Exchange of carbonyl sulfide (COS) between agricultural plants and the atmosphere: Studies on the deposition of COS to peas, corn and rapeseed

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Abstract. Young corn, pea and rapeseed plants were exposed to compressed synthetic air containing varying COS concentrations. The results suggest that COS exchange depends highly on the ambient COS mixing ratios. Ambient COS mixing ratios larger than 150 pptv resulted in a deposition of COS to all plant species studied. Significant (confidence level 95%) COS emission was only detected from rapeseed leaves at COS mixing ratios lower than 90 pptv. We computed COS compensation points around 90 (57—135) pptv and 144 (0—328) pptv COS for rapeseed and corn. For both plant species we found a close correlation between the photosynthetic CO_2 assimilation and the COS uptake. In contrast to the gas exchange studies with corn and rapeseed, experiments with pea plants revealed neither a change in response to increased COS concentrations of between 350 and 900 pptv COS nor any correlation with photosynthesis. However, for all three plants studied we found indications that COS is taken up preferentially over CO_2 under normal ambient conditions.

Introduction

During the last decade several investigations have revealed that plants are involved in the atmospheric sulfur cycle. Both uptake and emission of volatile reduced sulfur compounds by plants have been identified (Kluczewski et al. 1985; Taylor et al. 1983, De Kok et al. 1989; Brown et al. 1986; Fall et al. 1988; Rennenberg et al. 1990; Kesselmeier et al. 1992, 1993). In contrast to estimates of man-made sulfur emissions 93 ± 15 Tg S per year (according to Cullis & Hirschler 1980) exchange processes of naturally produced and consumed sulfur compounds are much less understood. Recent estimates of total natural sulfur emissions range around 65 ± 25 Tg S a^{-1} (Andreae & Jaeschke 1992). Uncertainties with these data may be attributed to several factors, including technical difficulties and gaps in knowledge of the plant physiology responsible for emission or de-

position (Kesselmeier 1991). We should be aware that for many trace gases deposition does not always result from uptake and consumption and emission does not automatically indicate production by vegetation because of possible adsorption to outer and inner plant surfaces (Kesselmeier 1992). Confusion results from investigations of trace gas emissions with boxes or cuvettes utilizing purified air for flushing. Many of the studies dealing with emissions of sulfur compounds from plants were conducted with sulfur-free air. Thus, Rennenberg et al. (1990) found a continuous emission of H_2S from spruces in the dark and in the light which was enhanced by light and correlates significantly with plant transpiration. Although interesting, such experiments should not be generalized because the experimental conditions are adjusted to an artificial environment and thus may exclude deposition. Furthermore, such a "zero-air" condition may even force sulfur emissions, which would not occur under normal environmental conditions. As a consequence, a number of investigations deal with emissions of reduced sulfur compounds simply because deposition was excluded by the experimental conditions. Some studies nevertheless revealed that the plants are a sink for reduced sulfur compounds (Taylor et al. 1983; Brown et al. 1986; Goldan et al. 1988; De Kok et al. 1989, 1991). However, some of these investigations were performed with atypically high concentrations of reduced S-compounds in the air, for example up to 125 ppbv H_2S (Taylor et al. 1983; De Kok et al. 1989, 1991). Here again, in parallel to emission, deposition and uptake values are of questionable relevance for a physiological or global scale extrapolation as the trace gas concentrations exceeded natural atmospheric conditions by a factor of 100—1000 and thus may force or at least enhance deposition. These problems are highlighted by recent investigations of soil emissions: Castro and Galloway (1991) showed that soils switch from acting as sources of COS and CS_2 under zero-air conditions to acting as sinks under atmospheric mixing ratios.

COS is the most abundant sulfur gas in the atmosphere. Because it is relatively inert in the atmosphere it may be transported into the stratosphere and is now believed to be a major source of stratospheric background aerosol (Crutzen 1976; Turco et al. 1980; Hofmann 1990). Therefore, the understanding and quantification of its sources and sinks are of considerable importance. COS has been shown to be a major sulfur compound emitted from vegetation (Lamb et al. 1987; Guenther et al. 1989). However, these measurements were conducted with sulfur-free air, thus they do not necessarily reflect natural exchange. Other laboratory studies have shown that COS is taken up by vegetation (Taylor et al. 1983; Kluczewski et al. 1985; Brown et al. 1986; Brown & Bell 1986; Fall et al. 1988; Goldan et al. 1988). A few field studies support these findings

(Goldan et al. 1987; Mihalopoulos et al. 1989; Hofmann et al. 1992a) and another found no evidence of COS uptake (Berresheim & Vulcan 1992).

