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Is Emission of Hydrogen Sulfide a Dominant Factor of SO_2 Detoxification? – A Comparison of Norway Spruce (*Picea abies* (L.) Karst.), Scots Pine (*Pinus sylvestris L.*) and Blue Spruce (*Picea pungens* Engelm.) in the Ore Mountains

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With 3 figures

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Summary

KINDERMANN G., HÜVE K., SLOVIK S., LUX H. & RENNENBERG H. 1995. Is emission of hydrogen sulfide a dominant factor of SO_2 detoxification? – A comparison of Norway spruce (*Picea abies* (L.) Karst.), Scots pine (*Pinus sylvestris* L.) and Blue spruce (*Picea pungens* Engelm.) in the Ore mountains. – Phyton (Austria) 35 (2): 255–267, 3 figures. – English with German summary.

The emission of reduced volatile sulfur compounds from Norway spruce (*Picea abies* (L.) Karst.), Scots pine (*Pinus sylvestris L.*) and Blue spruce (*Picea pungens* Engelm.) growing at high elevation in the Ore mountains (Kahleberg, Germany, altitude

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907 m) was measured in the field by cryosampling and gaschromatographic analysis. Twigs still attached to the trees were enclosed in a flow-through gas exchange cuvette and H_2S was detected as the predominant reduced sulfur compound in the effluent gas stream. Carbonylsulfide (COS) and, in a portion of the samples, dimethylsulfide were also detected. The mean H_2S emission rate was almost the same from twigs of Norway spruce (6.2 pmol kg^{-1} dw s^{-1}) and Blue spruce trees (5.9 pmol kg^{-1} dw s^{-1}) but it was approximately 18 times higher for Scots pine (110 pmol kg^{-1} dw s^{-1}). The percentage of SO_2 detoxification via H_2S emission was calculated on the basis of data on SO_2 fluxes. It is only about 1 % for Norway spruce and Blue spruce but about 10 % for Scots pine.

Zusammenfassung

KINDERMANN G., HÜVE K., SLOVIK S., LUX H. & RENNENBERG H. 1995. Stellt die Emission von Schwefelwasserstoff einen wesentlichen Faktor der SO_2-Entgiftung dar? Ein Vergleich zwischen Fichten (*Picea abies* (L.) Karst.), Kiefern (*Pinus sylvestris* L.) und Blaufichten (*Picea pungens* Engelm.) im Erzgebirge. – Phyton (Austria) 35 (2): 255–267, 3 Abbildungen. – Englisch mit deutscher Zusammenfassung.

Die Emission reduzierter flüchtiger Schwefelverbindungen von Fichten (*Picea abies* (L.) Karst.), Kiefern (*Pinus sylvestris* L.) und Blaufichten (*Picea pungens* Engelm.) wurde in einer Feldstudie untersucht. Das Untersuchungsgebiet liegt am Kahleberg auf 907 m üNN im östlichen Teil des Erzgebirges. Für die Messungen wurden jeweils ein am Baum verbliebener Ast in eine Glasküvette eingespannt, sodaß der Gasaustausch nicht beeinträchtigt war. Die Probengewinnung erfolgte mittels Kryofokussierung; die Analyse der Luftproben wurde am Gaschromatographen durchgeführt. Als die Hauptkomponente der emittierten reduzierten Schwefelverbindungen wurde H_2S ermittelt. Darüberhinaus konnte Carbonylsulfid (COS) und, in einem Teil der Proben, Dimethylsulfid nachgewiesen werden. Die mittlere H_2S-Emissionsrate war bei den Ästen der Fichten (6.2 pmol kg^{-1} dw s^{-1}) und den Ästen der Blaufichten (5.9 pmol kg^{-1} dw s^{-1}) fast gleich. Die Äste der Kiefer emittierten H_2S jedoch mit einer gegenüber den vorgenannten Baumarten nahezu 18-fach höheren Emissionsrate (110 pmol kg^{-1} dw s^{-1}). Der Prozentsatz der SO_2-Entgiftung durch die H_2S-Emission wurde basierend auf SO_2-Fluxdaten abgeschätzt. Fichte und Blaufichte entgiften demnach nur etwa 1 % des SO_2; die Kiefer hingegen zeigte eine Entgiftungsleistung von etwa 10 % des SO_2 durch H_2S-Emission.

