Chapter 2

SULFUR INTERACTIONS IN CROP ECOSYSTEMS

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INTRODUCTION

A comprehensive examination of adaptation of crop plants to changes in sulfur (S) supply begins with an analysis of the influence of pedogenetic and climatic factors. Sulfur supply has consequences for crop productivity and nutritional quality in terms of nutritive value and health-related properties. Factors affecting S supply and the subsequent impacts on crops are discussed in this chapter.

The soil S cycle is driven by biological and physico-chemical processes, which affect both flora and fauna. For example, the knowledge of S speciation in soils is required to provide information on plant available S forms and gives indications of likely interactions between the rhizosphere and the soil matrix. An additional complexity is the high spatio-temporal variability of sulfate occurring in soils (Schnug and Haneklaus 1998), and one consequence is that the plant available sulfate concentration in soils is a poor diagnostic criterion for the S supply. The presence of allelochemicals in the soil, including S-containing compounds, not only affects plants but also other organisms such as soil microorganisms, insects and herbivores, which will have impacts on all soil processes.

Both, severe S deficiency and S toxicity may occur in plants, foodstuffs, animal feed, and the human body. Macroscopic S deficiency is a major nutritional disorder in agricultural production in Europe, whilst the detrimental impact of S pollution on crop performance is a major concern in Asia. In East Asia, where under current legislation restrictions, SO_2

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emissions are expected to increase 34% by 2030 (Ichikawa *et al.* 2001), excessive S deposition is an inexorably increasing problem.

Crop productivity and nutritional quality of plants are closely related to mineral nutrition. In this chapter an attempt is made to summarize the response of crop plants to different regimes of S nutrition in terms of yield and composition in order to deliver a platform for evaluating their significance for nutritive value and health. Nutrigenomics acknowledges the prominent role of nutrition for disease protection by studying interactions between bioactive compounds and the genome (Ferguson 2006). A quality parameter for foodstuffs and animal feed is, in addition to the absence of S-containing antinutritives (e.g. glucosinolates) and allergens (e.g. cysteine proteinases), an adequate cysteine to methionine ratio and a high content of health promoting metabolites (e.g. glutathione, methylsulfonylmethane). The S supply is closely related to many of these compounds. *Brassica* crops contain characteristic glucosinolates, which are antinutritives because of their goitrogenic effect. Since the introduction of double low oilseed rape cultivars in the middle of the 1980s, higher doses of extracted rapeseed meal may be fed to animals without detrimental health effects. The S supply is one of the major factors influencing the glucosinolate content in vegetative and generative tissues of oilseed rape (Schnug 1990). Whilst a high glucosinolate content is undesired in animal feed, it is one of the secondary compounds with a strong anticarcinogenic potential in humans. The intake of sulforaphan, the degradation product of glucoraphanin in broccoli, has been linked to diminished risk of prostate cancer in several epidemiological studies (Cohen *et al.* 2000; Kolonel *et al.* 2000; Giovannuci *et al.* 2003).

Thiono-S (C = S or P = S) compounds may exhibit toxic properties such as lung and liver damage, and bone marrow depression (Neal and Halpert 1982). CS_2 is a thiono-S compound, which is used in agriculture as a nitrification inhibitor, others are constituents of pesticides and they may enter the human body. This stresses the advantage of ecologically sound agricultural production not only for environmental protection, but also for preventing adverse health effects. A naturally occurring thiono-S compound is goitrin, which can be found after degradation of progoitrin in *Brassica species* (Fenwick and Griffiths 1981). Pigs that were fed with extracted rapeseed meal showed goitrin levels in loin muscle that were rated as being inoffensive for human consumption (Thomke *et al.* 1998).

The ratio of S per gram of protein is similar in vegetable and animal proteins, but proteins in plant products have a lower nutritional quality for humans, because the cysteine to methionine ratio is imbalanced (Massey 2003). In vegetables the cysteine to methionine ratio is lowest with a ratio varying between 1:0.5 and 1:1 (Hands 2000). Soybeans and eggs show an

intermediate ratio of 1:1.3, while meat products have distinctly higher ratios of 1:2 to 1:2.8. In most plant species, the major proportion of S (up to 70% of the total S) is present in the reduced form in cysteine and methionine residues of proteins. The S-containing amino acids cysteine and methionine play a significant role in the structure, conformation, and function of proteins and enzymes in vegetative plant tissue, but high levels of these amino acids may also be present in seed storage proteins (Tabatabai 1986).

Glutathione is an antioxidant and may play a key role in the detoxification of xenobiotics and carcinogenesis in the human body (Richie 1992). During aging a faster oxidation of the physiological S pool can be observed and thus resulting in a higher physiological demand of antioxidants for maintaining the GSH to GSSG ratio (Miquel *et al.* 2006). Friedman (1994) outlines the significance of SH-containing amino acids and peptides as a means to combat adverse effects by other food compounds, for instance aflatoxins. Asparagus is rich in glutathione with 4 mg g^{-1} dry weight compared to other vegetables such as broccoli (0.7 mg g^{-1}), spinach (0.7 mg g^{-1}), or tomato (1.9 mg g^{-1}) (Pressman 1997). The glutathione content is closely related to the S nutritional status in such a way that an S application rate of 100 kg S ha^{-1} increased the glutathione content by about 65 nmol g^{-1} dry weight in leaves of oilseed rape and asparagus spears (Haneklaus *et al.* 2006).

Alliins (cysteine sulfoxides) are the characteristic S-containing secondary metabolites of *Allium* species such as onions, shallot, garlic, leek, and chives, which cause sensory characteristics and entail the pharmaceutical quality. The therapeutic effect of onions on vascular diseases such as thrombosis, arteriosclerosis, hyperlipidemia, and rheumatic arthritis of humans was attributed to the degradation of iso-alliin, which yields the lachrymatory factor (thiopropanal SO) and from this metabolite components are finally derived, which inhibit platelet aggregation (Kawakishi and Morimitsu 1994). Garlic is used against arteriosclerosis, high blood pressure, and has been shown to have antibacterial, antifungal, antiviral, and antiprotozoal activities. It also modulates the cardiovascular and immune system and has antioxidative and anticarcinogenic properties (Harris *et al.* 2001). S fertilization increased the isoalliin content in the leaves of onion up to 43-fold and doubled the alliin content in bulbs of onion and garlic (Bloem *et al.* 2001; Bloem *et al.* 2004).

After calcium (Ca) and phosphorus (P), S is the third most abundant mineral in the human body with about 0.25% (140 g S) of the total body weight (Clark 2002). While deficiency of S in the diet is rare, its toxicity has been identified as a relevant factor of concern (Komarnisky and Basu

2005). Grimble (2006) points out that high intake of L-methionine might increase the homocysteine level in plasma. Homocysteine may favor inflammatory centers, so that as a precautionary measure, increased intake of L-methionine should be avoided (Grimble 2006). High homocysteine increases the risk for cardiovascular disease, too (Borek 2006). An enhanced level of homocysteine intake is for instance possible by nutraceuticals. Methylsulfonylmethane (MSM) is a nutraceutical that alleviated symptoms of pain and physical function of humans suffering from osteoarthritis (Kim *et al.* 2006). Dietary supplements and nutraceuticals need to be critically evaluated because their regular intake may support, or even encourage, malnutrition with as yet unknown consequences for health. It is better to promote interest in and consumption of authentic foods, rich in bioactive compounds due to agro-technological measures such as S fertilization, to take advantage of the whole range of compounds in natural food and their synergetic effects.

This chapter provides an overview of various aspects of the adaptation of crop plants to changes in the S supply, in which special attention is paid to S in the rhizosphere and the effects of excessive S rates on crop performance. Previous monographs concentrated on S cycles at different scales (Haneklaus *et al.* 2003), diagnosis of the S nutritional status (Schnug and Haneklaus 1998), and various aspects of S in plant nutrition (Haneklaus *et al.* 2006). S transformation processes in the soil are closely related to management practices such as crop rotation and diversity of soil fauna. Measures, which foster plant health by combating soil-borne pathogens, as for example biofumigation, deserve a closer examination as they have the potential to substitute for pesticides by controlled amendment of S-containing allelochemicals. Data on the influence of variations in the S supply on crop productivity and quality are valuable for a better understanding of the long-term implications of anthropogenic activities causing excess or low S inputs. Even more importantly, such figures may enable an appraisal of the significance of S supply to crop plants for their nutritive value and possible health effects.

ADAPTATION OF THE PLANT RHIZOSPHERE TO CHANGES IN THE S SUPPLY

Lorenz Hiltner (1862 – 1923) coined the term rhizosphere and underlined the significance of microbial activities in this compartment for plant nutrition and plant health. Nicholas (1965) calculated that 1 g of soil of fertile arable land contains about 10^6–10^9 bacteria, 10^5–10^6 fungi, and 10^1–10^3

algae. The rhizosphere microflora, sustained by root exudates and root debris, affects plant growth in return by changing the availability of nutrients (Curl and Truelove 1986). The rhizosphere covers the space between the surface of plant roots and closely adhering soil particles and debris. Plant roots excrete among others sugars, amino acids, glycosides, organic acids, vitamins, and enzymes (Curl and Truelove 1986). The composition of the exudate varies in relation to plant species, growth stage and principal soil features (Curl and Truelove 1986). Biochemical speciation of S in soils in relation to plant species reflects interactions between root exudates and microflora.

