils (Tabatabai, 1986; Ernst, 1990). In general, plants rely on sulfate taken up by roots as the sulfur source for growth. In agro-ecosystems sulfur supply is not always optimal for plant growth and quality (Schnug, 1998). The abundance of sulfate in the pedosphere varies widely and may originate from weathering of rock, mineralization of organic sulfur, ground or runoff water, atmospheric deposition of sulfur gases and fertilizers. The majority of the sulfate taken up by the plant is reduced and metabolized into cysteine and methionine, both of which are highly important in proteins (De Kok et al., 2002a; Hawkesford and De Kok, 2006; Haneklaus et al., 2007b). Accordingly, the assimilation of sulfur and nitrogen are strongly interrelated and the organic molar N/S ratio may reflect the sulfur status of the plant, which usually ranges from 30 to 35 for sulfur-sufficient crop plants (Durenkamp and De Kok, 2003; Oenema and Postma, 2003). Plants contain a large variety of other organic sulfur compounds, which play an important role in plant functioning and adaptation to the environment (De Kok et al., 2002a).

In the present chapter, the role of sulfur for plant production in agro- and natural ecosystems will be evaluated. It is evident that the sulfur supply to the plant has a decisive effect on the growth, the performance and fitness, and the resistance of plants to biotic and abiotic stresses. Furthermore, sulfur strongly affects food quality of crop plants.

II. Uptake, Assimilation and Distribution of Sulfur

The uptake and reduction of sulfate in plants and its subsequent assimilation into organic sulfur compounds is highly coordinated (Hawkesford and De Kok, 2006). The uptake and distribution of sulfate in the plant is mediated by sulfate transporter proteins, which are encoded by a sulfate transporter gene family consisting of at least 14 members. The sulfate transporters have been classified in five different groups according to their cellular and subcellular expression and possible functioning (Davidian et al., 2000; Hawkesford, 2000; Hawkesford and Wray, 2000; Hawkesford et al., 2003a,b; Buchner et al., 2004; Hawkesford and De Kok, 2006; Chapter 2). There is a distinct group of sulfate transporters (Group 1), which mediate the uptake of sulfate by the roots that have a high affinity for sulfate (Km 1.5–10 μM). Another group of sulfate transporters (Group 2) are involved in the vascular loading and unloading of sulfate, however, these transporters have a lower affinity for sulfate. There are also distinct transporters (Group 4) involved in the vacuolar exchange of sulfate, whereas the functions of other transporter groups (Groups 3 and 5) are less well characterized (Buchner et al., 2004; Hawkesford and De Kok, 2006). The uptake and distribution of sulfate and the level of expression of the Groups 1, 2 and 4 sulfate transporter genes are directly controlled by plant sulfur status (Buchner et al., 2004; Hawkesford and De Kok, 2006). It needs to be further evaluated whether the local *in situ* sulfate concentration or that of a metabolic product of sulfate assimilation, such as cysteine or glutathione, is involved as signaling of the regulatory control of the different sulfate transporters.

The uptake of sulfate by the root is dependent on the plant sulfur requirement for growth, the shoot to root biomass partitioning, the different developmental stages of the plant *viz*. vegetative growth (herbaceous and crop plants), primary and secondary growth (woody plants), fruit and seed production, and varies widely between species (Hawkesford and De Kok, 2006). The plant's growth rate (1), sulfur requirement (2) and sulfate uptake (3) may be estimated as follows (derived from Durenkamp and De Kok, 2004):

$$\text{Growth rate} = (\ln W_2 - \ln W_1)/(t_2 - t_1) \qquad (1)$$

Sulfur requirement (μmol g^{-1} plant day^{-1}) =

growth rate (g g^{-1} plant day^{-1}) $\times$ sulfur content
    (μmol g^{-1} plant)   (2)

Sulfate uptake (μmol g^{-1} root day^{-1}) =
sulfur requirement (μmol g^{-1} plant day^{-1}) $\times$
    (S/R ratio + 1)   (3)

In (1) W_1 and W_2 represent the total plant weight (g) at time t_1 and t_2, respectively, and $t_2 - t_1$ the time interval (days) between harvests, and in (3) the S/R ratio represents the shoot (S) to root (R) biomass partitioning of the plant. Sulfate uptake by the roots of different crop species may for instance range from 8 to 40 μmol g^{-1} fresh weight day^{-1} (Westerman et al., 2000; Durenkamp and De Kok, 2004; Buchner et al., 2004), whereas that for tree species is presumably much lower (<5 μmol g^{-1} fresh weight day^{-1}; Kreuzwieser et al., 1996; Herschbach et al., 2000; van der Zalm et al., 2005). The sulfur requirement of a crop might be predicted by scaling up the sulfur requirement (2) in kmol sulfur ha^{-1} day^{-1} by estimating the crop biomass density ha^{-1} (Haneklaus et al., 2007a). The sulfur requirement (2) might have to be adjusted for woody species to allow for differences in growth rate and sulfur content among the roots, stems and branches, and the foliage (Johnson, 1984). The possible significance of mycorrhiza (symbiosis between roots and fungi) in the uptake of sulfate by roots of plants from natural ecosystems, e.g., forests, needs to be evaluated further (Rennenberg, 1999; Herschbach and Rennenberg, 2001; Tausz, 2007).

Generally the major proportion of the sulfate taken up is reduced and metabolized into organic compounds essential for structural growth, whereas the remaining sulfate in plant tissue is transferred into the vacuoles. The remobilization and in some species the redistribution of the vacuolar sulfate reserves may be rather slow and sulfur-deficient plants might still contain detectable levels of sulfate (Cram, 1990; Davidian et al., 2000; Hawkesford, 2000; Buchner et al., 2004).