Introduction

Emission of sulfur compounds by plants was first observed by MATERNA 1966 after fumigation of spruce trees with $^{35}SO_2$. These observations were confirmed in experiments with tomato, bean, and corn plants exposed to high concentrations of SO_2, where H_2S was identified as the main emitted sulfur compound (DE CORMIS 1968, 1969). Since these early observations, it has been shown in numerous studies that higher plants release H_2S into the atmosphere when they are supplied with an excess of sulfate, sulfite/sulfur dioxide, or L-cysteine (SILVIUS & al. 1976, WILSON & al. 1978, WINNER & al. 1981, FILNER & al.1984, RENNENBERG 1984, 1991). Depending on sulfur sources, H_2S is synthesized through different path-

ways of an intracellular sulfur cycle from which H_2S is released if the influx of sulfur exceeds the fluxes into protein, glutathione, methionine, or other sulfur containing compounds (SCHIFF & HODSON1973, SCHWENN & TREBST 1976, SCHMIDT 1979, ANDERSON 1980, GIOVANELLI & al. 1980, RENNENBERG 1991).

Exposure of plants to atmospheric SO_2 results in elevated sulfur levels in the shoots that can predominantly be ascribed to an accumulation of sulfate (GASCH & al. 1988, DE KOK 1990, DITTRICH & al. 1991, KAISER & al. 1993). Accumulation of sulfate at a site exposed to elevated levels of SO_2 in air was smaller in needles of Scots pine or Blue spruce trees than in Norway spruce (HÜVE & DITTRICH, unpubl. data). These species are generally thought to be more resistant to SO_2 than Norway spruce. It may therefore be hypothesized that high rates of H_2S emission may prevent sulfate accumulation and mediate resistance to SO_2 in Scots pine and Blue spruce. The present study was performed to test this hypothesis.

Material and Methods

Stand characteristics

The *Picea abies* (L.) Karst. (Spruce), *Pinus sylvestris* L. (Pine) and *Picea pungens* Engelm. (Blue spruce) trees used in this study are growing close to the summit of the Kahleberg (907 m above the sea level), which is located southwest of Dresden in the Ore mountains near the Czech border. Most of the Norway spruce trees at the Kahleberg declined in recent years. Blue spruce has been planted at this location during the last 30 years to replace the Norway spruce forest (RANFT 1982). Experimental trees were 20 to 40 years old. Detection of H_2S emission was performed during august 1992 on 1 to 2 different twigs per tree and 3 to 4 trees per species.

Gas Exchange Studies

Twigs with 1 to 4 needle generations were enclosed in a flow-through gas exchange cuvette of 2.9 liter volume (RENNENBERG & al. 1990). Unfiltered air was continuously passed through the cuvette at a flow rate of 33.3 mL s^{-1}. The temperature in the cuvette was automatically adjusted to the outside temperature. To avoid condensation of transpiration water in the cuvette, enclosed twigs were usually not exposed to full sunlight during the experiments. Rates of CO_2 fixation were calculated from the difference of the CO_2 concentration between the inlet and the outlet port of the gas exchange cuvette as determined with an infrared carbon dioxide analyser (LCA-2, ADC, Hoddesdon, UK).

Analysis of Volatile Sulfur Compounds

Quantification of volatile sulfur emissions was performed as described earlier (RENNENBERG & al. 1990). Sulfur compounds in cuvette air were trapped by cryo-enrichment in liquid argon (–186° C). Sulfur emission of the branches was corrected for volatile sulfur in ambient air by alternative usage of a second flow-through cuvette without an enclosed branch. Separation and detection of volatile sulfur compounds was achieved by GC analysis (Carbopack BHT-100, Supelco, Belafonte, PA)

with a flame photometric detector (FPD) sulfur analyser (Tracor, Bilthoven, The Netherlands). Identification and calibration was performed by means of standard permeation tubes (Dynacal, UPK, Bad Nauheim, Germany).