No chemical method, as far as the extractant or extracting procedure is concerned, has found universal acceptance for analyzing plant available S in soils. Site-specific differences of soil characteristics influence plant available sulfate quantitatively, while qualitative modifications could not be verified for different S fractions (Zucker 1987). Usually plant available sulfate concentrations provide no satisfactory relationship to the plant S status or yield. The reason has to be seen in the high spatio-temporal variability of sulfate in soils.

Plant-derived allelochemicals may influence plant growth, both, positively and negatively. Glucosinolates are prominent examples of allelochemicals and their effect on soil-borne pathogens has been studied extensively as cultivation of *Brassica* species as break crops and amendment with glucosinolate-containing plant material offers the possibility to reduce the input of pesticides.

S TRANSFORMATION PROCESSES AND S SPECIATION IN SOILS

The soil S cycle is driven by biological and physico-chemical processes, with both plants and soil biota being actively involved. The rhizosphere is a key zone with view to the mechanisms of soil S dynamics. Basic information about S speciation and transformation processes in soils is summarized below for a better understanding of soil/plant interactions and an evaluation of the chemical behavior of S species in the rhizosphere.

S transformation processes in soils

Two types of processes are involved in the mineralization of S, the biological and the biochemical mineralization (McGill and Cole 1981). The biological mineralization is considered to be driven by the microbial need for organic C to provide energy, and S released as sulfate is a by-product

of the oxidation of C to CO_2. Microbial-mediated processes are mainly responsible for S transformations, so that the factors affecting the microbial activity, such as temperature, moisture, pH, and substrate availability will also influence the process of mineralization, immobilization, oxidation, and reduction. From a nutritional point of view, the release of plant-available sulfate is of prime interest for plant growth. This process is faster the more recently the organic matter is formed (Ghani *et al.* 1993). In comparison, biochemical mineralization relies on the release of sulfate from the sulfate-ester pool through enzymatic hydrolysis. This implies that this process is linked to the S supply. Enzymes that catalyze the degradation of sulfate esters are: aryl, alkyl, steroid, gluco-, chondro-, and myco-sulfatases (Germida *et al.* 1993). In soils, only arylsulfatase activity has been determined (Germida *et al.* 1993). The hydrolysis of ester-bonded S follows the equation (Fitzgerald 1978):

$$R\text{–}C\text{–}O\text{–}SO_3^- + H_2O \rightarrow R\text{–}C\text{–}OH + H^+ + SO_4^{2-}$$

The sulfate-ester pool seems to be important for short-term and the carbon-bonded S pool for long-term mineralization of S (McGill and Cole 1981).

The edaphon constitutes about 5% of the total organic matter in soils (Topp 1981). The A_h horizon of soils typically comprises soil biota in the following ratio (dry matter m^{-2} in a no-till farm soil): bacteria (50 g), fungi (100 g), amoeba (5 g), nematodes (0.2 g), arthropods (0.5 g), and worms (1–20 g) (Anthoni 2000). Farm stock amounts to 50 g m^{-2} and is thus comparable to bacteria and earthworms, while fungi outweigh this number considerably (Anthoni 2000). Microbial biomass is in the range of 146 – 968 µg g^{-1} soil (Roembke *et al.* 2002) with an S content of 928 – 1,355 µg S g^{-1} (Saggar *et al.* 1981). Thus S in microbial biomass amounted to about 1–3% of the total organic S in agricultural soils (Saggar *et al.* 1981; Chapman 1987; Wu *et al.* 1994), but also values of up to 8.8% in vegetated soils were found (Hu *et al.* 2002). The turnover of the soil microbial biomass is fundamental for the incorporation of sulfate-S into soil organic matter. However, quantitative relationships between microbial immobilization of inorganic S, turnover of soil microbial biomass-S, and subsequent formation of organic S, as well as the extent of availability of these S fractions for plants have not been determined experimentally so far.

Mineralization of soil organic S can be influenced by farm management practices. The application of organic materials will lead to mineralization if the C:S ratio is <200:1 and immobilization at ratios of >400:1 (Eriksen *et al.* 1998). For ratios in between both processes are possible. Management

practices such as fertilization and crop rotation influence S dynamics (Tabatabai and Chae 1991) and should be steered in such way that the S supply is adapted to the S demand of the crop.

The contribution of mineralization to the S supply of plants is only small with about 1.7–3.1% of the organic S pool per year (Eriksen *et al.* 1998), because mineralization, immobilization, and possible leaching of S occur concurrently (Ghani *et al.* 1993). Thus, in soils with carbon contents between 1% and 4% C, net mineralization contributed 10–30 kg ha^{-1} $year^{-1}$ S to the S balance of an agricultural soil (Bloem 1998). The studies of Eriksen *et al.* (1998) and Bloem (1998) reveal that mineralization is an important, however not cardinal S pool for plants. High-yielding crops cannot satisfy their S demand solely by mineralization and atmospheric S depositions (Schnug and Haneklaus 1998).

S pools and transformation processes in the rhizosphere of different crops

Crop type was shown to influence S mineralization and immobilization in soils (Freney and Spencer 1960). The rhizosphere is a key zone with a view to the mechanisms of soil nutrient dynamics. Only limited data are, however, available about interactions between soil biota and plants and how they affect different S fractions in the rhizosphere. Biological and physico-chemical processes at the soil–root interface differ considerably from those in the non-rhizosphere soil. The evaluation of the bioavailability of different S fractions in various soil–plant systems is important for a better understanding of soil/crop interactions, which may be applied in models for predicting the contribution of organic matter to the S supply of crops. Additionally agronomic and ecological impacts in relation to the site-specific S cycling in agro-ecosystems could be assessed.

Ester-bonded S

The distribution of S fractions in the rhizosphere and non-rhizosphere varied depending on soil type and crop species (Hu *et al.* 2002). In general, the total S content in the soil was higher in the rhizosphere than in the non-rhizosphere. Plant S uptake and mass flow of sulfate from the non-rhizosphere to the rhizosphere most likely caused this variation. Another factor is the root system: oilseed rape with a coarse root system stimulates microbial biomass and thus enhances hydrolysis of ester-bonded S (Vong *et al.* 2002). The result was a positive and significant relationship between arylsulfatase activity and sulfate uptake of oilseed rape (Vong *et al.* 2002). Arylsulfatase released by microorganisms in the rhizosphere of oilseed rape was found to be more closely related to the S demand of the crop than was the case for barley (Vong *et al.* 2002 and 2003; Dedourge *et al.* 2003).

Knauff (2000) found a distinctly higher arylsulfatase activity in the rhizosphere of *Brassica* compared to gramineous crops. Correspondingly, the amount of ester-bonded S was lower in the rhizosphere than in the non-rhizosphere (Hu and Shen 1997; Hu *et al.* 2002). Oilseed rape showed a higher enzyme activity that increased with distance from the root, whilst for winter wheat, the inverse result was found. Additionally, micro-organisms in the rhizosphere have access to energy sources such as root exudates (Yan 1993) and it is possible that living roots enhance the activity of microorganisms and enzymes.

It is presumably the exudation of glucosinolates and their degradation by myrosinase, which yields a biocidal effect when oilseed rape is grown. During senescence oilseed rape roots may secrete myrosinase at up to 20 $\mu g\ kg^{-1}$ soil (Borek *et al.* 1996). The result is a lower amount of S bound in microbial biomass or immobilized (Dedourge *et al.* 2003). Dedourge *et al.* (2003) further assumed that only a part of the microbial population takes part in S mobilization and immobilization processes, as there was a close correlation between arylsulfatase activity and S bound in microbial biomass, but none for C bound in microbial biomass. The quality of root exudates creates a host-specific environment and influences microorganism populations selectively (Angus *et al.* 1994). Vančura and Hansliková (1972) found differences in the amount of root exudates of up to 30%. Though there are no conclusive results available that changes in microbial population are related to exudation patterns, differences in the quantity and composition of exudates exist, and are apparently greater among plants that are phylogenically unrelated (Curl and Truelove 1986). Such crop-specific exudation patterns and rates further strengthen the assumption of a demand-driven adaptation to soil conditions under a limited S supply.

Residual-S

The amount of residual-S was higher in the rhizosphere than in the non-rhizosphere (Hu *et al.* 2003). The content of plant-available S measured in 0.1 M $CaCl_2$ and adsorbed sulfate in the rhizosphere and non-rhizosphere of oilseed rape and radish were significantly lower than those of wheat when grown on a Haplic Acrisol. The reason for these differences was presumably the significantly higher biomass production of oilseed rape and radish compared to wheat (Hu *et al.* 2002). In general, it may be expected that sulfate will accumulate in the rhizosphere when S uptake is lower than mass flow of sulfate. Vong *et al.* (2002) also determined lower sulfate concentrations of organic origin in the rhizosphere and non-rhizosphere of oilseed rape than barley. They identified the rapid S acquisition of oilseed rape as the driving force. This effect was consistent at high mineral S

conditions. The results of Hu *et al.* (2002) and Vong *et al.* (2002) suggest that crop-specific discrepancies in S uptake and crop-related differences of microbial and enzymatic activities in the root zone influence S transformation processes in soils.