The chloroplast is the predominant site of sulfate reduction; however, root plastids are also able to reduce sulfate, since all enzymes of sulfate assimilation are present (Heiss et al., 1999; Lappartient et al., 1999; Lee and Leustek, 1999; Yonekura-Sakakibara et al., 2000; Chapter 3). At least for most herbaceous and crop plants, as with nitrate reduction (Scheurwater et al., 2002), sulfate reduction in the root as a proportion of the whole plant sulfur assimilation is limited, since here the shoot to root ratio generally exceeds 2 to 6. Sulfate needs to be activated by ATP to adenosine 5′ phosphosulfate (APS) catalyzed by APS sulfurylase before it is reduced to sulfite by adenosine 5′ phosphosulfate reductase with glutathione as a reductant (Leustek and Saito, 1999; Kopriva and Koprivova, 2003; Fig. 1). Subsequently the sulfite is reduced to sulfide by sulfite reductase with ferredoxin as a reductant. The formed sulfide is incorporated into cysteine with *O*-acetylserine as the substrate. This reaction is catalyzed by *O*-acetylserine(thiol)lyase, which is associated as an enzyme complex with serine acetyltransferase (the *O*-acetylserine synthesizing enzyme) named cysteine synthase (Droux et al., 1998; Hell, 2003; Chapters 4 and 5) and is the primary direct coupling step between sulfur and nitrogen assimilation in plants (Brunold, 1990, 1993; Brunold et al., 2003; Fig. 1).

The *in situ* sulfate concentration in the chloroplast (plastid) may be one of the limiting/regulatory steps in the reduction of sulfate, because the affinity of ATP sulfurylase for sulfate is rather low (K_m approximately 1 mM; Stulen and De Kok, 1993). Moreover, the expression and activity of APS reductase is highly responsive to the sulfur status of plant, with metabolic products of sulfate assimilation, such as cysteine or glutathione, as the likely regulating signals (Brunold, 1990, 1993; Leustek and Saito, 1999; Kopriva and Koprivova, 2003; Saito, 2003; Chapter 5).

The reduced sulfur in the shoot may be distributed from the source to the sink as glutathione (Rennenberg et al., 1979) or in some plant species
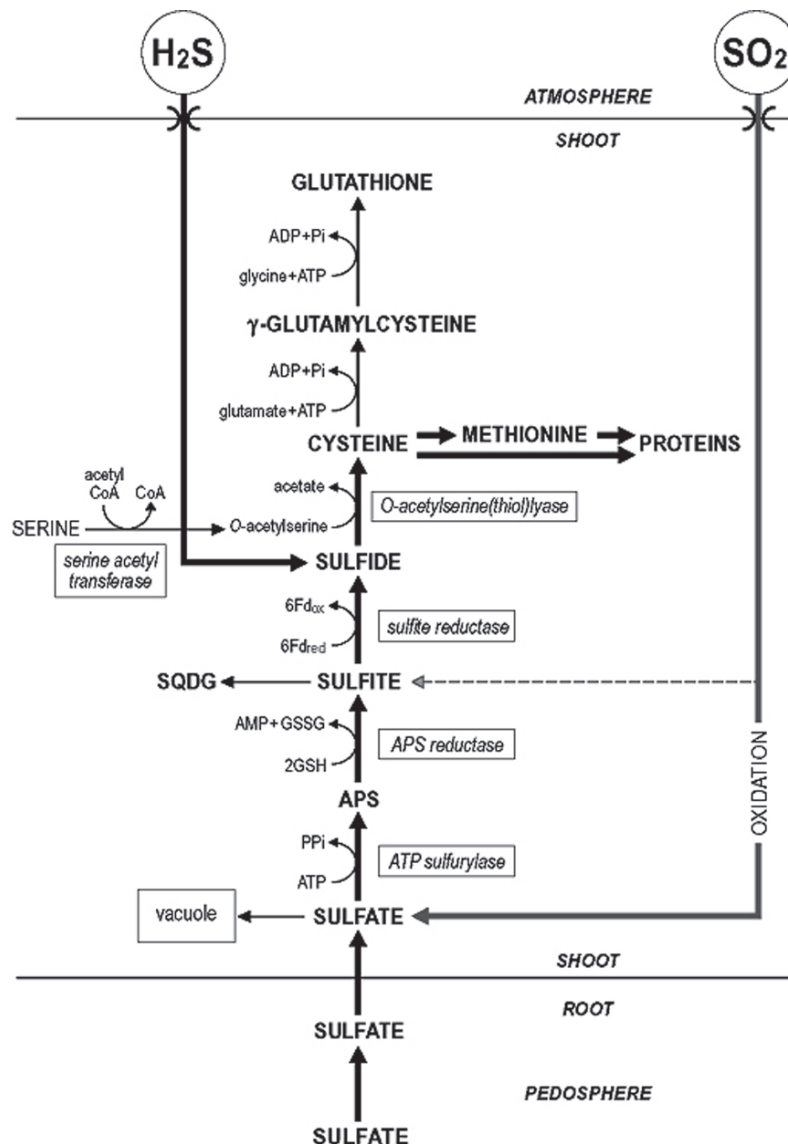
Fig. 1. Metabolism of sulfate and atmospheric sulfur gases in plants (adapted from De Kok et al., 2002a). APS, adenosine 5′-phosphosulfate; Fd_{red}, Fd_{ox}, reduced and oxidized ferredoxin; GSH, GSSG, reduced and oxidized glutathione; SQDG, sulfoquinovosyl diacylglycerol.

as *S*-methylmethionine via the phloem (Bourgis et al., 1999). The reduced sulfur formed in the roots may be transported as methionine and to a lesser extent as cysteine and glutathione to the shoot via the xylem (Pate, 1965). In contrast to annual herbaceous plants, the distribution of sulfur in perennial species and particularly trees is considerably more complex due to their specific features (Tausz, 2007). In trees there are large storage tissues in trunks, long distances between

uptake in roots and consumption/reduction in foliage, and long life spans subject to seasonal changes. Compared to fast-growing herbaceous species, sulfur distribution has only been investigated in a few tree species in detail. A comparison of beech (*Fagus sylvatica*), a deciduous broadleaf, and spruce (*Picea abies*), an evergreen conifer, revealed basic differences in sulfur distribution (Rennenberg and Herschbach, 1995; Herschbach and Rennenberg, 2001; Herschbach,