SO_2 concentration measurements

SO_2 concentration in the atmosphere was measured (APSA-350 E, Alcyon Tecan Systems S.A., Renens, Switzerland) continuously at a field station of the University of Dresden close to Oberbärenburg, approximately 8 km from the Kahleberg. SO_2 concentrations at this site were shown to be very similar to SO_2 concentrations at the Kahleberg (LIEBOLD & DRECHSLER 1991).

Aqueous extraction and determination of water-soluble sulfate in soil and needles

Because the surface of the needles was often contaminated with visible deposits of insoluble salts (mainly $CaCO_3$), each needle was wiped with 5 % acetic acid and rinsed immediately with distilled water. The needles and soil samples were dried using a microwave-oven for 6 to 8 minutes and ground to a fine powder by a mill working with teflon pots and teflon balls (mill MM2, Retsch GmbH, Haan, Germany). Two mL of deionized water (Nanopure, 18.2 Megaohm-cm) were added to about 40 mg of dry sample powder. The samples were boiled for 5 min in a heating block and then vigorously mixed for another 2 min. The extracts were cleared by centrifugation (12.500 g for 5 min). To minimize contamination with phenolic compounds, 50 mg of purified insoluble PVPP (polyvinylpolypyrrolidone, M_r 500,000, Sigma Chemical Co., St. Louis, USA) was added to 1 mL of the water solution and the samples were again mixed vigorously for 30 min. The extracts were cleared again by centrifugation (12.500 g for 5 min) and subsequent pressure filtration through 0.45 µm micromembrane filters (Ultrafree-MC filter, Millipore Products Division, Bedford, MA, USA). Aliquots of the aqueous extracts were diluted and subjected to suppressed anion chromatography ((IC 100, Biotronik, Maintal, Germany) fitted with an automatic sampler injector (BHT 7041, Biotronik, Maintal, Germany), a conductivity meter and UV detector (210 nm) (BT 0330, Biotronik, Maintal, Germany) and an intregrator (Shimadzu C-R1B, Tokyo, Japan)). After every six samples, a standard containing sulfate at a concentration of 0.1 mM was measured for external standardization.

Total sulfur and organic sulfur content in the needles

The total sulfur content in the needles was determined in the dry needle powder after pressure ashing in concentrated HNO_3 by inductively coupled plasma (ICP) atomic emission spectrophotometry (Model JY 70 PLUS, ISA Jobin-Yvon, France). The organic sulfur content of the needles was calculated by the difference in total sulfur content minus water soluble sulfate content. The quantity of oxidized water-soluble thiols is negligible compared to watersoluble sulfate and hence is not considered in this calculation, though these thiols might be extracted together with sulfate.

Results and Discussion

Emission rates of H_2S from twigs of the three conifer species investigated varied considerably with day time, species and individual tree (Fig. 1–3). Ambient SO_2 concentration changed during a day with high

