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Ecological significance of H_2S emissions by plants - a literature review

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Abstract

The emission of several volatile reduced sulfur gases (H_2S, COS, DMS, CS_2 and methylmercaptan) from various plant species was determined in various experiments. From these volatile substances H_2S is one of the most important sulfur gases emitted by higher plants in response to an excess of sulfur. So far, a correlation between soil applied sulfur fertilization and H_2S emission of agricultural crops was not proven, but it was shown in field experiments that sulfur fertilization and the sulfur nutritional status, respectively had a significant effect on fungal infections in oilseed rape. These findings underline the concept of sulfur-induced resistance (SIR) of plants. H_2S is highly fungi toxic and therefore a relationship between increasing hydrogen sulfide emissions of plants and a higher resistance of crops against pests and diseases can be assumed. A better understanding of the natural defense system of domesticated plants based on the release of H_2S may contribute to a significant reduction of the input of fungicides in agriculture and thus to more sustainability in crop production. In organic farming, sulfur induced resistance may play a major role for maintaining plant health. From environmental point of view the degradation of toxic surface ozone concentrations by plant-released H_2S is another process of ecological relevance.

Key words: hydrogen sulfide, sulfur induced resistance, SIR, surface ozone

Sulfur induced resistance – release of H_2S

The significance of sulfur (S) for the resistance of crops against pests and diseases became evident at the end of the 1980's. At this time macroscopic S deficiency became a widespread nutrient disorder because of the desulfurization of industrial emissions in Western Europe (Booth et al., 1991). At the same time infections of oilseed rape with *Pyrenopeziza brassicae* spread out in regions which where never infected before (Schnug and Ceynowa 1990; Schnug et al., 1995a).

It has been known since long time that S has protective effects against pests and diseases. Most of this knowledge is, however, restricted to the effects of foliar-applied elemental S (Jolivet, 1993). In comparison, little is known about soil-applied S in sulfate form, which may have a strong influence on plant resistance by directly stimulating biochemical processes in the primary and secondary metabolism (Schnug, 1997). In fertilizer experiments under field conditions it could be shown that soil-applied S fertilization significantly reduced fungal infections of oilseed rape with light leaf spot (*Pyrenopeziza brassicae*), grapes with powdery mildew (*Uncinula necator*) and potato tubers with stem cancer (*Rhizoctonia solani*) (Schnug et al., 1995a; Bourbos et al., 2000; Klikocka et al., 2004). The results of these experiments indicate that different S metabolites are involved in disease resistance, which were induced by S fertilization and thus underpinning the concept of sulfur induced resistance (SIR) (Schnug et al., 1995a; Haneklaus et al., 2004). An improved understanding of how S is involved in the stress resistance of plants together with efficient fertilizer strategies are a challenge for future agricultural production techniques. The aim of S fertilizer strategies will be to maximize the inherent potential stress resistance, which otherwise would not be expressed due to an insufficient S supply, whilst maintaining an environmentally and economically sustainable farming (Schnug, 1997).

The mechanisms of SIR are not yet fully understood. Mechanisms to tackle with biotic stress, which are provided by the S metabolism involve among others glutathione, phytoalexins and glucosinolates (Haneklaus et al., 2004). The release of volatile S compounds is putatively an important mechanism in SIR, too. The emission of several volatile reduced S gases (H_2S, COS, DMS, CS_2 and methylmercaptan) from various plant species was determined (Schröder, 1993). Under growth conditions with an excessive S supply significant amounts of gaseous S compounds are released into the atmosphere from which H_2S is the most abundant gas emitted (Rennenberg, 1991). The release of H_2S is thought to be actively regulated by the plant metabolism rather than being a metabolic side-product. An indication for the first hypothesis is that H_2S emissions could be observed also under field conditions with a moderate sulfur supply (Rennenberg, 1991). Anyway, an excess S supply by atmosphere and pedosphere induces the emission of volatile S compounds by plants. The release of H_2S occurs when the influx of S compounds via leaf or root in the form of cysteine, sulfate, SO_2 or COS exceeds the conversion of these S sources into protein, glu-

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tathione, methionine and other S containing compounds (Rennenberg, 1991). The emission of H_2S is comparable with a pressure valve for the plant to dispose of excess S (Filner et al., 1984). It has been suggested that the release of H_2S regulates, homeostatically the size of the cysteine pool and thus maintains it at a low level because of its cytotoxicity. H_2S may be released prior or after cysteine formation (Giovanelli, 1990), but the question is still open which enzymes catalyze the release of H_2S. Another possible mechanism, which induces the H_2S emission by plants could be the involvement in the natural defense system of crop plants against fungal infections (Haneklaus et al., 2004).