In addition to exchange studies, investigations on the metabolic processes are necessary. In recent work (Protoschill-Krebs & Kesselmeier 1992), the physiological basis for COS uptake and absorption by plants was characterized. The isolated CO_2-consuming enzymes Ribulose-1,5-bisphosphate-carboxylase, Phosphoenolpyruvate-carboxylase, and carbonic anhydrase, the most efficient of all, increased the in vitro COS hydrolyzation rate significantly. According to this mechanism, COS metabolization is strictly linked to the CO_2 assimilation pathway. In a contrasting interpretation, Fall et al. (1988) suggested the uptake of COS to be not directly tied to CO_2 assimilation, based on experiments using varying CO_2 mixing ratios in the flush gas.

In the present study our objective was to obtain information (1) about the influence of ambient COS mixing ratios on the exchange rates between intact leaves and air and (2) about the relation between the photosynthetic rate and COS exchange. This was of special interest for it facilitated a comparison between results obtained with intact plants and results obtained with isolated enzymes (Protoschill-Krebs & Kesselmeier 1992). The fumigation experiments were conducted with single leaves, still attached to the plant, using a dynamic gas exchange system. This allowed the concomitant measurement of transpiration and net assimilation rates.

Materials and methods

Gas exchange system

A commercially available system for measuring the gas exchange of plants (Miniküvette, Fa. Walz, Effeltrich, Germany) was modified in order to allow the quantification of sulfur compounds. The gas exchange chamber was made of plexiglass (15 × 10 × 9 cm), whereas the rear side was made of a 5 mm thick copper plate with the side facing the chamber being teflon coated. A control and data acquisition unit mediated the regulation and measurement of temperature and relative humidity inside the chamber and the gas flow into the chamber. Air pressure inside the chamber was equal to the pressure outside. Single leaves were enclosed by removing the upper part of the chamber and inserting the petiole through a slot in the front wall which was then sealed with Terostat No 9 (TEROSON, Germany). The air inside the chamber was mixed by a fan made of PTFE mounted on the bottom of the chamber and driven by a magnetically coupled motor situated outside the chamber. Under steady state condi-

tions a maximum temperature gradient of 0.1 °C was observed in the chamber. Gas flow rates through the chamber ranged from 0.5 l/min to 2 l/min, resulting in residence times of 15 to 60 sec.

Gas exchange measurements

The transpiration and net assimilation by the enclosed leaves were derived from the difference in the water vapour content and the CO_2 concentration between the incoming and outgoing cuvette air. These were measured with an infrared gas analyzer (BINOS 100, Leybold-Heraeus, Hanau). The transpiration rate and the net assimilation rate were calculated following the method of Ball (1987).

Plant material

Plant species used for this study were corn (*Zea mays*, var. Gelber Badischer Landmais), peas (*Pisum sativum*, var. Arvika) and rapeseed (*Brassica napus*, subspec. napus, Sommerraps). The plants were grown in commercially available potting soil (Floratorf, Torfprodukt acc. to DIN 11540-F80, pH 6.0—6.5) in a growth chamber (Heraeus, Germany) within a 12 hr day-night cycle for 3—4 weeks (corn and peas) and 4—6 weeks (rapeseed). Chamber conditions were as follows: daytime PAR 300 $\mu E\ m^{-2}\ s^{-1}$, T = 23 °C, RH (relative humidity) = 70%; nighttime: T = 18 °C, RH = 75%. The plants were watered each day with a Hoagland solution (Hoagland & Arnon 1950). Only the youngest, fully expanded leaves were investigated in these gas exchange measurements. Variability within the species is expressed with the data fluctuations, as 3—4 different experiments were done with different plants.