2003). *Picea abies* takes up sulfate and transports it to older needles, apparently the predominant site of sulfur reduction. Buds and young needles rely on reduced sulfur supplied by older needles as glutathione transported in xylem and phloem. Under normal conditions, spruce trees do not seem to transfer reduced sulfur from their foliage to the trunk and roots. These tissues may rely on reduced sulfur produced by root sulfur reduction. Upon exposure to high atmospheric sulfur input, however, spruce trees seem capable of transferring organic sulfur (most probably as glutathione) from the needles into the roots (Tausz et al., 2003b). In deciduous beech, both reduced organic sulfur in the form of thiols (mainly cysteine and some glutathione) and sulfate are supplied via xylem to the developing young leaves until they can meet their own sulfur reduction requirements. The cysteine seems to be supplied by the breakdown of storage proteins in the trunk. These storage proteins are synthesized during the vegetation period using sulfur imported as glutathione and sulfate (rather than cysteine) from leaves into the trunk. It should be noted that the specific modifications of sulfur distribution pathways in spruce and beech are closely related to the rhythms in flushing, shedding of foliage, and dormancy periods typical of a strictly seasonal climate, and that not much is known about the sulfur metabolism of trees in other climate zones.

In addition to sulfate taken up by the root, plant shoots are also able to absorb and metabolize sulfur gases, viz. SO_2 and H_2S, and use them as a sulfur source for growth (De Kok, 1990; De Kok et al., 1997, 1998, 2000, 2002a,b, 2007; Westerman et al., 2000, 2001; De Kok and Tausz, 2001; Tausz, 2007; Fig. 1). The foliar uptake of SO_2 is generally directly dependent on the degree of opening of the stomata, and the internal resistance to the SO_2 gas is low due to its high solubility in water. In general there is a linear relationship between the uptake of SO_2 by the plant shoot and the atmospheric concentration of SO_2. Once the SO_2 gas diffuses to the mesophyll, it dissociates in water and forms bi(sulfite). The absorbed SO_2 in the mesophyll may enter the sulfur reduction pathway as either sulfite or, after its oxidation as sulfate. Generally, SO_2 exposure results in an enhanced sulfur content of the foliage, mainly because of an accumulation of sulfate presumably in the vacuole, even at relatively low atmospheric concentrations (De Kok, 1990; De Kok and Tausz, 2001; Tausz, 2007). Plants are able to utilize atmospheric H_2S as a sulfur source. The uptake of H_2S by the shoot is largely determined by the rate of its metabolism into cysteine and exposure generally results in rapid accumulation of cysteine and glutathione in the shoot (De Kok, 1990; De Kok et al., 1998, 2002a,b; De Kok and Tausz, 2001). Exposure of plants to atmospheric sulfur gases may depress the uptake of sulfate by the root and its reduction in the shoot (De Kok and Tausz, 2001; De Kok et al., 2002a,b). It has been estimated that at atmospheric levels of $\geq 0.03\,\mu l\, l^{-1}$ SO_2 or H_2S, foliarly absorbed sulfur may contribute substantially (>10–40%) to the sulfur requirement for growth of crop plants (De Kok et al., 2007).

III.   Significance of Sulfur in Plant Functioning and Adaptation to Stress and Pests

Cysteine is the sulfur donor for the synthesis of methionine, and the precursor of several other sulfur compounds, such as glutathione, coenzyme A, biotin and secondary sulfur compounds in plants (Giovanelli, 1990; Noji and Saito, 2003; Chapter 6). The predominant proportion of the organic sulfur in plant tissue is present as cysteine and methionine residues in proteins, which may account for up to 60% and 90% of the total and the organic sulfur fraction, respectively (Heinz, 1993; Stulen and De Kok, 1993). The sulfur-containing amino acids are of great significance in the structure, conformation and function of proteins and enzymes. High levels of these amino acids may also be present as storage proteins, e.g., in seeds (Tabatabai, 1986). The thiol groups of the cysteine residues are highly significant in various functional reactions. In proteins the thiol groups can form covalent bounds upon oxidation resulting in disulfide bridges with other cysteine side chains and/or linkage of polypeptides to form cystine residues. The thiol groups of cysteine residues in enzymes are also of great importance in the binding of substrates by enzymes, in metal-sulfur clusters in proteins (e.g., ferredoxins, metallothionins) and in regulatory proteins (e.g., thioredoxins (Jacquot et al, 1997; Verkleij et al., 2003).

Plants contain water-soluble non-protein thiol compounds, which account for 1–2% of the total sulfur, with concentration in plant tissue ranging from 0.1 to 3 mM. Cysteine and the tripeptide glutathione (γGlu-Cys-Gly; GSH) or its homologues, e.g., homoglutathione (γGlu-Cys-βAla) in Fabaceae, hydroxymethylglutathione (γGlu-Cys-βSer) in Poaceae, are the major water-soluble non-protein thiol compounds present in plant tissues in glutathione/cysteine ratio generally exceeding 10 (De Kok and Stulen, 1993; Rennenberg, 1997; Grill et al., 2001; Chapter 11). Glutathione and its homologues are enzymatically synthesized in two steps, both of which are ATP dependent reactions (Fig. 1). First, γ-glutamyl-cysteine is synthesized from cysteine and glutamate by γ-glutamylcysteine synthetase and second, glutathione is synthesized from γ-glutamylcysteine and glycine (in glutathione homologues, β-alanine or serine) catalyzed by glutathione synthetase.