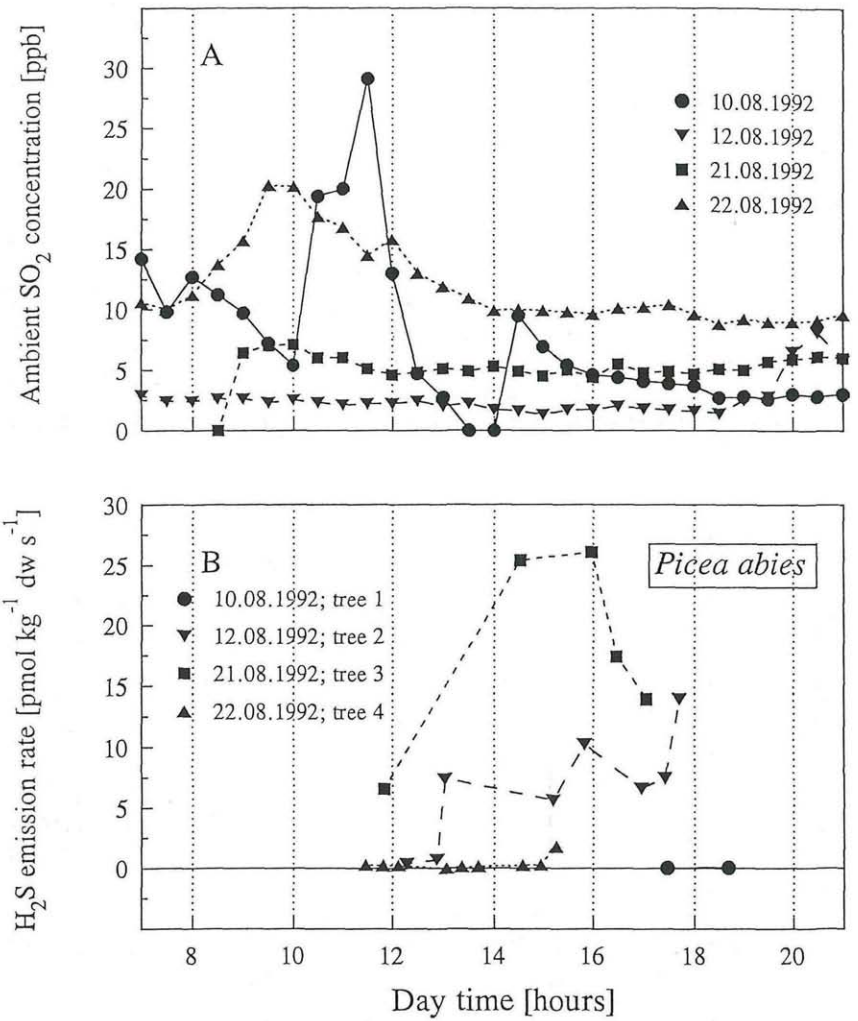

Fig.1. Diurnal variations in the ambient SO_2 concentration (A) and the H_2S emission rates (B) of four twigs of Norway spruce (*Picea abies* (L.) Karst.) which were measured on four different days (different symbols). Each point in Panel B represents a single measurement made with one twig containing 1 to 4 year old needles.

concentrations of SO_2 in the air especially in the morning hours until noon (Fig. 1–3). In addition to H_2S emission, emissions of trace amounts of carbonylsulfide, dimethylsulfide, and carbon disulfide from twigs of Norway spruce were also found in a few measurements. Emission of methylmercaptan was not detected in Norway spruce. Twigs of Blue spruce emitted trace amounts of carbonylsulfide, methylmercaptan and carbon disulfide.