Exposure, sampling and analytical procedure

Enclosed leaves on intact plants were exposed either to nonpurified pressurized air (Linde 5.0) or to pressurized air enriched with COS, resulting in mixing ratios of about 400 to 500 pptv at the inlet port of the gas exchange chamber. COS was provided from a permeation tube placed in a two-stage dilution system. Air samples were taken directly from the outlet port of the gas exchange chamber at a flow rate of 200 ml/min. The samples were dried by commercially available Nafion driers (Permapure) and cryogenically trapped into a glass cryo trap (volume ca. 25 ml) which was submerged in liquid argon. For further details and GC analysis see Hofmann et al. (1992b). Prior to the exposure of leaves, the empty system was flushed, in order to determine gas contamination and absorption

effects by the empty cuvette. From this flushed but empty system, five samples for the determination of blank concentrations were taken. For all experiments with enclosed leaves, the parameters temperature, relative humidity, light intensity and flow rate of the flushing gas, were identical with those of the empty cuvette system. Collection of samples started after an equilibration time of one hour. Fluxes of sulfur compounds were calculated by subtracting the average blank concentration from the corresponding average concentration found with a leaf enclosed in the cuvette. These differences were checked by statistical analysis (t-test). All data used were at least within the 95% confidence level. Leaf area (one-sided basis) was measured by projecting the leaf area on millimeter paper, then cutting and weighing the corresponding paper area.

Results and discussion

COS exchange in relation to the ambient COS concentration

The results of fumigation experiments with varying COS concentrations suggest that COS exchange depends highly on the ambient COS mixing ratios. Ambient COS mixing ratios larger than 150 pptv resulted in a deposition of COS to all plant species studied as indicated by a decrease of the COS concentrations. A significant (confidence level 95%) COS emission was only detected from rapeseed leaves at COS mixing ratios lower than 90 pptv (Fig. 1). Deposition of COS to the plant species on a leaf area basis in the light (100—1200 μmol photons m^{-2} s^{-1}) varies from 6.3 to 94 [nmol S/m^2*h), 9.4 to 94 [nmol S/m^2*h], and 47 to 75 [nmol S/m^2*h] for pea, corn, and rapeseed leaves respectively (Table 1).

The uptake rates of COS by rapeseed and corn varied with ambient concentrations in agreement with studies of Goldan et al. (1988) with

Table 1. Deposition ranges of carbonyl sulfide (COS) on a leaf area basis in the light (PAR*) during all experiments.

Plant species	COS [nmol S m^{-2}h^{-1}]	Light intensities (PAR*) [μmol m^{-2}s^{-1}]
Rapeseed	47 —75	600
Pea	6.3—94	100— 800
Corn	9.4—94	150—1200

* Photosynthetic active radiation in μmol photons m^{-2}s^{-1}

Glycine max at COS mixing ratios ranging between 100 pptv and 1 ppbv and of Kluczewski et al. (1985) and Brown et al. (1986), who investigated the COS uptake of *Lolium perenne* and *Raphanus sativus* with mixing ratios of 4 ppbv. An increase in COS mixing ratios caused an increase in the COS uptake by corn and rapeseed (Fig. 1). Using linear regression, we computed compensation points around 90 (57—135) pptv and 144 (0—328) pptv COS for rapeseed and corn, respectively (confidence level 95%). These COS compensation points are consistent with the findings of Goldan et al. (1988) who found that the uptake resistance of soybean increased if ambient COS concentrations are below 200 ppt, suggesting that COS uptake approaches zero at non-zero COS concentrations. Our data for rapeseed and corn further show a more or less constant increase in deposition correlating with the COS mixing ratios up to the 800 pptv tested. We assume that this increase in relation to the ambient concentration is sustained even up to high COS mixing ratios. This assumption is in accordance with studies by Taylor et al. (1983) of plant species like *Glycine max*, *Lolium esculentum* and *Phaseolus vulgaris*, which, in the presence of 125 ppb COS, had very high COS deposition rates, roughly three orders of magnitude higher than those we measured.