Conditions determining the H_2S emission by plants are physiological factors such as the growth stage (Seykia et al., 1982a; Rennenberg and Filner 1983; Filner et al., 1984; Lakkineni et al., 2003) and metabolic activity of the plant tissue, but also nutritional and environmental factors (Fall et al., 1988; Rennenberg 1991; Schröder 1993; Lakkineni et al., 2003). Generally, the emission of S gases increases with temperature and illumination (Lamb et al., 1987; Seykiya et al., 1982b; Fall et al., 1988). The strategy to dispose of excess S depends on a concentration gradient for H_2S between plant and atmosphere. The presence of high atmospheric H_2S concentrations prevents H_2S emission, so that it is not surprising that H_2S fumigation resulted in a rapid accumulation of thiols, including cysteine in the plant tissue (Rennenberg, 1991; De Kok et al., 1998).

Data for the natural release of gaseous S-compounds reported in literature vary over a wide range (Seykia et al., 1982a, b, c; Rennenberg and Filner 1982, 1983, 1984; Filner et al., 1984; Fall et al., 1988; Schröder 1993; Collins 1996; Lakkineni et al., 2003). Filner et al., (1984) calculated a worldwide S emission from plants of 7.4 Tg S yr^{-1}, while Winner et al. (1981) came to a value of 54 Tg S yr^{-1}. Globally, Crutzen (1983) calculated the annual S emissions of H_2S, DMS and methylmercaptan from agricultural fields to be in the range of < 4 Tg S yr^{-1}. One reason for the large discrepancies observed for S emissions are analytical problems. H_2S measurements are difficult to conduct if emissions are low, because analytical systems need to be extremely sensitive so that there is only a few data available that provides information about the release of gaseous S compounds in the low range (Wilson et al., 1978; Seykia et al., 1982b; Lakkineni et al., 1990; Bloem et al., 2004a). Another problem of H_2S measurements is that most experiments were conducted under artificial conditions, e.g. with cut plant parts that were fed with concentrated S solutions (Wilson et al., 1978; Seykia et al., 1982b; Rennenberg and Filner 1983). Therefore such estimates need to be treated carefully. The metabolism of living crops and cut plant parts reacts completely different, and consequently higher H_2S emissions were measured from detached leaves and leaf discs than from whole plants. Extrapolation of H_2S emissions, which were measured from detached leaves or plant parts will therefore lead to an overestimation of the H_2S emission by the crop (Bloem et al., 2004a). In the laboratory it was possible to stimulate leaves to emit H_2S at 1000 times higher rates than under field conditions (Filner et al., 1984). When sulfate was fed to intact roots of whole plants, the increase in the H_2S emission was usually much lower (Rennenberg and Filner, 1982, 1983; Filner et al., 1984). Apparently, the root system constitutes a barrier for the influx of sulfate into the plant, and hence prevents an immediate release of H_2S from excessive sulfate in the soil (Rennenberg and Lamoureux, 1990). In some experiments the H_2S emissions were stimulated by injuring the roots, but for the same reason as in case of the cut leave these results are also not suitable to calculate the H_2S emissions by plants under natural conditions.

Although it is generally assumed that H_2S can be reliably determined using cryogenic trapping with gas chromatographic analysis, slight variations of the analytical procedure may result in significant losses of H_2S (Rennenberg, 1991). Despite these analytical problems that have to be overcome, the determination of H_2S emissions from intact plants in dependence on the S supply and infections with fungal diseases will be a milestone for addressing key metabolites involved in SIR. The role of S nutrition and fungal infections for the potential release of H_2S emissions was shown in field experiments with *Brassica napus* L. (Bloem et al., 2004b). For instance, the activity of the H_2S releasing enzyme L-cysteine desulfhydrase significantly increased in infected plant tissue and, to a lower extent in plants with a higher S nutritional status. (Bloem et al., 2004b).