Glutathione functions in sulfur metabolism in the reduction of APS (as a reductant), storage and transport of reduced sulfur and regulation of sulfate assimilation in plants (Grill et al., 2001; Chapter 11). Furthermore it functions as a reductant in the enzymatic detoxification of reactive oxygen species in the glutathione-ascorbate cycle and as thiol buffer in the protection of proteins via direct reaction with reactive oxygen species, e.g., superoxide, hydrogen peroxide and lipid hydroperoxides, or by the formation of mixed disulfides (De Kok and Stulen, 1993; Grill et al., 2001; Tausz et al., 2003a; Fig. 2). All these reactions occur via a sulfide/disulfide exchange reaction of its cysteine residue generally in combination with glutathione reductase, an NADPH-dependent enzyme. The redox state of glutathione (GSH/GSSG ratio) in plant tissue generally exceeds a value of 7 (Rennenberg, 1997; Foyer and Noctor, 2001; Tausz, 2001). Variation in glutathione levels, its redox state and the activity of glutathione reductase have been related to the adaptation of plants in agro- and natural ecosystems to stress and a
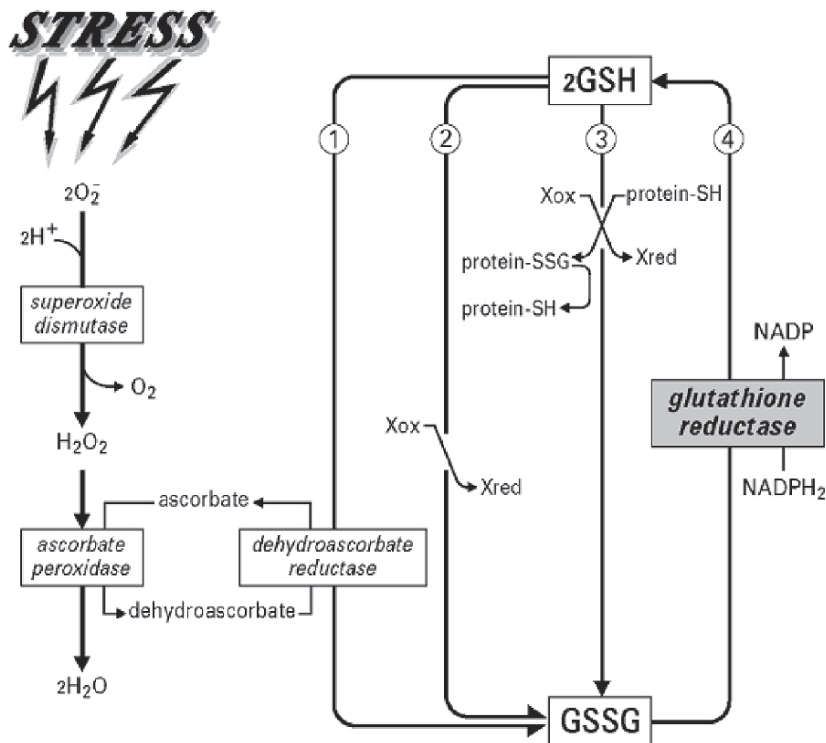

Fig. 2. Significance of glutathione and glutathione reductase in the enzymatic detoxification of reactive oxygen species in the glutathione-ascorbate cycle (1) and as thiol buffer in the protection of proteins via direct reaction with reactive oxygen species, e.g., superoxide, H_2O_2 and lipid hydroperoxides (2), or by the formation of mixed disulfides (3) (adapted from De Kok and Stulen, 1993).

changing environment, e.g., air pollution, drought, low temperature, UV-B radiation (Grill et al., 2001; Chapter 11).

Moreover, glutathione is the precursor of phytochelatins ((γGlu-Cys)$_n$Gly), which are synthesized by a inducible phytochelatin synthase. The number of γ-glutamyl-cysteine residues (γGlu-Cys)$_n$ in phytochelatins generally ranges from 2 to 5 (though sometimes up to 11). Phytochelatins play an important role in the detoxification of cadmium, and possibly also arsenic (Cobbett and Goldsbrough, 2002). Cadmium exposure was found to stimulate sulfate uptake by maize roots through enhanced expression of a high affinity sulfate transporter, as a result of the increased demand for sulfur in the biosynthesis of phytochelatins (Nocito et al., 2002, 2006). Although several other metals or metalloids (e.g., Cu, Hg, Ag, Zn and Ni) can also induce synthesis of phytochelatins, there is no direct evidence that phytochelatins are responsible for their detoxification (Cobbett and Goldsbrough, 2002). It is assumed that the cadmium-phytochelatin complex is transported into the vacuole in order to sequester the potentially toxic cadmium (Rauser, 1993, 2000, 2001). Glutathione is also involved in the detoxification of xenobiotics (Schröder, 1998, 2001; Gullner and Kömives, 2001). Different xenobiotics may induce distinct isoforms of the enzyme glutathione *S*-transferase, which catalyzes their conjugation with glutathione. Under natural conditions, glutathione *S*-transferases are assumed to have significance in the detoxification of lipid hydroperoxides, in the conjugation of endogenous metabolites, hormones and DNA degradation products, and in the transport of flavonoids, but in agro-ecosystems they may have great significance in herbicide detoxification and tolerance.

Sulfoquinovosyl diacylglycerol is the predominant sulfolipid present in plants, and in leaves it accounts for up to 3–6% of the total sulfur content (Heinz, 1993; Benning, 1998; Harwood and Okanenko, 2003). It is a constituent of plastid membranes and is likely to be involved in chloroplast (plastid) functioning. Sulfite is the likely sulfur precursor for the formation of the sulfoquinovose group of this lipid (Harwood and Okanenko, 2003). Despite quantitative and qualitative changes in sulfolipid content and its fatty

acid composition upon exposure to stress and pests, its actual significance in adaptation needs further evaluation.