Such crop-related differences in S fractions of the rhizosphere and non-rhizosphere were not only found on aerated soils, but also under waterlogged conditions (Hu *et al.* 2003). Rice utilized residual-S more intensely than oilseed rape (Hu *et al.* 2003), because its aeration tissues warrant oxidizing conditions and thus promote activity of microbes and sulfatase from the top to the roots (Han and Yoshida 1982).

Ratios of inorganic sulfate in the non-rhizosphere compared to the rhizosphere varied between 1:1.3 and 1:3.1, indicating an enrichment of sulfate in the rhizosphere (Hu *et al.* 2003). When growing oilseed rape, the ester-bonded and carbon-bonded S increased by 47% and 25% in the rhizosphere compared to the control (Hu *et al.* 2003). In contrast, the two fractions decreased by 75% and 30% in the rhizosphere of rice (Hu *et al.* 2003). These findings provide further evidence that the mineralization of organic S is related to crop type and that all fractions of organic S are on principle bioavailable.

Influence of S fertilization on microbial populations and on S transformation processes

The release of organic acids by plant roots promotes growth of bacteria, and attracts bacteria and fungi towards roots (Jones 1998). Microbial arylsulfatase activity was stimulated by increasing sulfate concentrations in contrast to barley arylsulfatase activity (Ganeshamurthy and Nielsen 1990). With increasing mineral sulfate fertilization the uptake of S by barley from organic sources declined after 3 weeks (Vong *et al.* 2002). On a long-term basis, the application of compost had the strongest effect on the arylsulfatase activity when compared to manure and mineral fertilizers (Knauff *et al.* 2003). Concomitantly with an increase in organic matter, the arylsulfatase activity increased in these experiments so that a higher availability of soil organic S to plants can be expected.

The influence of elemental S applications on S-oxidizing *thiobacilli* and heterotrophic bacteria has been studied comprehensively. There exists a wide spectrum of S-oxidizing microorganisms in soils: the majority of 273 different bacteria and 70 fungi that were collected from the rhizosphere of summer oilseed rape were able to oxidize elemental S (Grayston and Germida 1991). Nevertheless, the oxidation rate of soil-applied elemental S is regularly limited because of a restricted population size. The efficacy of elemental S depends on the particle size, application rate, soil, and

climatic factors including the number as well as the activity of S-oxidizing microorganisms (Watkinson and Bolan 1998). Li *et al.* (2005) reported that repeated applications of elemental S increased the oxidation rate. Lee *et al.* (1990) found that the oxidation rate was independent of the initial number of *Thiobacillus* spp. present during incubation, while under field conditions reapplication of elemental S resulted in an increased oxidation rate because of a higher number of *Thiobacillus* spp. remaining from the first application of elemental S (Lee *et al.* 1987). Repeated applications of elemental S increased the *Thiobacillus* spp. count and population of aerobic heterotrophic S-oxidizing bacteria consistently and achieved a maximum value of 1.0×10^8 g^{-1} and 5.0×10^4 g^{-1} soil after the seventh and fourth application, respectively (Yang *et al.* 2006). These results suggest that soils which receive regular applications of elemental S have a higher number of S-oxidizing microbial populations and thus a substantially higher oxidation potential.

Gupta and Germida (1988) investigated the acidifying effect of repeated elemental S rates of 44 kg ha^{-1} over 5 years as the reason for a decline of microbial biomass by 40%. Whilst fungi were reduced, bacteria and actinomycetes were unaffected. This resulted in a reduced number of mycophagous amoebae so that a negative impact on the control of phytopathogenic fungi cannot be excluded.

S speciation in soils

The spatial speciation of nutrients is relevant to soil analysis. Gassner *et al.* (2002) showed that different environmental factors resulted in the spatial speciation of P. It was possible not only to separate different pools, but also, based on the analysis of their spatial continuity, to extract different environmental parameters that resulted in the formation of these pools. For S, no correspondent investigations have been carried out so far. Usually, the speciation comprises the following S pools: total S, organically bonded S (labile and stable S fractions), and inorganic S.

Most of the S in terrestrial soils is bound in the organic fraction, which amounts usually to more than 95% of the total S content (Eriksen *et al.* 1998). Organic S in soils is a heterogeneous mixture of soil organisms, partly decomposed plant material, animal, and microbial residues. The nature of soil organic matter is highly complex and any procedure attempting to divide organically bound S into only a few biologically meaningful fractions will never match the variation of individual chemical compounds. Many different approaches were developed empirically to separate soil organic S into major fractions representing distinct forms and properties as for instance: (i) chemical extraction followed by physical-

chemical separation into humic acids, fulvic acids, and humins (Bettany *et al.* 1980); (ii) reactivity with reducing agents: carbon-bonded S (C–S) and sulfate esters (C–O–S; C–N–S and C–S–S) (Tabatabai 1982); (iii) physical separation into organo-mineral size fractions (Hinds and Lowe 1980; Anderson *et al.* 1981); and (iv) molecular weight fractionation (Scott and Anderson 1976; Keer *et al.* 1990). Details about the different procedures for fractionating different S forms are given by Eriksen *et al.* (1998).

Sulfate released from labile S fractions and microbial biomass is important for the S nutrition of crops. A soil feature, which affects the plant-available S pool is soil texture. A relative increase of the sulfate-ester pool with decreasing particle size indicates a protection of organic S from mineralization (Eriksen *et al.* 1998) and it results in a decreased availability of S to plants. This hypothesis is supported by the findings of Anderson *et al.* (1974) who showed that high molecular weight components were preferably adsorbed to clay particles and Keer *et al.* (1990) who proved that more than 75% of the total organic S was present in the form of sulfate esters with a molecular weight of >200,000 Da. These findings are in agreement with those of Bettany *et al.* (1979 and 1980), who found that a fractionation of organic matter delivered a higher percentage of S in ester form in the fulvic acid fraction that was not associated with clay minerals on arable soils than on grassland as the organic material in this fraction is usually younger and not yet bonded to clay-associated humic acids (Eriksen *et al.* 1998).

SPATIO-TEMPORAL VARIABILITY OF S IN SOILS

Adaptations of the plant rhizosphere to changes in the S supply can be followed up by assessing the spatio-temporal variability of S species in soils. The largest scale reflects differences between soil types, the lowest scale that within a single field.

The typical range of S in agricultural soils of humid and semi-humid regions is 100–500 μg g^{-1}, or 0.01–0.05% S (Stevenson 1986). The total S content of soils may be as low as 20 μg g^{-1} (0.002%) in highly leached and weathered soils of humid regions or as high as 35 mg g^{-1} (3.5%) in marine marsh soils and up to 50 mg g^{-1} (5%) in calcareous and saline soils of arid and semiarid regions (Stevenson 1986, Chapter 1). Examples for differences in S speciation for different soil types are given in Table 1. Notably the proportion of carbon-bonded S can be lower than 0.1% of the total S content (Table 1). The proportion of ester-bonded S ranged from 15% to

52% of the total S. The plant-available sulfate content varied between 1.2 µg and 40.4 µg SO_4-S g^{-1}. It has been outlined previously that inorganic sulfate content is of prime relevance for the plant S supply. S transformation processes are dynamic and the high spatio-temporal variability of sulfate reflects this (Figure 1, Schnug and Haneklaus 1998; Bloem *et al.* 2001).

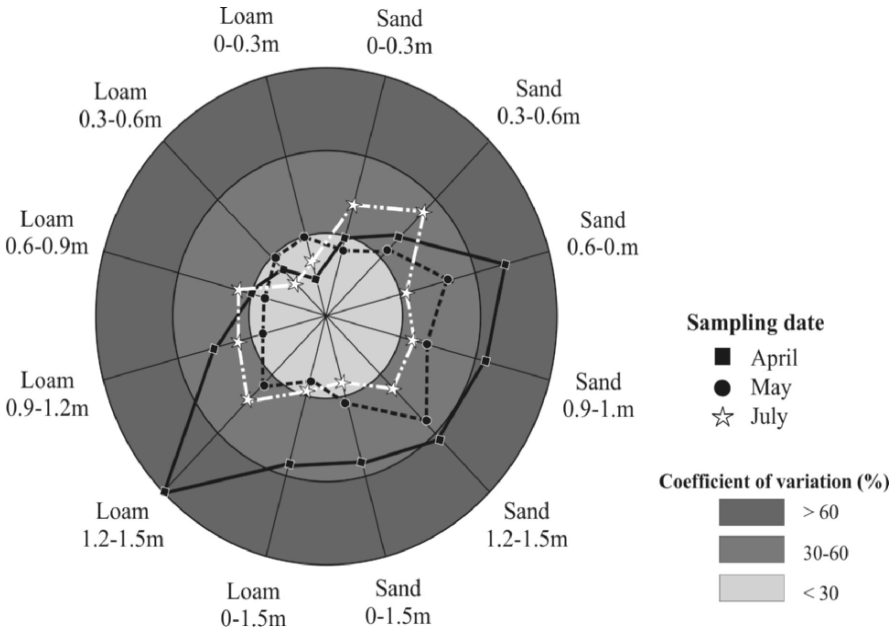

Figure 1. Spatio-temporal variability of the sulfate contents in different soil layers on two soil types. (Adapted from Bloem *et al.* 2001.)