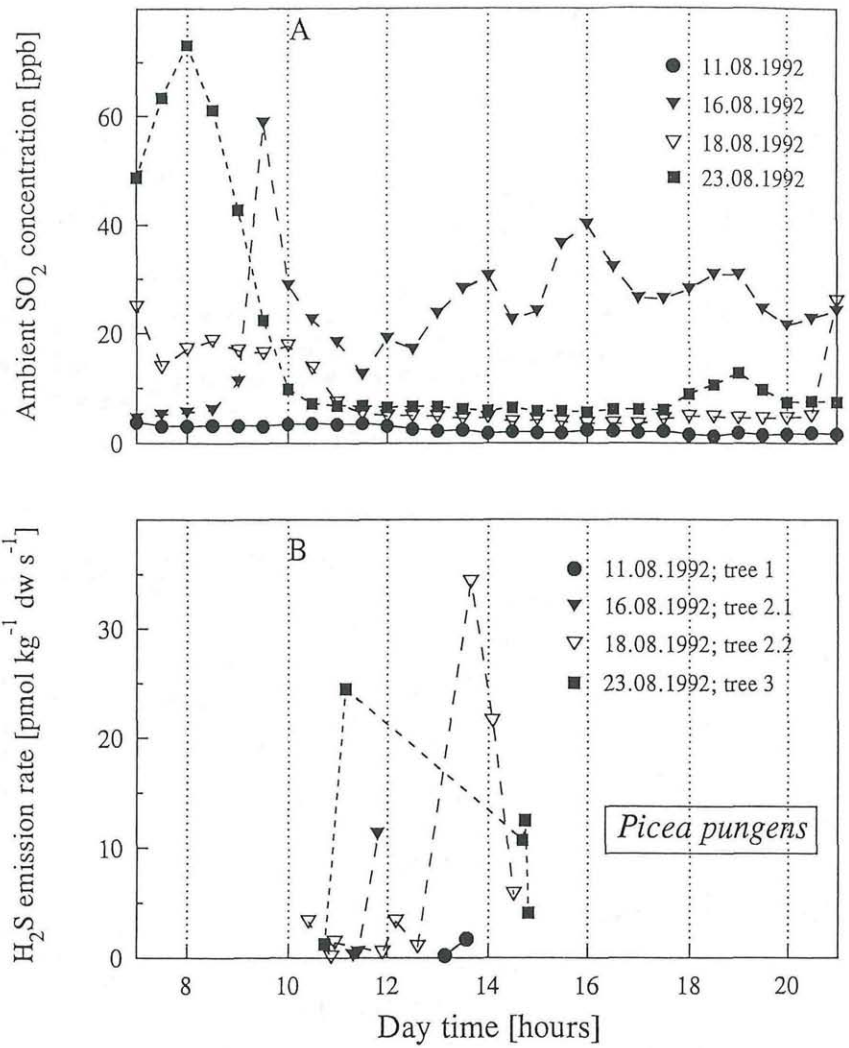

Fig. 2. Diurnal variations in the ambient SO_2 concentration (A) and the H_2S emission rates (B) of four twigs of Blue spruce (Picea pungens Engelm.) which were measured on four different days (different symbols). Two different twigs were measured on two different days per tree (open and closed symbol). Each point in Panel B represents a single measurement made with one twig containing 1 to 3 year old needles.

Emission of sulfur dioxide and dimethylsulfide were not detected. In addition to H_2S, twigs from Scots pine emitted trace amounts of carbonylsulfide and carbon disulfide. Emission of sulfur dioxide, methyl mercaptan and dimethylsulfide was not found. The mean H_2S emission rates of Nor-