Some plant species contain secondary sulfur compounds, such as glucosinolates in *Brassica* (Schnug, 1990, 1993; Rosa, 1997; Graser et al., 2001; Glawisching et al., 2003) and γ-glutamyl peptides and alliins (*S*-alk(en)yl cysteine sulfoxides; Chapter 13) in *Allium* (Lancaster and Boland, 1990; Randle et al., 1993, 1995; Randle, 2000; Randle and Lancaster, 2002; Coolong and Randle, 2003a,b). Glucosinolates account for 1–6% of the total sulfur in the leaves of oilseed rape (Blake-Kalff et al., 1998). There are at least 120 glucosinolates identified in 16 families of dicotyledonous plants, which vary in the side chains and are derived from 8 different amino acids (Fahey et al., 2001; Halkier and Gershenzon, 2006). Upon tissue disruption glucosinolates are enzymatically degraded by myrosinase and yield a variety of biologically active products such as isothiocyanates, thiocyanates, nitriles and oxazolidine-2-thiones (Rosa, 1997, 1999; Kushad et al., 1999; Graser et al., 2001; Petersen et al., 2002; Reichelt et al., 2002; Wittstock and Halkier, 2002). The glucosinolate-myrosinase system is assumed to play a role in plant–herbivore and plant–pathogen interactions. Furthermore, glucosinolates are responsible for the flavor properties of Brassicaceae and recently have been shown to have significance as phytopharmaceuticals in view of their potential anti-carcinogenic properties (Zhang et al., 1992; Fahey et al., 1997, 2002; Kushad et al., 1999; Graser et al., 2001; Petersen et al., 2002; Reichelt et al., 2002).

In *Allium* the content of γ-glutamyl peptides and alliins is strongly dependent on the stage of development of the plant, temperature, water availability and the level of nitrogen and sulfur nutrition (Lancaster et al., 1986, 2000; Lancaster and Shaw, 1989, 1991; Randle et al., 1993, 1995; Randle, 2000; Randle and Lancaster, 2002; Coolong and Randle, 2003a,b; Durenkamp and De Kok, 2002, 2003, 2004). Bloem et al. (2004) observed that in onion bulbs the content of iso-alliin may account for up to 74% of the total sulfur content. γ-Glutamyl peptides may be synthesized from cysteine (via γ-glutamylcysteine or glutathione) and can be metabolized into the corresponding alliins via oxidation and subsequent

hydrolyzation by γ-glutamyl transpeptidases, although other possible routes of their synthesis cannot be excluded (Granroth, 1970; Lancaster and Boland, 1990; Edwards et al., 1994; Randle and Lancaster, 2002). The alliins and their breakdown products (e.g., allicin) are the flavor precursors for the odor and taste of the *Allium* species. A wide variety of volatile and non-volatile sulfur-containing compounds are released from the tissue by alliinase, an enzyme that is released from the vacuole upon disruption of the tissue (Lancaster and Collin, 1981; Block, 1992). The physiological functions of γ-glutamyl peptides and alliins are still largely unresolved, but may have significance in chemical defense against insects and pathogens and in the storage of nitrogen and sulfur (Lancaster and Boland, 1990, 1991; Schnug, 1993; Lancaster and Shaw, 1991; Randle and Lancaster, 2002). Furthermore, these compounds may have potential value as phytopharmaceuticals (Haq and Ali, 2003).

Several other sulfur metabolites may play a role in the resistance of plants against stress and pests, e.g., phytoalexins, sulfur-rich proteins (thionins) and localized cellular deposition of elemental sulfur (Cooper and Williams, 2004; Hell and Kruse, 2007) and even the possible release of volatile sulfur compounds as H_2S (Schnug, 1997; Städler, 2000; Glawisching et al., 2003; Haneklaus et al., 2003; Haq and Ali, 2003; Hell and Kruse, 2007; Tausz, 2007). However, their significance in "sulfur-induced-resistance" is not yet fully understood and needs further to be assessed (Schnug, 1997; Haneklaus et al., 2003). For instance, plants grown under normal sulfur conditions may emit minute amounts of H_2S, which may be formed prior to or after the synthesis of cysteine, in the latter case by cysteine desulfhydrase (Schröder, 1993; Haneklaus et al., 2003; Riemenschneider et al., 2005). However, the rate H_2S release is a negligible proportion of the total sulfur flux in plants (Stulen and De Kok, 1993). The H_2S emission may be strongly enhanced when plants are previously exposed to high levels of atmospheric sulfur gases (Rennenberg, 1984; Schröder, 1993; Haneklaus et al., 2003; Tausz, 2007). However, its physiological significance under natural conditions appears be unclear (Ernst, 1990).

IV. Plant Sulfur Requirement and Nutrition in Agro- and Natural Ecosystems

Sulfur requirement varies greatly among agricultural crops. *Brassica* crops have a high demand for S (1.5–2.2 kmol ha^{-1}), followed by *Allium* crops such as leek and onion (1–1.2 kmol ha^{-1}), whereas cereals and legume crops require relatively small quantities of S (0.3–0.6 kmol ha^{-1}) (Zhao et al., 2002). The high requirements of *Brassica* and *Allium* crops are partly due to the synthesis of S-containing secondary metabolites, glucosinolates in *Brassicas* and *S*-alk(en)yl-L-cysteine sulfoxide in *Allium* crops. In addition, the high sulfur requirement of *Brassicas* may also be attributed to a large accumulation in the vegetative tissue of sulfate, which is remobilized slowly in response to sulfur deficiency (Blake-Kalff et al., 1998). Sulfur requirement is also dependent on crop yield; a high yielding crop requires more nutrients including S.