The variability of sulfate concentrations within one field can be as high as variations between different soil types in different climatic areas (Table 1, Schnug and Haneklaus 1998). This high spatio-temporal variation of plant-available sulfate concentrations under humid conditions was shown to be closely related to soil physical and hydrological parameters (Bloem 1998). Severe S deficiency in crops can occur on all soil types and is generally exacerbated by high yields, soils with a light soil texture, high permeability and low organic matter content, sites poorly connected to capillary ascending groundwater, leaching; reduced root growth and rooting intensity in acid soils, soil compaction, or low soil temperatures. In addition to the spatial variability, rapid temporal changes in soil sulfate are

a causal reason for a lack of relationship between soil analytical data and plant S status or crop yield (Schnug and Haneklaus 1998).

S-CONTAINING ALLELOCHEMICALS

Molisch (1937) defined allelopathy as chemicals being transferred from one plant to another; these chemicals may exert positive or negative effects. Allelochemicals are secondary compounds, which affect plants, soil microorganisms, insects, and herbivores. S-containing allelochemicals are closely related to adaptations of the plant rhizosphere to changes in the S supply as they influence soil microorganisms and other plants.

Root exudates may directly affect seed germination of another plant, either by promoting the process, or inhibiting it (Curl and Truelove 1986). Bell and Koeppe (1972) showed that giant foxtail inhibited growth of maize by about 35% due to an allelopathic effect. The allelopathic effect of plants from the orders *Cruciferae*, *Resedaceae*, and *Capparidaceae* on weeds and soil-borne diseases usually focusses on the release of volatile isothiocyanates (ITCs). The degradation of glucosinolates (GSLs) by myrosinase delivers not only ITCs, but also organic cyanides, nitriles, oxazolidinethiones, and ionic ITCs all of which have allelopathic potential (Brown and Morra 1996; Mizutani 1999). Myrosinase activity was proven on fields where *Brassica* species were grown (Borek *et al.* 1996) and Yamane (1991) showed that the microorganism *Rhizopus* that can be found in the rhizosphere of *R. sylvestris* produced extracellular myrosinase. The release of about 13 µg plant^{-1} day^{-1} hirsutin and 9.3 µg plant^{-1} day^{-1} pyrocatechol by the weed yellow fieldcress (*Rorippa sylvestris*) inhibited germination of lettuce seedlings (Yamane *et al.* 1992). At lower concentrations hirsutin proved to have an inhibitory effect exclusively on noncruciferous crops (Kawabata *et al.* 1989).

ITCs may interfere with seed enzymes (Drobnica *et al.* 1977). Petersen *et al.* (2001) assumed that low concentrations induce a secondary dormancy, while high concentrations prevent germination. Basically, ITCs were shown to inhibit germination and growth of both, monocotyledonous and dicotyledonous plants (Petersen *et al.* 2001). In pot experiments, Norsworthy and Meehan (2005a, b) found the sensitivity of *Panicum texanum*, *Digitaria anguinalis, Senna otusifolia*, and *Amaranthus palmeri*, *Ipomoea lacunose*, and *Cyperus esculentus* to be related to chemical structure and concentration of ITCs. Under field conditions mustard, summer and winter oilseed rape were mixed at flowering after mowing with the soil to test their effect on seed germination (Haramoto and

Gallandt 2005). These authors could not verify any significant effect of *Brassica* crops on the delay of seed germination by weeds when compared to non-*Brassica* cover crops.

GSLs may be released by root exudates of living plants and exert their allelopathic effects. Another option is their degradation after decomposition of separated plant parts or harvest residues. Their effect on soil-borne pathogens is summarized by the term and phenomenon of biofumigation. Biofumigation might advance to a promising and ecologically sound alternative for crop protection if its efficiency can be directed.

Biofumigation

The efficiency of GSLs and/or ITCs against soil-borne fungal diseases, nematodes, and weeds is related to the kind of pathogen and pathotype. Additionally, GSL content and type, and quantitative release of ITCs are relevant factors (Sarwar and Kirkegaard 1998; Rosa and Rodrigues 1999; Smolinska *et al.* 2003). The toxicity of ITCs is based on their nonspecific, irreversible interactions with sulfhydryl groups, disulfide bonds, and amino groups of proteins and amino acids; thiocyanates interfere with the tertiary structure of proteins through electrostatic interaction (Brown and Morra 1996). Their, toxicity is, however lower than that of ITCs (Rosa and Rodrigues 1999). For aliphatic ITCs Sawar *et al.* (1998) found a decreasing toxicity with increasing length of side chain. The GSL content of different *Brassica* species increased in the order *B. napus* < *B. juncea* < *B. nigra* (Sarwar and Kirkegaard 1998). Propenyl-GSL was found at higher levels in *B. carinata*, *B. nigra*, and *B. juncea* and phenylethyl-GSL in *B. napus* (Kirkegaard and Sarwar 1998). Smith and Kirkegaard (2002) tested the susceptibility of 75 fungi and oomycetes, and 41 bacterial isolates against 2-phenylethyl-ITC. For fungi that showed a low susceptibility against 2-phenylethyl-ITC, the effective dose for a reduction of the mycelial growth was high and vice versa. In general, the GSL content and efficacy of *B. napus* decreased from 20.5 to 0.7 in shoots and from 31.0 µmol to 0.8 µmol g^{-1} dry weight in roots from flower primordium to harvest (Kirkegard *et al.* 1996, Sarwar and Kirkegaard 1998). This dilution effect was attributed to a higher biomass production (Sarwar and Kirkegaard 1998). S fertilization was shown to significantly increase the GSL content in vegetative and generative plant materials (Schnug 1990; Haneklaus *et al.* 2006). The effect of ITCs on soil-borne fungal pathogens under laboratory conditions is summarized in Table 2.

Table 1. Distribution of S species in the upper layers of different soils.

Location	Soil type	Depth (cm)	Total S	Organic S	C-bonded S	Ester-bonded S	Sulfate S[1]	Reference
					(μg g^{-1})			
China	Haplic Staganic Anthrosol (aerated[2])	0–20	134	91.4	13.8	20.1	28.8	(1)
China	Haplic Staganic Anthrosol (waterlogged[2])	0–20	133	87.8	14.4	27.0	40.4	(1)
China	Haplic Acrisol[3]	0–20	182	144	18.1	75.3	28	(2)
China	Hortic Anthrosol[3]	0–20	130	106	0.1	32.4	24	(2)
USA	13 soils	0–15	56–618	55–603.8	8.0–87.7	29.3–286.8	1.0–14.2	(3)
Canada	Aridic Haploboroll	0–15	312	310.2	48	163	1.8	(4)
	Typic Haploboroll	0–15	338	336.0	49	171	2.0	(4)
	Udic Haploboroll	0–15	463	461.8	52	220	1.2	(4)
	Transitional	0–15	225	223.8	65	77	1.2	(4)
	Typic Cryoboralf	0–15	144	141.8	63	52	2.2	(4)
Denmark	Typic Hapludalf	0–20	202	169	99	67	27.1	(5)
	Typic Haplorthod	0–20	122	146	81	49	1.1	(5)

[1]soluble sulfate; [2]soil material from nonvegetated non-rhizosphere soil; [3]soil material from fallow non-rhizosphere soil; (1) Hu *et al.* (2003), (2) Hu *et al.* (2002), (3) Tabatabai and Bremner (1972), (4) Bettany *et al.* (1973), (5) Eriksen (1996).

The fungicidal or fungitoxic effect depended on the ITC concentration in agar and headspace, respectively (Sawar *et al.* 1998). The lowest fungitoxic concentration on *Gaeumannomyces graminis* was 1.6 µmol $l^{-1}$of 2-propenyl-ITC in the headspace and 5 µmol l^{-1} benzyl-ITC in agar (Sawar *et al.* 1998). With 6.2 µmol l^{-1} *Bipolaris sorokiniana* proved to be least sensitive against 4-Pentenyl-ITC in the headspace and *Pythium irregulare* with 90 µmol l^{-1} in the agar (Sawar *et al.* 1998). The results of these experiments showed that the toxicity of ITCs was different when incorporated into agar, or released in gaseous form. Compared to aliphatic ITCs, aromatic ITCs had a higher toxicity in agar than in gaseous form because of different vapor pressures (Sawar *et al.* 1998). Under laboratory conditions, a fungicidal/fungitoxic effect of ITCs lasted no longer than 6 days; only a continuous exposure reduced colony growth efficiently (Smolinska *et al.* 2003). In comparison, allyl-ITC had a half-life of only 20 to 60 h in soils (Borek *et al.* 1995). Another impairment of the efficacy occurs when GSL-containing plant material is used instead of pure chemicals. Only 1–8% of the potential ITC concentration was found after incorporation of plant material into soil (Brown and Morra 1996; Morra and Kirkegaard 2002). Myrosinase concentration in plant tissue was sufficient for degradation of GSLs and supplementing additional myrosinase yielded no higher fungitoxicity (Lazzeri *et al.* 2004a). Soil moisture content and a sufficient decomposition of the plant material were obviously major limiting factors for the release of ITC (Morra and Kirkegaard 2002). Another limiting factor might rely on the reaction of ITCs with inherent plant proteins and amino acids (Warton *et al.* 2001).