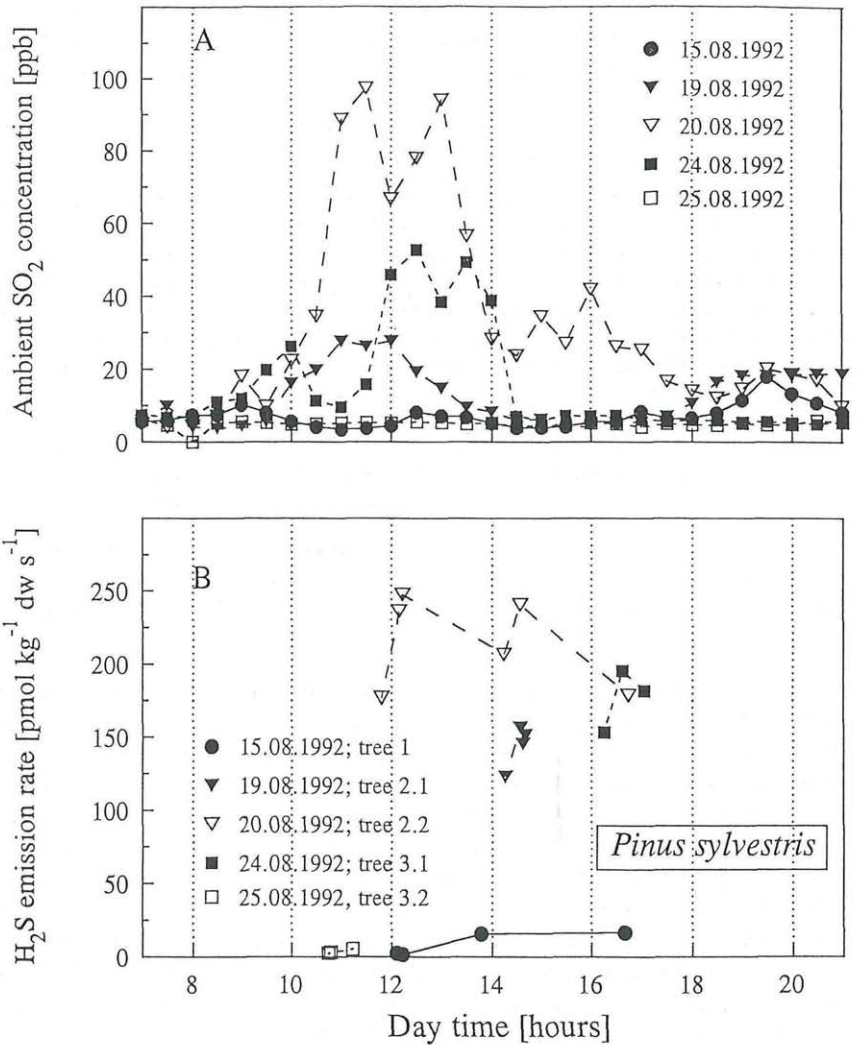

Fig. 3. Diurnal variations in the ambient SO_2 concentration (A) and the H_2S emission rates (B) of five twigs of Scots pine (*Pinus sylvestris* L.) which were measured on five different days (different symbols). Two different twigs were measured on two different days per tree (open and closed symbol). Each point in Panel B represents a single measurement made with one twig containing 1 to 2 year old needles.

way spruce (6.21 pmol kg^{-1} dw s^{-1}) and Blue spruce (5.88 pmol kg^{-1} dw s^{-1}) were comparable (Tab. 1). The mean H_2S emission rate of Scots pine (110 pmol kg^{-1} dw s^{-1}) was approximately 18 times higher. Mean SO_2 concentrations varied only by a factor of two. Mean rates of CO_2 fixation,

given in µmol CO_2 kg^{-1} dw s^{-1}, were low (Tab. 1) and did not match the mean values reported by other authors for spruce (BEYSCHLAG & al. 1987, LANGE & al. 1989). This could be due to the shading of the cuvettes and to partial closure of the stomata.

Table 1

Mean H_2S emission and CO_2 uptake rates in twigs of Pine (*Pinus sylvestris* L.), Blue spruce (*Picea pungens* Engelm.) and Spruce (*Picea abies* (L.) Karst.) in response to mean atmospheric SO_2 concentrations. Values are presented as means ± SE (standard error). For H_2S emission and CO_2 uptake rates the values in parentheses depict the number of replicate twigs used in the calculation of each mean, whereas for SO_2 concentration measurements the values in parentheses depict the number of replicate measurements. The number of trees studied for H_2S and CO_2 exchange were 4, 3 and 3 for Spruce, Blue spruce and Pine, respectively.

Species	H_2S emission rate [pmol kg^{-1} dw s^{-1}] ± SE	Net CO_2 uptake rate [µmol kg^{-1} dw s^{-1}] ± SE	SO_2 concentration [ppb] ± SE
Scots pine	110 ± 43.6 (5)	5.45 ± 0.93 (5)	13.1 ± 0.66 (145)
Blue spruce	5.88 ± 2.13 (4)	9.12 ± 6.78 (4)	11.8 ± 0.75 (116)
Norway spruce	6.21 ± 4.17 (4)	4.83 ± 4.11 (4)	6.82 ± 0.37 (116)