Sulfur deficiency occurs when sulfur supply from the environment does not match the requirement by the crop. Incidences of sulfur deficiency in agricultural crops or grassland have been reported in different regions of the world (Pasricha and Fox, 1993; Dobermann et al., 1998; Blair, 2002; Zhao et al., 2002; Edmeades et al., 2005; Malhi et al., 2005). *Brassica* crops and multiple-cut grass are generally more prone to sulfur deficiency than other crops, because of their high requirements for sulfur. In Western Europe, sulfur deficiency has become more common in recent decades mainly because of a dramatic reduction in the sulfur inputs from the atmosphere (McGrath et al., 2002). For example, in many areas in the United Kingdom, atmospheric sulfur deposition decreased from 70 kg ha^{-1} year^{-1} in the 1970s to less than 10 kg ha^{-1} year^{-1} in the early 2000s. Other contributing factors include the use of sulfur-free compound fertilizers and the increasing trend of crop yield. Sulfur deficiency usually occurs as a result of a nutrient imbalance, particularly with regard to nitrogen, and one of the common indicators that are used to diagnose sulfur deficiency is the nitrogen to sulfur ratio (Dijkshoorn and van Wijk, 1967). A nitrogen to sulfur ratio of greater than 17:1 (molar ratio 39:1) in wheat grain generally indicates that the crop had been supplied with inadequate sulfur (Randall et al., 1981). In leaf tissues, the critical

value of the ratio is approximately 15:1 (molar ratio 34:1) for cereals and 6–10:1 (molar ratio 14–23:1) for oilseed rape (Spencer and Freney, 1980; McGrath and Zhao, 1996; Blake-Kalff et al., 2000; Blake-Kalff et al., 2002). Recently, Blake-Kalff et al. (2000) proposed the use of the malate to sulfate ratio in leaf tissues as a reliable diagnostic method for crops such as cereals and oilseed rape. A sulfur-deficient crop utilizes nitrogen inefficiently, which subsequently leads to increased nitrogen losses to the environment. For example, Brown et al. (2000) showed that the application of sulfur reduced nitrate leaching to drainage water by 5–72% at a sulfur-deficient grassland site. Therefore, correcting sulfur deficiency in agricultural crops not only benefits yield but also the environment.

Sulfur deficiency can be easily corrected by the application of sulfur fertilizers. Sulfur fertilizers are available in a number of chemical forms; the most common are sulfate and elemental sulfur. The sulfate form is readily available to plant uptake, but sulfate is very mobile in near neutral and alkaline soils and is thus prone to leaching losses when rainfall exceeds evatranspiration. In contrast, elemental sulfur is not available to plant uptake until it is oxidized to sulfate. Oxidation of elemental sulfur is mediated by both autotrophic chemolithotrophs, including some species of *Thiobacillus*, and a wide range of heterotrophic bacteria and fungi in soil (Lawrence and Germida, 1991; Germida and Janzen, 1993). The oxidation is affected by: (a) presence of microorganisms capable of oxidation of elemental sulfur, (b) effective surface area of the elemental sulfur particles, (c) soil temperature, (d) soil water potential and (e) soil aeration (Janzen and Bettany, 1987; McCaskill and Blair, 1987; Watkinson and Blair, 1993; Watkinson and Lee, 1994; Haneklaus et al., 2007a). For annual agricultural crops, sulfate fertilizers are generally a better option than elemental sulfur because the rate of oxidation of elemental sulfur may not match crop demand (Riley et al., 2000; Zhao et al., 2002; Malhi et al., 2005). On the other hand, elemental sulfur is suitable as a maintenance fertilizer for pasture (Blair, 2002).

The sulfur supply to plants in natural ecosystems originates from weathering of rocks, mineralization of organic sulfur and ground or runoff water (Edwards, 1998; Haneklaus et al., 2003).

Atmospheric sulfur inputs may contribute substantially to the sulfur influx in natural ecosystems, where the total of dry and wet sulfur deposition may range from 0.06 to 1 kmol ha^{-1} year^{-1}, though locally in heavily polluted areas these values can be much higher (Johnson, 1984; Cappellato et al., 1998; Edwards, 1998; Haneklaus et al., 2003). It is generally assumed that, in contrast to agroecosystems, plants in natural ecosystems have an adequate sulfur supply (Ernst, 1990, 1993, 1997; Haneklaus et al., 2003). For example, in lowland and wetland ecosystems, the sulfate concentrations in ground or runoff water and the sulfur content in the soils and sediments burials are presumed to be sufficient for natural plant growth (Haneklaus et al., 2003). The sulfur uptake necessary for tree growth ranges from 0.1 to 0.2 kmol ha^{-1} year^{-1}, whereas the total sulfur content of mineral soils in upland ecosystems ranges from 10 to 100 kmol ha^{-1} (and forest floors 0.6 to 1.8 kmol ha^{-1}) (Haneklaus et al., 2003). However, most of the soil total sulfur might not be available for plant uptake (Edwards, 1998). Soil soluble sulfate-S in forest soils ranges from 0.15 kmol ha^{-1} at a conifer site remote from pollutant inputs (*Pseudotsuga menziesii* plantation in southeastern Australia) to more than 50 kmol ha^{-1} at a deciduous forest site with high sulfur pollution input (*Quercus prinus* in TN, USA; Johnson, 1984). Because sulfur requirements of forest stands are low, sulfur deficiencies in forests have only been reported from areas remote from pollutant inputs, e.g., from southeastern Australia and northwestern United States (Johnson, 1984). Atmospheric sulfur inputs as low as 0.03 kmol ha^{-1} year^{-1} may be sufficient to sustain growth of a *Pinus radiata* stand in Australia (Johnson, 1984). Although a recent large scale survey suggested that the effect of atmospheric sulfur deposition is still measurable at many forest sites across Europe (Augustin et al., 2005), decreasing atmospheric sulfur inputs in conjunction with increasing nitrogen deposition may lead to an increased probability of sulfur limitation of forest ecosystems in the future (Johnson and Mitchell, 1998). It has to be pointed out that the cited forest studies dealt with overall ecosystem budgets and not with specific tree physiological measurements. Instantaneous sulfur requirements of forest stands may deviate significantly from annual averages, e.g., during development of new foliage or when storage

proteins are laid down. Physiological studies indicated such changes and showed contributions of internal redistribution (see above), but currently do not allow quantification on whole tree or stand basis (Rennenberg and Herschbach, 1995). Adsorption/desorption properties of sulfate in forest soils lend themselves to causing temporary limitations in available sulfate during periods of increased requirements (Johnson and Mitchell, 1998). Hence, the instantaneous requirements of forest trees in relation to their growth stage warrant further interest.