The efficacy of plant materials to yield a fungitoxic or fungistatic effect was related to crop type. *B. juncea and Sinapis alba* delivered better results compared to *B. napus* (Smolinska and Horbowicz 1999). Not only vegetative, but also generative plant material had a fungitoxic effect. Seed meal of mustard inhibited completely mycelial growth of *R. solani*, *G. graminis*, and *Fusarium graminearum* (Kirkegard *et al.* 1996).

As expected, the efficiency of ITCs for biofumigation declined clearly in the order *in vitro* >> pot experiment >> field experiment. Price *et al.* (2005) found an increase in the allyl-ITC concentration in relation to soil texture, soil temperature, and soil coverage, and a decrease in relation to microbial population and time after incorporation of a standardized mustard plant material. A significant decline was found after 8 h, which underlines the narrow time slot for a phytosanitary effect of ITCs. In addition, microbial degradation in soils decreased the allyl-ITC concentration. A higher allyl-ITC concentration was found on a more sandy soil, which the authors attributed to a presumably lower adsorption to the organic matter fraction (Price *et al.* 2005). With higher soil

temperature and soil coverage, a higher allyl-ITC was found, while soil water content and soil pH had no influence on the release of allyl-ITC (Price *et al.* 2005).

Under field conditions Smith *et al.* (2004) found no significant relationship between GSL content in roots of oilseed rape and phytosanitary effects, and yield of the following wheat crop in the rotation. Kirkegaard *et al.* (2000) proved that *Brassica* crops reduced the inoculum of *Gaeumannomyces graminis*. This effect coincided with root decay and a reduced content of intact GSLs at maturity (Kirkegaard *et al.* 2000), but it was also not persistent in the following wheat crop.

Under field conditions, radish showed resistance against *Meloidogyne javanica* and *Meloidogyne arenaria* that was comparable to resistant fodder sorghum, while *Brassica* crops also reduced reproduction of these nematodes (Pattison *et al.* 2006). The contribution of ITCs from *Raphanus sativus* to this resistance remains uncertain. The nematicidal effect of individual GSLs and their degradation products on *Meloidogyne incognita* and *Globodera rostochiensis* was tested *in vitro* (Buskov *et al.* 2002; Lazzeri *et al.* 2004a). ITCs differed in their nematicidal effect by factor 400; their efficacy was usually higher when exposure time was exalted (Lazerri *et al.* 2004).

Research in the field of biofumigation has shown that GSL content and pattern vary in relation to plant species, plant part, growth stage, and S supply. The potency of ITCs was found to be distinctly higher under laboratory than field conditions if at all. Soils are open systems with a much higher volume than that of sealed containers in the lab, resulting putatively in a lower ITC concentration in the headspace of pathogens. Additional obstacles under field conditions are that the incorporation of the break crop is not homogenous; the GSL content is lower in plant residues than in younger plant material and degradation of GSLs is incomplete as it requires mechanical disruption to destroy cell structures and sufficient water for a sufficiently high myrosinase activity. A solution to these problems might be a functional biofertilizer, which consists of material from different plants with highest concentrations of GSLs releasing most biocidal ITCs. Different coatings of the fertilizer will facilitate a continuous release of GSLs and ITCs.

ADAPTATION OF PLANT GROWTH TO CHANGES IN THE S SUPPLY

S requirement differs highly between species and it varies during plant growth. The S requirement can be defined as “the minimum rate of the S

uptake and utilization, which is sufficient to obtain the maximum yield, quality and fitness", which is for crop plants equivalent to "the minimum content of S in the plant associated with maximum yield" and is regularly expressed as kg S ha^{-1} in the harvest products (Haneklaus *et al.* 2006). The S demand of agricultural crops may be as low as 1 kg S t^{-1} for sugar beet and as high as 17 kg S t^{-1} for *Brassica* crops (Haneklaus *et al.* 2006). In physiological terms the S requirement is equivalent to the rate of S uptake, reduction and metabolism needed per gram plant biomass produced over time and can be expressed as mg S g^{-1} plant day^{-1} (Haneklaus *et al.* 2006). The S requirement of a crop may be predicted by scaling up the S requirement in μg S g^{-1} plant day^{-1} to g S ha^{-1} day^{-1} by estimating the crop biomass density ha^{-1} (tons plant biomass ha^{-1}). When a plant is in the vegetative growth period, the S requirement ($S_{requirement}$) can be calculated as follows (De Kok *et al.* 2000):

$$S_{requirement} = S_{content} \cdot RGR$$

with $S_{requirement}$ (μg S g^{-1} plant day^{-1}), S content (μg S_{total} g^{-1} plant biomass), and relative growth rate (RGR) of the plant (g biomass g^{-1} plant day^{-1}). The RGR can be calculated by:

$$RGR = (\ln W_2 - \ln W_1) \cdot (t_2 - t_1)^{-1}$$

with the total plant weight in g, W_1 and W_2, at time t_1 and t_2, respectively, and the time interval (days) between two samplings t_2 and t_1.

When all other essential plant nutrients are sufficiently supplied and abiotic growth conditions are optimum, the S requirement of different crop species varies between 0.3 and 3.2 mg S g^{-1} plant dry weight day^{-1}. Generally, the major proportion of the sulfate taken up is reduced and metabolized into organic compounds, which are essential for structural growth. However, in some plant species a large proportion of S is present as sulfate. Here, organic S content may be a better parameter for the calculation of S requirement (Haneklaus *et al.* 2006, see section below).

YIELD STRUCTURE

Roots

The influence of S nutritional status on root growth is commonly neglected, though it is a major factor influencing S uptake of crops. Restricted root growth can, for instance regularly be found on headlands

due to soil compaction. Here, symptoms of S deficiency regularly appear first. Reduced root growth limits the ability of the plant to explore the soil spatially for available S and hampers its access to S resources in subsoil water (Bloem *et al.* 2000). Under humid conditions, sulfate can be leached from the root zone due to precipitation in autumn particularly on light soils, so that young plantlets do not have access to sulfate-rich capillary ascending water or groundwater. Although crops with a high S demand, such as oilseed rape, have a coarse root system which favors microbial activity and microbially-mediated degradation of ester-bonded S, this morphological modification alone might not deliver sufficient amounts of sulfate to satisfy the S demand. Whenever S supply is insufficient, this will result in the occurrence of macroscopic S deficiency symptoms, even during the very early growth stages. An increasing problem in agriculture is the enhancement of S deficiency where Tebuconazol was applied as a fungicide, as it apparently reduces not only the growth of the aboveground vegetative plant parts, but also reduces root depth and density (Bloem *et al.* 2000). Apparently this effect is also consistent in crop rotation.

Lange (1998) showed that S fertilization to leguminous crops significantly increased shoot, root, and nodule biomass of alfalfa, crimson clover, and faba bean; in the case of peas this effect was significant for shoot and nodule biomass (Figure 2). The improved root growth due to S fertilization yielded a higher number of nodules, while nodulation itself was not affected (Scherer and Lange 1996; Lange 1998).

These results strengthen the significance of a sufficient S supply in intensive farming as root growth may be inhibited and thus the risk of S deficiency enhanced. In S-deficient legumes, N that was fixed in nodules was not assimilated which caused disturbance of protein synthesis and finally resulted in the appearance of macroscopic symptoms of S deficiency (Lange 1998). At present the question cannot unequivocally be answered as to whether S deficiency affects plants and/or microsymbionts as S fertilization increased number and size of nodules, and nitrogenase activity (Singh and Raj 1988; Lange 1998).

Yield components

During the very early growth stages of winter cereals, severe S deficiency caused an irreversible reduction of generative yield components (Haneklaus *et al.* 1995, Figure 3). Such severe disorder could only be counterbalanced by S fertilization prior to tillering (Haneklaus *et al.* 1995). Grain yield was reduced by up to 93% if no S was applied (Haneklaus *et al.* 1995). The S nutritional status had the strongest effect on the number of kernels per ear. Cereal plants obviously retain the number of

inflorescence bearing culms at the expense of grain setting under conditions of S deficiency.

The S rate significantly influenced the number of pods per plant and seeds per pod of oilseed rape under greenhouse conditions (Schnug 1988). When the N supply was low, S fertilization had no effect on the number of pods and number of seeds per pod. When the N supply was high, S fertilization nearly doubled the number of seeds per pod. Neither variations in the N, nor in the S supply had a significant influence on the thousand grain weight (TGW). Asare and Scarisbrick (1995) could verify no significant influence of S fertilization on TGW of oilseed rape under field conditions, either. In contrast, Shukla *et al.* (2005) found a significant increase of only TGW by 9% after S fertilization under field conditions, while other changes in yield components such as the number of branches and pods per plant, seeds per pod, and seed yield were not significant so that the question arises in how far climatic conditions influenced this result.

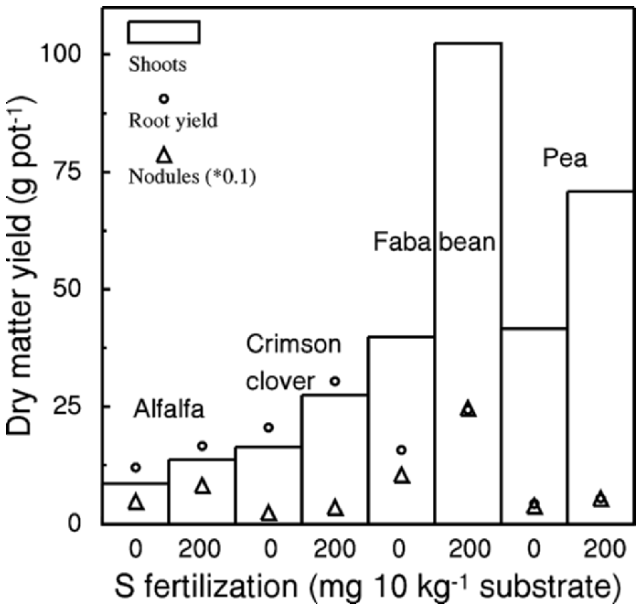

Figure 2. Influence of S fertilization on shoot and root biomass, and number of nodules of alfalfa, crimson clover, faba bean, and pea. (Adapted from Lange 1998.)