Surface ozone concentrations

H_2S emissions by plants may degrade toxic surface ozone and thus be of high ecological significance (Schnug 1997). Surface ozone concentrations increased in rural areas over the last decade on an average by 1.8 g m^{-3} yr^{-1} (Figure 1). At the same time plant S concentrations declined at a constant rate of 0.45 mg yr^{-1} (Figure 1; Schnug, 1993, Schnug, 1997).

Assuming that: a) H_2S emissions from plants decline linearly together with the S supply (Collins 1996, Rennenberg 1984) at a rate of 0.57 nmol m^{-2} h^{-1} (calculated from the data of Schnug and Haneklaus 1994); b) crops have an average leaf area index of 1; c) crops assimilate and reduce S during an av-

erage of 100 days a year and 10 h a day; and d) H_2S degrades O_3 in a 1:1 ratio; then up to 75% of the observed increase of surface ozone could be attributed to the decrease in the total amount of S-turnover in the "green part" of the ecosystem (Schnug, 1997).

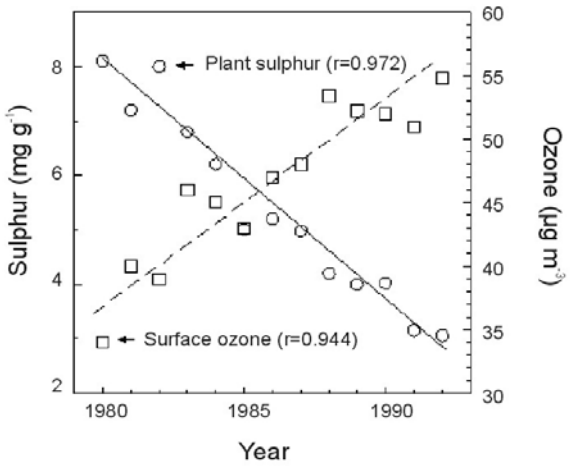

Figure 1:
Atmospherical surface ozone concentrations and total sulfur in younger, fully developed leaves of field grown *Brassica napus* varieties in northern Germany from 1980-1992 (Schnug 1993).

These figures here are only an estimate and may change depending on the actual input parameters, but they still outline the important function of S assimilation and reduction in ecosystems. Despite the significance of these findings for air quality, higher S inputs in the past century enabled plants to adapt to increasing environmental stress caused by higher surface ozone concentrations and, vice versa, the decline of the S supply within only one decade (Schnug, 1991, 1993) may have serious consequences for the stability of recent ecosystems. For example, S deficiency is thought to be one of the reasons why 50% of all forests are damaged. These damages are caused by a reduced resistance against abiotic stress because of a continuously declining S supply on the one hand, and steadily increasing environmental stress on the other hand (Williams, 1982, Zhao, 1996).

Conclusions

So far there is no scientific proof for a correlation between the rate of soil-applied S and the amount of H_2S released by plants. In the case of other secondary S compounds such as glutathione and glucosinolates significant positive relationships were found (De Kok et al., 1998; De Kok and Stulen, 1993, Schnug et al., 1995b; Haneklaus et al., 1999; Bloem et al., 2004). H_2S is highly fungi-toxic (Pavlista, 1995) and therefore a relationship between increasing H_2S emissions and the resistance of crops against pests and diseases is likely (Seykia et al., 1982c; Beauchamp et al., 1984; Schröder 1993). All these findings clearly show that extensive field measurements are required to evaluate the impact of different nutritional conditions and fungal diseases on the emission of H_2S. It is the aim of a joint research project financed by the DFG (German Research Foundation) to determine the release of H_2S in relation to the S nutritional status of agricultural crops and to answer the question whether such relationship is involved in SIR. The identification of the mechanisms causing SIR will be an important milestone for a sustainable agricultural production as the input of fungicides could be minimized or completely waived (Haneklaus et al., 2004). Consumers are increasingly concerned about the contamination of foodstuff with pesticide residues and consequently markets for plant production from farming systems avoiding such contaminations are expanding (Schnug, 1997). Thus, SIR may become an important strategy to efficiently combat pathogens in sustainable farming systems, favorably organic farming. An important advantage of SIR compared to pesticides is that the resistance will not be rapidly broken by new pathotypes (Haneklaus et al., 2004). And an indirect effect of an increased release of H_2S could be the detoxification of toxic surface ozone concentrations by which oxidative stress would be lowered outside the organism (Schnug, 1993, 1997).

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