In some natural ecosystems plants have to cope with excessive sulfur in oxidized (sulfate) or reduced form (sulfite, sulfide), which may be available to the plant via (i) the pedosphere from sulfur-emitting fumeroles, gypsum-rich soils and waterlogging, (ii) the hydrosphere from salinity and (iii) the atmosphere from dry and wet deposition of atmospheric sulfur. Excessive sulfur may negatively affect plant growth, for instance as the consequences of sulfate salinity. However, plants may be adapted and are able to cope with excessive sulfur by accumulating it as sulfate in the vacuole (so-called thiophores), or by its elimination (avoidance of sulfur accumulation) by secretion from the shoot via salt glands in halophytes or emission of sulfur gases as H_2S and dimethyl sulfide (DMS; Ernst, 1990, 1993, 1997; Stefels, 2000, 2007). The latter emission is highly significant in some plant species from marine ecosystems, e.g., *Spartina*, which may accumulate high levels of dimethylsulfoniopropionate (DMSP) in leaves upon exposure to excessive sulfur. DMSP may be enzymatically degraded to yield DMS emission by the shoot (Ernst, 1990, 1993, 1997; Hanson and Gage, 1996; Stefels, 2000, 2007). Specific species (e.g., *Allium* and *Brassica*) may emit a variety of other organic sulfur gases including DMS, which are likely degradation products of secondary sulfur compounds (Lanzotti, 2006).

Permanent or temporary potentially phytotoxic levels of dissolved H_2S in the rhizosphere may occur in marshes and tideland wetlands, and in poorly drained and waterlogged soils, e.g., rice paddies (Trudinger, 1986; Van Diggelen et al., 1987; Bates et al., 1992; Armstrong et al., 1996; Armstrong and Armstrong, 2005). In these anoxic soils, H_2S is produced from biological decay of organic sulfur and the activity of dissimilatory sulfate-reducing bacteria and is accumulated under anoxic conditions. Levels from 0.02 to 1.4 mM sulfide may occur in the soil solution around the root zone (Allam and Hollis, 1972; Carlson and Forrest, 1982; Van Diggelen et al., 1987). Levels as low as 0.002 mM sulfide may negatively affect root respiration and nutrient uptake (Allam and Hollis, 1972; Joshi et al., 1973, 1975). Sulfide levels higher than 0.08 mM may reduce root growth and development or result in root and bud death, lignification and blockages within the root arenchyma and vascular tissue (Ford 1973; Armstrong et al.,1996; Armstrong and Armstrong, 2005). The tolerance to high H_2S levels under anoxia is most likely determined by the *in situ* sulfide level in the roots, which is dependent on the rate of oxidation of sulfide in the rhizosphere by bacteria such as *Beggiotoa* or in the plant, and by the sulfide resistance of metabolic processes in the plant species (Joshi et al., 1973, 1975; Joshi and Hollis, 1977; Carlson and Forrest, 1982; Fry et al., 1982; Van Diggelen et al., 1987; Armstrong et al., 1996; Armstrong and Armstrong, 2005). Despite the toxicity of sulfide, there is evidence on basis of the $^{34}S/^{32}S$ ratio in plant tissue that some species from saline habitats are able to use the abundant sulfide upon anoxia directly or indirectly as sulfur source (Raven and Scrimgeour, 1997).

V. Sulfur and Food Quality

Quality requirements of agricultural products vary widely and are determined mainly by the end use of the product. The sulfur nutrition of a crop often has strong and diverse influences on the quality of the produce, because of its essential role in the synthesis of amino acids, proteins and some secondary metabolites.

Legume seeds are important sources of protein for humans and animals. However, their nutritional value is limited by the low contents of the essential amino acid methionine (Friedman, 1996). Different storage proteins of legume seeds vary considerably in their contents of the S-containing amino acids. For example, the pea storage proteins vicilin and lectin contain no cysteine and methionine, whereas legumin contains 1.7% S-containing amino acids (Spencer et al., 1990). Soybean seed has two major storage proteins, glycinin and β-conglycinin. Glycinin is

rich in S-containing amino acids (1.8%), whereas β-conglycinin is poor in these amino acids (0.6%) (Shortwell and Larkins, 1989). In general, sulfur deficiency decreases the synthesis of S-rich storage proteins, but increases the synthesis of S-poor proteins concomitantly (Blagrove et al., 1976; Gayler and Sykes, 1985; Spencer et al., 1990; Naito et al., 1995). As a result, sulfur deficiency in legume crops reduces the nutritive value of the seeds (Eppendorfer, 1971; Eppendorfer and Eggum, 1995).

The disulfide and thiol groups of gluten proteins are essential for viscoelasticity of the wheat dough during breadmaking (Shewry and Tatham, 1997; Zhao et al., 1999b,c). Studies in Australia established that sulfur nutrition plays an important role in the breadmaking quality of wheat (Moss et al., 1981, 1983; Wrigley et al., 1984; MacRitchie and Gupta, 1993). These studies showed that sulfur increased synthesis of S-rich storage proteins, such as the α-, β-, and γ-gliadins and the low-molecular-weight glutenin subunits, and decreased the proportion of S-poor proteins, such as the ω-gliadins and the high-molecular-weight glutenin subunits. Furthermore, the concentration of sulfur in flour correlated positively with dough extensibility, but negatively with resistance to stretching. Similarly, several studies in Europe showed that the S status of wheat has a profound effect on the composition of gluten proteins, the rheological properties of dough and breadmaking performance (Schnug et al., 1993; Zhao et al., 1999a,b,c; Wieser et al., 2004; Flaete et al., 2005). In general, increasing S concentration in wheat grain is associated with increasing dough extensibility and increased loaf volume of bread. It is clear that maintaining an adequate sulfur status for wheat is important for breadmaking quality.