Investigations on the timing of S fertilization and initiation of S deficiency in oilseeds, revealed that in both cases a close and significant relationship existed between duration of S deficiency and all yield components (number of branches, number of pods per plant, number of seeds per pod, seed and straw yield) except TGW (Schnug 1988). A comparison between single and double low varieties showed that the double low cultivars had reduced components of yield structure consistently more than did the single low varieties (Schnug 1988). On average only 44% of the relative seed yield were obtained when double low plants were grown for 50% of the vegetation period under conditions of S deficiency, while the corresponding value was 57.5% for single low varieties (Schnug 1988). An assessment of the differential effect of the point of timing when S deficiency affected plant growth revealed that components of yield structure were more reduced when S deficiency occurred later during growth. From the viewpoint of plant production the area-related seed yield was reduced equally by both scenarios (Schnug 1988). Under field conditions, Nuttall and Ukrainetz (1991) recommended S fertilization to spring oilseed rape at sowing in order to avoid yield losses; otherwise with every 10 days of delay, a net yield loss of up to 7% may be incurred.

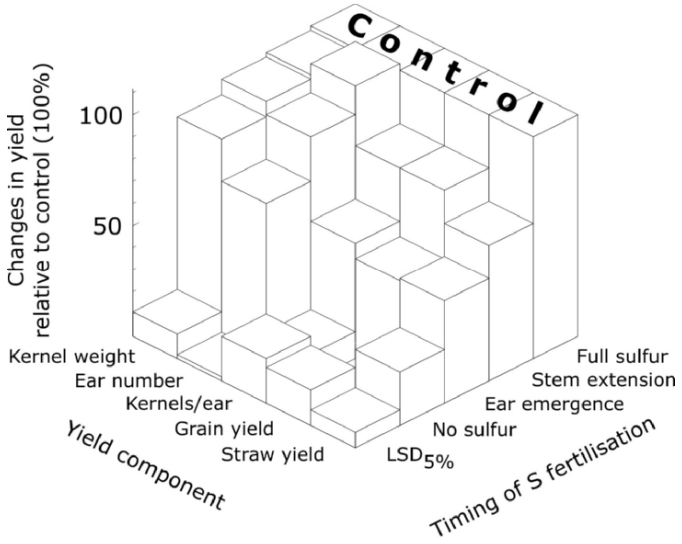

Figure 3. Influence of timing of S application, under conditions of severe S deficiency, on kernel weight, ear number, kernels per ear, and on grain and straw yield of wheat in comparison to a sufficiently supplied crop. (Adapted from Haneklaus *et al.* 1995.)

Table 2. Influence of ITCs on soil-borne fungal pathogens, bacteria, and nematodes under laboratory conditions.

Pathogen	Effect	Ref.
Aphanomyces euteiches[a]	inhibition of mycelial growth and germination of encysted zoospores reduced disease severity	(1,2)
I. Bipolaris sorokiniana[a]	retardation of mycelial growth	(3)
II. Fusarium graminearum[a]	retardation of mycelial growth (vegetative material)	
III. Gaeumannomyces graminis[a]	inhibition by mustard seed meal (25 mg)	
IV. Pythium irregulare[a]	inhibition of mycelial growth by mustard shoots (500 mg) and seed meal (5 mg)	
V. Rhizoctonia solani[a]	retardation of mycelial growth (vegetative material) inhibition by mustard seed meal (25 mg)	
Gaeumannomyces graminis[a]	inhibition of mycelial growth; effect decreased with age of mycelium	(4)
Fusarium oxysporum[a]	inhibition of germination of chlamydospores	(5)
Pythium irregulare[a] *Rhizoctonia solani*[a]	inhibition/retardation of mycelial growth	(6)
Sclerotinia sclerotiorum[a]	retardation of germination of sclerotia	(5)
Sclerotium cepivorum[a]	inhibition of germination of sclerotia	(5)
41 isolates of bacteria[b]	growth inhibition in relation to concentration	(7)
75 isolates of fungi and oomycetes[b]	inhibition of mycelial growth by 50% and 90% in relation to concentration	(7)
Bipolaris sorokiniana[b] *Fusarium graminearum*[b] *Gaeumannomyces graminis*[b] *Pythium irregulare*[b] *Rhizoctonia solani*[b]	fungitoxic to mycelium	(8)
Fusarium oxysporum[b]	inhibition of mycelial growth	(9)
Fusarium oxysporum[b]	suppression of conidial and chlamydospore germination	(9)
Leptosphaeria maculans[b]	inhibition of growth (except for progoitrin)	(10)
Globodera rostochiensis[b]	100% mortality of 2nd stage juveniles	(11)
Globodera rostochiensis[b]	100% mortality of 2nd stage juveniles	(12)

[a]Plant material; [b]ITCs; (1) Smolinska *et al.* (1997), (2) Muehlchen *et al.* (1990), (3) Kirkegaard *et al.* (1996), (4) Angus *et al.* (1994), (5) Smolinska and Horbowicz (1999), (6) Lazzeri *et al.* (2004b), (7) Smith and Kirkegaard (2002), (8) Sarwar *et al.* (1998), (9) Smolinska *et al.* (2003), (10) Mithen and Lewis (1986), (11) Serra *et al.* (2002), (13) Pinto *et al.* (1998).

Table 3. Influence of excessive S supply on yield components and selected plant characteristics.

Crop	Highest S rate		Effect of highest S rate	Ref.
Bean	600	mg pot^{-1}	reduced biomass (–58%), amino acid (–59%) and protein content (–50%) in leaves	(1)
Broccoli	180	mg kg^{-1}	reduction of (market) yield and total biomass	(2)
Cabbage	360	mg kg^{-1}	reduction of (market) yield and total biomass	(2)
Cabbage	90	kg ha^{-1}	reduction of (market) yield	(3)
Cabbage	100	kg ha^{-1}	reduction of (market) yield	(4)
Grass	300	kg ha^{-1}	increased shoot and root biomass	(5)
Kidney beans	6,000	kg ha^{-1}	no effect on yield components and protein content of seeds (S application in previous year)	(6)
Maize	120	kg ha^{-1}	reduction of yield components with S >60 kg ha^{-1}	(7)
Onion	115	mg kg^{-1}	no influence on yield	(2)
Pea	400	mg kg^{-1}	reduced seed yield in 1 out of 3 genotypes (reduced seed number and seed weight)	(8)
Pea	75	kg ha^{-1}	reduced vegetative biomass, seed yield, seed protein, no of effective nodules, leghaemoglobin content	(9)
Potato	150	kg ha^{-1}	reduced tuber yield	(10)
Soybean	90	kg ha^{-1}	highest grain yield (regular fertilization over 6 years)	(11)
Soybean	60	kg ha^{-1}	S fertilization increased number of nodules/plant, active nodules, d.w. of nodules, and chlorophyll content	(12)
Soybean	240	kg ha^{-1}	reduced biomass and seed yield (strength of effect N-related)	(13)
Tomato	222	mg l^{-1}	Ca imbalance in plants; no significant influence on fruit yield and quality	(14)
Tomato	666	mg pot^{-1}	reduced photosynthetic capacity and protein N content; no effect on biomass	(15)
Wheat	224	kg ha^{-1}	decrease of forage and grain yield in relation to year and location (regular application over 7 years)	(16)
Cultivation on post-mining land/amelioration of salinity and alkalinity				
Alfalfa	4,730	mg kg^{-1}	high plant available sulfate-S in soils did not yield over-proportional S uptake (0.23–0.48% S); accumulation of non-protein-N compounds with higher S level	(17)
Alfalfa	2,800	mg kg^{-1}	gypsum amendment enhanced salt tolerance and thus maintained yield	(18)
Tomato	1,700	mg l^{-1}	decreased fruit weight and size	(19)
Tomato	900	kg ha^{-1}	increased yield and fruit weight; less unripe fruit	(20)
Pawpaw	3,500	kg ha^{-1}	up to 73% higher lateral branch extension and 100% higher dry matter production	(21)

(1) Ruiz *et al.* (2005), (2) Blankenburg (2002), (3) Rhoads and Olson (2001), (4) McKeown and Bakker (2003), (5) Olson and Jacobsen (1999), (6) Hojjati (1976), (7) Khan *et al.* (2006), (8) Randall *et al.* (1979), (9) Singh and Raj (1988), (10) Singh *et al.* (2001), (11) Saha *et al.* (2001), (12) Ganeshamurthy and Reddy (2000), (13) Abbès *et al.* (1992), (14) Lopez *et al.* (2002), (15) Xu *et al.* (1996), (16) Girma *et al.* (2005), (17) Pucek and Pys (1999), (18) Vaughan *et al.* (2002), (19) Cerda *et al.* (1984), (20) Di Candilo *et al.* (1993), (21) Picchioni *et al.* (2004).