Emission of H_2S in response to excess sulfur is a common feature of higher plants (RENNENBERG 1991). The measured rate of H_2S emission from spruce twigs at the Kahleberg is similar to the emission rate reported for spruce grown in the German alps in the absence of significant atmospheric SO_2 and with low sulfate content in the soil (RENNENBERG & al. 1990). In contrast mean H_2S emission rates from twigs of Norway spruce, measured at different locations during the same sampling period in august 1992 varied considerably. The mean emission rate detected from twigs at Würzburg (NW-Bavaria) was about 155 times lower compared to that detected at the Kahleberg. The SO_2-concentration in the air (annual mean) at Würzburg is about 1/7 the SO_2-concentration measured at the Kahleberg (KINDERMANN 1994, KINDERMANN & al. 1995).

At the Kahleberg, the SO_2 concentration in the air, mainly originating from Czech power plants is still very high (up to 30 to 40 ppb SO_2, annual means). Nevertheless, our results demonstrate that SO_2 is not capable of dramatically enhancing H_2S emission rates from spruce twigs. As in the Alps, the sulfate content in the soil of the Kahleberg was low (1.92 ± 0.63 mmol sulfate kg^{-1} dw soil). For pine, the maximum H_2S emission rate in the field (240–250 pmol kg^{-1} s^{-1}) after a short exposure time to high concentrations of SO_2 (80–100 ppb SO_2, Fig. 3) was about four times higher than reported by HÄLLGREN & FREDERICKSSON 1982 for trees fumigated with approximately the same SO_2 concentration for two days and nights.

Not only SO_2/sulfite but also sulfate can be a substrate for the generation of H_2S by plants (SPALENY 1977). Eight to nine day old spruce seedlings, irrigated with 5 % K_2SO_4 released H_2S into the atmosphere at a rate of 18.1 pmol H_2S kg^{-1} dw s^{-1} (SPALENY 1977). The rate of H_2S emission of spruce seedlings may depend on the availability of sulfate in the soil. Also, the emission rate of H_2S depends on the developmental stage of plants (RENNENBERG & FILNER 1983). The root system constitutes a barrier for the influx of sulfate into the plant, and hence prevents an immediate emission of H_2S from excess sulfate supply (RENNENBERG 1991). Since all three species investigated here are growing on the same site, the differences of H_2S emission rates cannot depend on available sulfate in the soil. It may, however, depend on differences in sulfate uptake and transport to the leaves. As shown in Tab. 2, the sulfate content of the needles of the three species analyzed differed considerably. Highest sulfate contents were found in spruce, intermediate contents in pine and lowest contents in Blue spruce. In contrast to pine trees and Blue spruce trees, Norway spruce accumulates sulfate in the needles after exposure to high concentrations of SO_2 in the air (DITTRICH & al. 1991, KAISER & al. 1993) (Table 2). Apparently, there is no correlation between the rate of H_2S emission and leaf sulfate content in general. The organic sulfur content of the needles of the three species was similar (Table 2) and this did not reflect differences in H_2S emission.

Table 2

Levels of total sulfur, sulfate and organic sulfur in needles of the twigs of Pine, Blue spruce and Spruce which were used in the gas exchange measurements reported in Table 1. Values are presented as mean ± SE (standard error). The value in parenthesis following the species name denotes the number of replicate twigs used in each measurement.

Species	Total sulfur [mmol kg^{-1} dw] ± SE	Sulfate [mmol kg^{-1} dw] ± SE	Organic sulfur [mmol kg^{-1} dw] ± SE	Ratio inorg/org sulfur
Scots pine (5)	48.3 ± 1.92	20.1 ± 1.35	28.1 ± 2.42	0.72
Blue spruce (4)	36.3 ± 2.56	11.9 ± 1.96	24.5 ± 0.72	0.49
Norway spruce (4)	56.7 ± 4.19	32.9 ± 6.36	23.7 ± 2.30	1.39