In contrast to the gas exchange studies with corn and rapeseed, experiments with pea plants revealed no change in response to increased COS
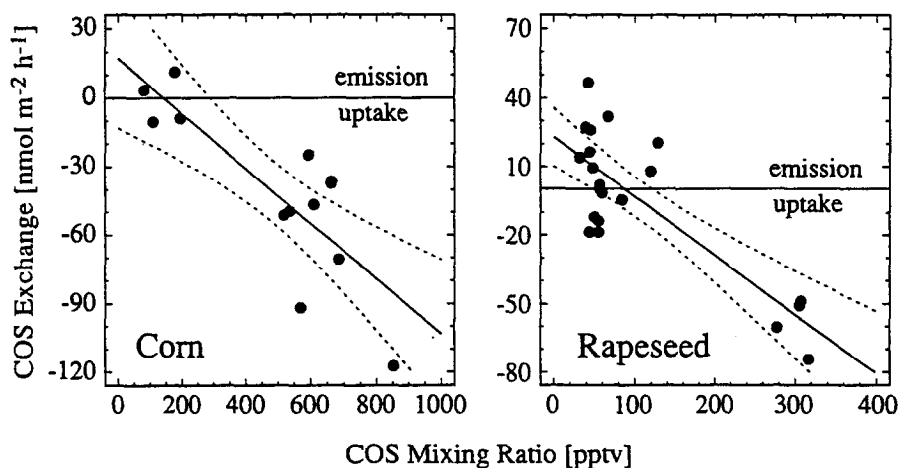

Fig. 1. Exchange of carbonyl sulfide (COS) between corn or rapeseed leaves when exposed to different COS mixing ratios in flushed ambient air. Both plant species were fertilized with Hoagland solution. Solid lines show linear regression ($r^2 = 0.67$ for corn; $r^2 = 0.66$ for rapeseed); dotted lines express 95% confidence level. Compensation points calculated were 89 (57—135) pptv and 144 (0—328) pptv for rapeseed and corn, respectively.

concentrations between 350 and 900 pptv COS (Fig. 2). Nutritional effects responsible for this behaviour can be excluded, as fertilized and non-fertilized plants did not show a correlation between ambient COS mixing ratios and exchange behaviour (Fig. 2). Fertilized plants, however, with likely an enhanced protein synthesis, exhibited a higher deposition (Fig. 2) which we interpret as a demand for sulfur due to an optimized nitrogen supply. An explanation for the difference between the behaviour of pea plants and corn or rapeseed plants remains to be identified.
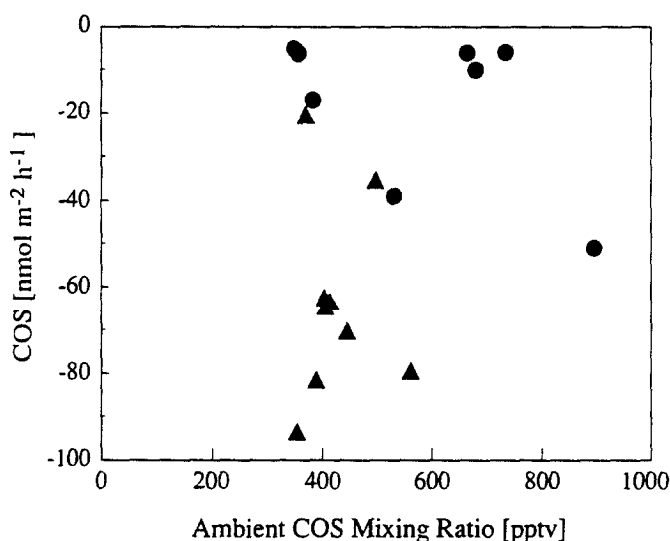

Fig. 2. Exchange of carbonyl sulfide (COS) between pea leaves when exposed to different COS mixing ratios in flushed ambient air. Closed circles, non fertilized plants (watered with tap water); closed triangles, fertilized plants (watered with Hoagland solution).

The COS sulfur absorbed by plants is partly incorporated into organic compounds (Brown et al. 1986). Some of the sulfur is assumed to be reemitted in the form of H_2S, as is observed with cyanobacteria (Miller et al. 1989). This would agree with recent findings that carbonic anhydrase isolated from pea plants catalyzes the reaction of COS with H_2S and splits COS to H_2S and CO_2 (Protoschill-Krebs 1991; Protoschill-Krebs & Kesselmeier 1992). In the present study we found no significant H_2S emissions even at high COS uptake rates. Thus, we cannot validate that COS uptake directly initiates an emission of H_2S by higher plants. However, a cleavage of COS with a subsequent production of H_2S need not be excluded. Carbonic anhydrase is located in the chloroplast stroma of C3-plants and/or in the cytoplasm of C4-plants. Therefore, in plants

exposed to light the H_2S arising from COS hydrolysis is likely to be trapped in the alkaline chloroplastic stroma, which can exhibit pH values above 8.0. This explanation is supported by the work of Spedding et al. (1980a, b) who found that S^{-2} is taken up rapidly and irreversibly by isolated illuminated spinach chloroplasts.