In sunflower, S deficiency delayed floret initiation and anthesis, but not maturity under controlled growth conditions (Hocking *et al.* 1987). Additionally, the number of seeds per plant and TGW were reduced. The authors concluded that a sufficient S supply before floret initiation is important for initiating a maximum number of florets and thus potential seeds.

BIOMASS DEVELOPMENT

There are small differences in patterns of uptake of different macronutrients during the vegetation period. S uptake runs more or less parallel to biomass development and is proportional to seed yield. Oilseed rape for instance may take up about one-third of its total S demand before winter resting. Usually, under conditions of S deficiency, S fertilization significantly increases vegetative and generative plant biomass production. Lack of response is often related to experimental conditions such as site and climatic conditions (Kowalenko 2000).

Growing leguminous crops such as soybean, which have been previously multiplied on S-deficient soils, increases the susceptibility of young plantlets against an insufficient S supply, as the proportion of S-containing storage proteins is reduced (Hitsuda *et al.* 2005). S deficiency in the vegetative stage reduced biomass (Randall and Wrigley 1986) and a lower plant dry matter of sunflower was closely related to the N supply in such a way that no impact was found at a low N input, however, severe losses were recorded when the N supply was high (Hocking *et al.* 1987).

The influence of S deficiency on vegetative and generative yield has been studied in detail for agricultural crops and is comprehensively summarized for instance by Pedersen *et al.* (1998) and Aulakh (2003).

Plant growth under excessive S availability

While numerous studies have investigated the influence of S fertilization on crop productivity under limiting conditions, the impact of excessive S input in temperate regions has only been dealt with sporadically. An exception is the influence of atmospheric S pollution on plant growth. In comparison, extremely high S rates are applied, for instance, in desert agriculture for the amelioration of salinity and alkalinity, and in the course of cultivating post-mining land (Table 3).

S is commonly considered as being highly biocompliant such that excess S neither diminishes productivity, nor impairs quality of the plant products. There are, however, indications that overrated S fertilization may

reduce crop yield and that this effect is related to crop type (Table 3). A major handicap of a proper attribution of effects to an excessive S rate (Table 3) is the lack of information about other growth limiting factors, antagonistic effects with other essential plant nutrients, and the S nutritional status itself.

Even more important than detrimental effects of an excess S supply on crop parameters is a possibly detrimental effect on animal health. Prominent examples of adverse effects of high S intake on ruminants are polioencephalomalacia, a neurological disorder and haemolytic anaemia (Stoewsand 1995; Gould *et al.* 2002). The risk of polioencephalomalacia exists when grass which contains more than 0.38% S is eaten by the animals (Gould *et al.* 2002).

Excess S may cause a premature leaf fall (Motavalli *et al.* 2006). Even a uniform application rate of 134 kg ha^{-1} S causes site-specifical yield increases and depressions as was shown for forage grass (Kowalenko 2000). These results fit to the observations of Donald and Chapman (1998) who found indications of S toxicity at rates of 200 kg ha^{-1} S to grass and clover. Forage yield at stem extension was reduced by about 5% at 224 kg ha^{-1} S, while the corresponding value for grain yield was even as high as 11% (Girma *et al.* 2005). Khan *et al.* (2006) found that 120 kg ha^{-1} S reduced dry-matter yield of maize significantly compared to a sufficiently supplied crop, such that the yield level equaled that of the S deficient control plots. Excessive S produced the lowest grain yield, and also TGW (Khan *et al.* 2006). This growth-depressive effect was observed at total S concentrations of about 6–9 mg g^{-1} S dry weight at silking stage.

Other reports from McKeown and Bakker (2003) and Sanderson (2003) delivered contradictory results. Cabbage yield decreased when S rates exceeded 55 kg ha^{-1} S; this effect was not significant for the harvest products of broccoli though biomass production was reduced 8–10 times (McKeown and Bakker 2003). In contrast, S rates of up to 670 kg ha^{-1} S proved to be compliant for broccoli (Sanderson 2003). In both experiments the S source was gypsum so that a Ca effect might be excluded. Using a different S source it might be possible that excessive S rates induce Ca deficiency as was shown for tomatoes in hydroponics, which revealed blossom end, rot symptoms (Lopez *et al.* 2002). In further experiments, S fertilizer rates of 45–90 kg ha^{-1} S reduced cabbage yield with the head size being affected in particular (Rhoads and Olson 2001); in the pot experiments of Blankenburg (2002) a change of the S supply from sufficient to excess resulted in a reduction of head and floret yield of cabbage and broccoli by 16.5% and 18.4%; the corresponding increase of the total S content was from 7.9 to 9.6 mg g^{-1} S and 8.8 to 10.9 mg g^{-1} S, respectively.

Disproportionate S rates significantly reduced shoot biomass of beans in a pot experiment with the S concentration in the leaf tissue more than doubled with values of 1.25% S under optimum supply increasing to 2.71% S dry weight under excessive S supply (Ruiz *et al.* 2005).

The effects of extreme S applications when used in desert agriculture are also not consistent (Table 3). For pawpaw, Picchioni *et al.* (2004) found that 15 t ha^{-1} gypsum significantly improved growth parameters; the total S concentration in roots (1.9 mg g^{-1} S) and trunks (0.7 mg g^{-1} S) was not significantly increased because of a dilution effect through increased plant growth. In comparison, stems of tomato plants were thinner, leaves darker green and smaller when grown under excessive S and symptoms became more pronunced with plant age and affected the aboveground biomass more than root growth (Cerda *et al.* 1984, Table 3). Fruit yield, both fruit weight and size, was reduced by up to 52%, whilst the number of fruits was not affected. In comparison, severe S deficiency reduced fruit yield by 58% (Cerda *et al.* 1984). Relative increases in organic S concentrations in different plant parts, for instance from 0.2 under conditions of S deficiency to 0.33% S under excess S in leaves at flowering were determined, but which were distinctly lower than the corresponding values found for sulfate (0.1% and 1.79% SO_4-S, respectively).

Critical nutrient values and ranges

For the evaluation of S nutritional status and prognosis of crop yield, different S species such as organic S, sulfate, total S, and the N:S ratio of various plant parts are determined, usually during the vegetation period and results are interpreted by employing diverse statistical approaches. It is the large variation in experimental conditions and mathematical procedures which make it more or less impossible to compare results from different experiments (Haneklaus *et al.* 2006). Thus the main objective, the reliable deduction of critical values is confronted with major limitations. Important threshold markers for the S supply are: the symptomatological value, which reflects the S concentration below which deficiency symptoms become visible; the critical nutrient value, which stands for the S concentration above which the plant is sufficiently supplied with S for achieving the maximum potential yield or yield reduced by 5%, 10%, and 20%; and the toxicological value, which indicates the S concentration above which toxicity symptoms can be observed. A comprehensive overview of crop-specific deficiency and sufficiency ranges of S supply has been compiled by Haneklaus *et al.* (2006), and the major outcome can be summarized as follows: severe to moderate S deficiency is indicated generally by sulfate concentrations of <0.15 mg g^{-1} sulfate-S and total S

concentrations of <1.7 mg g^{-1} S; for *Poaceae* and non-*Brassica* vegetables total S concentrations may be lower with 0.9 mg g^{-1} S or higher with 2.9 mg g^{-1} S, respectively. An adequate S supply is reflected by total S concentrations of 1.7–4 mg g^{-1} S; *Brassica* crops show a higher optimum range with values of 4.8 (oil crops) to 7.5 (vegetables) mg g^{-1} S. For N:S ratio and sulfate concentrations, values of 16–20 and 150–1,600 mg kg^{-1} sulfate-S, respectively reflect a sufficient S supply. In the literature, S concentrations, which impair crop performance are rare for S. An excessive S supply can be expected if plants contain more than 2.8 mg g^{-1} sulfate-S; for fodder crops total S concentrations of only 3.2 mg g^{-1} S may be already excessive, while the corresponding value for non-*Brassica* vegetables would be 10 mg g^{-1} S (Haneklaus *et al.* 2006). In general, it can be expected that yield depressions occur at lower S concentrations in plants when green matter is harvested, such as forage grasses and cabbage (see Table 3).

The boundary line approach is a robust tool to evaluate without bias the relationship between individual growth factors and yield and to determine optimum values and ranges of the soil and plant nutrient status of a crop (for a detailed description of *Bolides*, the upper boundary line development system see Haneklaus *et al.* 2006). The boundary line approach has been applied to determine threshold values for S deficiency, sufficiency, and excess in oilseed rape, cereals, and sugar beet (Table 4). The interpretation of cereal and oilseed rape values is based on more than 5,000 data pairs from greenhouse and field experiments as well as field surveys which have been compiled since 1973 and 1980, respectively. Details for sugar beet are given by Haneklaus *et al.* (1998).