The estimated percentage of SO_2 detoxification via H_2S emission for the period of our measurements is summarized in Tab. 3. Literature data of stomatal conductance for pine (HÄLLGREN & al. 1982) are not consistent to our data, respectively they are lacking for Blue spruce trees. Estimates of the mean stomatal conductance during the experiments can be made on the basis of the rate of photosynthesis in Table 1. Assuming that the CO_2 gradient across stomata is similar for all three species, the mean sto-

matal water conductance during the experiments can be estimated (Table 3). Based on these estimates, the rate of SO_2 uptake by the needles can be calculated using the measured mean SO_2 concentration data during the experiments (calculation according to Taylor & Tingey 1983, Table 3, further explanations in the footnotes to Table 3). The percentage of SO_2 detoxification by H_2S emission was different for the tree species. Blue spruce

Table 3

Calculation of the percentage of SO_2 which was detoxified via H_2S emission from twigs of Pine, Blue spruce and Spruce. CO_2 uptake rate relative to spruce, mean stomatal water conductance, mean stomatal conductance of SO_2, needle surface area, SO_2 uptake rate, H_2S emission rate, and percentage of SO_2 detoxification by H_2S emission are shown for the different tree species. Calculations and further explanations are given in the footnotes.

Item	Parameter	Units	Pine	Blue spruce	Spruce
1.	CO_2 uptake rate relative to Spruce[a]	–	1.1	1.9	1.0
2.	Stomatal water conductance[b]	[mmol m^{-2} s^{-1}]	(11)	(19)	10
3.	Stomatal SO_2 conductance[c]	[mmol m^{-2} s^{-1}]	5.8	10.1	5.3
4.	Needle surface area[d]	[m^2 kg^{-1} dw]	14.0	10.5	14.4
5.	SO_2 uptake rate[e]	[nmol kg^{-1} dw s^{-1}]	1.06	1.25	0.52
6.	H_2S emission rate	[pmol kg^{-1} dw s^{-1}]	110	5.88	6.21
7.	Percentage of SO_2 detoxified via H_2S emission	[%]	10.4	0.5	1.2

[a] based on data of Table 1. CO_2 uptake rate of spruce was set 1.0.

[b] Mean stomatal water conductance of Norway spruce after Kaiser & al. (1993). For the other species, values in parenthesis were estimated by multiplication of mean stomatal water conductance of Spruce with CO_2 uptake rate relative to Spruce (item 1), assuming that the CO_2 gradient across stomata is similar for all three species.

[c] The stomatal conductance of SO_2 is 0.53 times the stomatal water conductance (Taylor & Tingey 1983).

[d] The specific needle surface area of Norway spruce and Blue spruce were determined for trees at the Kahleberg. The specific needle surface area of pine was determined for trees at the Botanical Garden of the University of Würzburg, but is consistent to the specific needle surface area of pine trees at the Kahleberg.

[e] SO_2 uptake rate is the result of the multiplication of SO_2 concentration in the air (Table 1) with item 3 and item 4 of Table 3 (stomatal SO_2 conductance and needle surface area) for the different tree species.

detoxified 0.5 %, Norway spruce 1.2 % and pine 10.4 % of the SO_2 taken up during the experiments by emission of H_2S. The varying capability of H_2S production may contribute to the observed differences of SO_2 sensitivity of the tree species. Early investigations in the surroundings of steelworks and in the Ore mountains showed a succession of increasing sensitivity to SO_2 in the sequence Blue spruce, pine, and Norway spruce (Schröder &

REUSS 1883, RANFT 1982). The absolute rates of H_2S emission are low for all three species. However, pine, in contrast to the two spruce species, seems to be capable of reducing an appreciable proportion of SO_2 that enters the needles, and to emit reduced sulfur as H_2S. Reduction requires light and occurs in the chloroplasts which appear to be mainly responsible for detoxifying SO_2 (DITTRICH & al. 1992, VELJOVIC-JOVANOVIC & al. 1993).

None of the species studied detoxifies SO_2 in general mainly by emission of H_2S. Especially in Norway spruce, accumulation of sulfate anions in the needles remains the major fate of SO_2 taken up by the needles.

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