Sulfur deficiency has been found to result in a large accumulation of asparagine in cereal leaves and grain (Shewry et al., 1983; Zhao et al., 1996). A recent study has shown a startling increase in the levels of free asparagine in the grain of wheat grown under sulfur deficiency and the formation of high levels of acrylamide during heating of flour derived from sulfur-deficient grain (Muttucumaru et al., 2006). The level of acrylamide produced from the sulfur-deficient flour was approximately 5–10-fold higher than that from the sulfur-sufficient flour. The presence of acrylamide in a range of fried and oven-cooked foods has caused worldwide concern because this compound has been classified as probably carcinogenic in humans; acrylamide also has neurological and reproductive effects (Friedman, 2003). Acrylamide found in cooked foods is formed during heat treatment of food components as a result of the Maillard reaction between amino acids, particularly asparagines, and reducing sugars (Mottram et al., 2002; Stadler et al., 2002). This explains why sulfur deficiency has such a marked effect on acrylamide formation in heat-treated wheat flour, and highlights the importance of sulfur nutrition in terms of food safety.

Sulfur deficiency can also affect the quality of sugar beet storage roots. Using a hydroponic system to grow sugar beet, Bell et al. (1995) showed that withholding sulfur supply for two months increased the concentration of α-amino-N in the beet roots more than 2-fold. The increased concentration of amino acids in roots reduces juice purity, and therefore the extraction yield of white sugar.

Malting quality of barley and brewhouse performance are assessed in terms of ease of processing and flavor characteristics (Palmer, 1989). During malting of barley grain, large molecular weight components of the endosperm cell walls, the storage proteins and starch granules are hydrolyzed (modified) enzymatically, rendering them more soluble in hot water during mashing. Variability in malting quality is due to factors such as the rate of enzyme synthesis during germination, the composition of the endosperm, and the packing of starch granules (Palmer, 1989). A recent study by Zhao et al. (2006) showed that sulfur applications significantly increased the activities of hydrolytic enzymes and improved endosperm modification during malting. As a result, the concentration of β-glucan in the wort was decreased, which is beneficial for the filtration of wort. Furthermore, sulfur applications also increased the concentration of *S*-methylmethionine (the precursor of the flavor compound dimethylsulfide) in kilned malt, which is expected to impact on beer flavor.

The presence of high levels of glucosinolates in rapeseed can restrict its use in animal feed. One of the predominant glucosinolates in rapeseed is 2-hydroxy-3-butenyl glucosinolate (progoitrin), which forms oxazolidine-2-thione

upon hydrolysis. This hydrolytic product has goitrogenic and anti-nutritional effects in animals (Fenwick et al., 1983; Griffiths et al., 1998). The glucosinolate content in rapeseed has been much decreased by breeding of the double-low (low erucic acid and low glucosinolates) varieties. However, even in these varieties glucosinolates can account for up to 30% of the total sulfur in the seeds. Sulfur supply is one of the most important environmental factors that influence the synthesis and accumulation of glucosinolates in seeds (Schnug, 1990; Zhao et al., 1993). In general, use of sulfur fertilizer to oilseed rape at a normal recommended rate is unlikely to increase the glucosinolate concentration to an unacceptable level, but applying more S than required by the oilseed rape crop must be avoided (Zhao et al., 2002). In contrast to the undesirable effects of hydroxyalkenyl glucosinolates mentioned above, certain glucosinolates have been identified as possible cancer prevention agents in model animals and might have significance as phytopharmaceuticals. In particular, sulforaphane, the isothiocyanate produced from the hydrolysis of 4-methylsulfinylbutyl glucosinolate, which is present in broccoli, has been found to induce anticarcinogenic protective enzymes (phase II enzymes) (Zhang et al., 1992; Fahey et al., 1997; Fahey et al., 2001). Sulforaphane reduced the incidence, delayed the appearance of, and reduced the size of tumors in a rat mammary tumor model (Fahey et al., 1997), and showed potential for treating *Helicobacter pylori*-caused gastritis and stomach cancer (Fahey et al., 2002). Therefore, sulfur nutrition could play a role in enhancing the health promoting properties of *Brassica* vegetables.

The nutritional quality of sulfur deficient grass silage is poor. For animal feeding, a N:S ratio below 15:1 is considered satisfactory (Murphy and O'Donnell, 1989). Applications of sulfur fertilizer increased the proportion of total N in grass present as protein-N, and decreased the contents of nitrate and free amino N (Murphy and O'Donnell, 1989; Richards, 1990; Murphy and Quirke, 1997; Murphy et al., 2002). These effects are beneficial to animal nutrition. Sheep are more sensitive to S deficiency than cattle because of the special requirements for wool production. Early studies showed that sheep performance was improved by sulfur fertilization of forage (Rendig and Weir, 1957). Too much sulfur in grass may have an adverse effect on animal health. Sulfur may induce copper deficiency in cattle, by forming thiomolybdate compounds in the rumen which bind copper and make it unavailable to the animal (Leach and Thornton, 1987). This appears to occur when the copper status of the animal diet is marginal and the concentrations of molybdenum and sulfur are high. The critical concentrations of Mo and S in herbage that can cause an antagonism on Cu metabolism are >3 mg kg^{-1} and >0.3–0.4% on a dry matter basis, respectively. The other antagonistic effect of sulfur is to decrease selenium uptake by plants (White et al., 2007). Selenate is a chemical analogue of sulfate and is taken up by the plant root via sulfate transporters. Sulfur fertilization decreased herbage Se concentration, which subsequently resulted in a significantly lower blood Se level in the cattle grazing the S-treated pasture (Murphy and Quirke, 1997). Selenium supplementation can be practiced by addition to animal feeds or by the inclusion of selenium in fertilizers (White et al., 2007).

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