Comparing these threshold values with median values from literature (Haneklaus *et al.* 2006), it is striking that total S concentrations which can be found when macroscopic symptoms are visible are in good agreement. The same applies for threshold concentrations indicating a sufficient S supply of cereals and sugar beet, although for oilseed rape significantly higher values were determined. The reason is most likely that the yield of oilseed rape crops was distinctly lower in many studies; only for the 75% percentile of literature data was there a sufficient S supply indicated by a S concentration of 6.7 mg g^{-1} S (Haneklaus *et al.* 2006). For the first time upper critical S concentrations in cereals and oilseed rape, which result in yield depressions of 10% have been calculated by a robust statistical procedure. For sugar beet upper critical S concentrations were determined before by *Bolides* (Haneklaus *et al.* 1998).

Table 4. Threshold values for total S concentrations (mg g^{-1} S, d.w.) in younger leaves of oilseed rape and sugar beet, and whole aboveground biomass of cereals at start of stem extension and canopy closing.

	Deficiency	Sufficiency		Excess
Crop	Symptomatological threshold	Lower critical value (–5% yield)	Maximum yield[1]	Upper critical value (– 10% yield)
Cereals	<1.2	3.2	4.0	>7.5
Rape	<2.8[2] and <3.5[3]	5.5	6.5	>14.0
Sugar beet	<1.7	3.0	3.5	>4.5

[1]seed (oilseed rape), grain (cereals), root and sugar (sugar beet) yield; [2]single low and [3]double low varieties

At present the physiological background of sulfate toxicity is unknown but some speculations about regulatory mechanisms may be formulated. A first hint of possible metabolic dysfunctions comes from the fact that excessive S supply to tomatoes induces Ca deficiency which becomes visible as blossom end rot (Cerda *et al.* 1984). May *et al.* (1998) assumed interactions between Ca and redox based signaling processes. The reactivity of the enzyme serine acetyltransferase, which catalyzes the first reaction in the biosynthesis of cysteine from serine was regulated by Ca-dependent protein kinase phosphorylation in soybean (Liu *et al.* 2006). Kim and Kim (2002) showed that sulfhydryl containing metabolites controlled the increase of cellular Ca^{2+} under conditions of S amino acid deprivation in rat heptoma cells, which is a further reference to a redox-state regulation of Ca. Additionally, pool sizes of ascorbic acid and GSH, and functional and regulatory interactions between them might be involved in growth inhibition under excessive S stress; a similar mode of action was proposed for boron deficient plants (Lukaszewski and Blevins 1996). Thus it might be possible that under excessive S stress crosstalk between Ca and S metabolic pathways hampers S homeostasis and thus unfolds its toxic effects. The identification of genes that govern the plant ionome might elucidate the mechanisms controlling S accumulation.

DRY MATTER COMPOSITION

The dry matter composition of plant products is an important quality parameter of foodstuffs and animal feed. The S nutritional status of crops has a significant influence on the nutritive value and sensory features of

plant products. S-containing flavor compounds are, for example, cysteine in fruits (Shankaranarayana *et al.* 1973), asparagusic acid, 3-mercaptoisobutyric acid, 3-methylthioisobutyric acid, diisobutyric acid disulfide, and 3-*S*-acetylthio-methacrylic acid in asparagus (Tressel *et al.* 1977), and glucosinolates and alliins in mustard, radish, onion, and garlic (Bloem *et al.* 2004). The influence of S fertilization on secondary S-containing compounds has been comprehensively summarized by Haneklaus *et al.* (2006).

Cysteine and methionine

Vegetable proteins have been recognized as being of lower nutritional value than animal proteins. The reason is the imbalanced cysteine to methionine ratio rather than the lower S content per gram of protein (Massey 2003, see above). The amino acids cysteine and methionine are the major end products of sulfate assimilation in plants and bind up to 90% of the total S (Giovanelli *et al.* 1980). A significant relationship between S supply and S-containing amino acids exists only under extreme S deficiency where macroscopic symptoms are visible (Haneklaus *et al.* 2006). Under conditions of S deficiency, firstly a decrease of S-containing amino acids in proteins is found (Schnug 1997). As the amino acid composition is genetically determined this effect is, however limited, and thereafter the total protein content will be reduced (Schnug 1997). The transition point to a reduced protein content matches the appearance of severe S deficiency symptoms (Schnug 1997). An insufficient S supply in the vegetative stage reduced biomass, the amino acid composition was only slightly influenced, however significant changes were observed in generative parts (Randall and Wrigley 1986). The authors attributed this to the fact that leaf proteins are mainly functional, while seed proteins are mainly for storage.

Eppendorfer and Eggum (1992) found the biological value of proteins in potatoes reduced from 94 to 55 by S deficiency at high N supply and from 65 to 40 and 70 to 61 in kale and field beans, respectively. Whilst the essential amino acid concentrations declined due to S deficiency, the content of amino acids of low nutritional value, such as arginine, asparagines, and glutamic acid, increased (Eppendorfer and Eggum 1992). The final influence of the S nutritional status is closely related to the N supply and they should therefore be assessed together. At low N supply, S deficiency increased the starch content in vegetative parts of kale and ryegrass, and seeds of oilseed rape, while this effect was not found at high N input. At high N levels, S deficiency reduced the methionine content in vegetative tissue of kale and ryegrass more severely than the cysteine

content, whereas in seeds of oilseed rape and field bean the cystine content was more strongly reduced (Eppendorfer and Eggum 1992).

The composition of seeds reflects an adaptation of plants to the S supply. Species with a low TGW, such as oilseed rape, typically rely on oil and fat as energy sources for the embryo. The total protein content of their seeds is uniform and more or less independent of the S supply. An increase of cysteine and methionine in total protein from about 0.8% to 1.1%, and 0.75% to 1.4%, respectively with increasing S supply from moderate deficiency towards sufficient supply (Mortensen *et al.* 1992), did not cause any significant changes in total S bound in the protein fraction. This was confirmed using the X-RF method for the indirect determination of GSLs by determining the total S content (Schnug and Haneklaus 1990). Adaptation of the metabolic sink to the S supply is maintained solely by the number of seeds produced (Schnug and Haneklaus 1994).

The endosperm of cereals which has a distinctly higher TGW, consists mainly of carbohydrates as the main energy reserve. S deficiency impairs the baking quality of wheat before crop productivity is reduced and a lack of protein or S could partly be compensated by increased concentrations of either compound (Haneklaus *et al.* 2006). The supply before anthesis is critical for wheat grain yield and quality as results of Haneklaus and Schnug (1992), Haneklaus *et al.* (1992 and 1995), and Anderson and Fitzgerald (2001) reveal. So, the S content of plants deprived of S from start of anthesis equaled that of plants fully supplied with S throughout the vegetation period, whereby sulfate was derived presumably from uptake by roots and GSH translocation from flag leaves (Anderson and Fitzgerald 2001).

In legumes, which have a high TGW, the cotyledons have a major storage function, whilst the proportions of embryo and endosperm are minor. Krishnan *et al.* (2005) found that soybean cultivars with high protein content had a low content of S-containing amino acids and vice versa. Under conditions of S deficiency these plants reduce the amount of the S-rich fractions. In pea seeds, legumin-type globulin proteins contained a higher proportion of S-containing amino acids than vicilin-type globulins (Randall *et al.* 1979). Extreme S deficiency yielded a decrease in the legumin content, whilst both increases and reductions were found when S was excessively applied to different genotypes (Randall *et al.* 1979). Excess S was accumulated as sulfate and the nonprotein amino acid *S*-methylcysteine in lupin and peas (Randall and Wrigley 1986). Sexton *et al.* (2002) showed that pods and seeds seemed to be the major sites of S reduction and that it was the S supply during reproductive growth which influenced protein-S in soybean seeds. In accordance with these results, Sunarpi and Anderson (1997) determined that 87% of the S in seeds was

taken up by roots during seed filling, with the balance coming from redistribution. A sufficient S supply before floret initiation proved to be nevertheless important for inserting maximum number of florets in sunflower (Hocking *et al.* 1987). Schroeder (1984) suggested that a sufficient S supply during seed filling might contribute to a significant improvement of the nutritive value of peas.

TGW, protein, and fat content of oilseed rape seeds were only affected by the S supply under conditions of extreme S deficiency (Schnug 1988), otherwise no significant influence could be verified under field conditions (Schnug 1988; Asare and Scarisbrick 1995). In contrast, Eppendorfer and Eggum (1992) and Shukla *et al.* (2005) found a significant increase in TGW by S fertilization. S deficient sunflower plants produced seeds with a lower TGW, while the oil content was not influenced (Hocking *et al.* 1987).

Crosstalk between S and N metabolic pathways will not only influence yield structure, biomass development, and dry matter composition, but also N-use efficiency of agricultural crops. Under conditions of S deficiency, nitrate and non-S-containing amino acids accumulate which may reduce the nitrate reductase activity (Srivastava 1980; Schnug 1997). Randall and Wrigley (1986) determined an increase from <5% to 30% of nonprotein N in seeds under conditions of severe S deficiency. S fertilization promotes nitrate reduction and thus reduces the nitrate content in vegetative plant tissues. Disproportionate N fertilization enforces the negative impact of an insufficient S supply on plant quality and it is inevitably linked to avoidable N losses to the environment. On average, per kilogram of insufficient S required to satisfy the demand of the crop, 15 kg of N are prone to be lost to the environment (Schnug 1997). The solution of this problem cannot be an excess S dose as adverse effects on crop productivity and quality are possible, and in any case, this is not compliant with a sustainable use of resources. A holistic appraisal of S interactions in crop ecosystems from field to fork should therefore always be a part of the farm management system.

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