COS exchange in relation to photosynthetic CO_2 assimilation

Based on enzymological studies (Protoschill-Krebs & Kesselmeier 1992; Kesselmeier 1992) metabolic pathways for the consumption of COS by plants are known to be principally the same as those for the assimilation of CO_2. Therefore a clear correlation between the uptake of COS and CO_2 assimilation in cuvette studies is anticipated. As shown in Fig. 3, COS uptake rates by rapeseed and corn leaves increased approximately linearly with increasing net CO_2 assimilation rates. The correlation is significant at the 95% confidence level for both species. COS exchange by pea leaves did not correlate with the net CO_2 assimilation rate, but showed almost constant COS uptake rates over a wide range of photosynthetic activity ($1.4-15.2$ μmol CO_2 m^{-2} s^{-1}; data not shown).
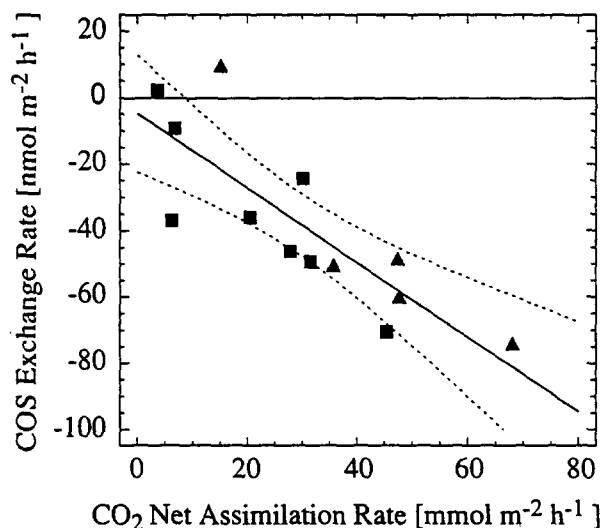

Fig. 3. Exchange of carbonyl sulfide (COS) in correlation with the CO_2 net assimilation for fertilized (watered with Hoagland solution) corn (squares) and rapeseed (triangles). Solid line represent linear regression ($r^2 = 0.69$); dotted lines express 95% confidence level. COS concentrations during this experiment were 625 pptv ($\pm$ 51, $n = 8$) for corn and 302 ($\pm$ 15, $n = 5$) for rapeseed.

The observed increase in COS deposition with increasing CO_2 net assimilation rates agrees with recently published investigations on the metabolic background for the uptake of COS by higher plants (Protoschill-Krebs & Kesselmeier 1992) which shows that carbonic anhydrase catalyzes the hydrolysis of COS to H_2S and CO_2. Interestingly, further experiments (Protoschill-Krebs 1991; Kesselmeier 1992) showed that carbonic anhydrase (CA) isolated from pea plants had a significantly higher affinity to COS than to CO_2:CA prefers COS to CO_2 by three orders of magnitude, indicating that plants may prefer COS to CO_2. Since this is of considerable consequence to our understanding of COS uptake under atmospheric conditions, we correlate the uptake of COS with the uptake of CO_2 by intact leaves to compare enzymological studies with our investigation of intact leaves. We calculate the ratio of CO_2 net assimilation to COS uptake ($[CO_2]_{ass}/[COS]_{upt}$; or, R_{ass}) and compare this ratio to the ratio of atmospheric concentrations ($[CO_2]_{ambient}/[COS]_{ambient}$; or, R_{amb}). R_{ass}/R_{amb} provides an insight into the behaviour of different plants in consuming COS in the presence of CO_2. If COS and CO_2 uptake by leaves is close to the ambient mixing ratios, then R_{ass}/R_{amb} will have a value near 1 ($R_{ass} = R_{amb}$). Where $R_{ass}/R_{amb} > 1$, we conclude that CO_2 assimilation is favoured over COS uptake, whereas $R_{ass}/R_{amb} < 1$ indicates that COS uptake is favoured over CO_2 assimilation. The results of such a comparison are shown in Table 2. For rapeseed leaves, R_{ass} approximated R_{amb}. For pea and corn leaves from fertilized plants, COS uptake was clearly favoured over CO_2 uptake. Without fertilization pea leaves favoured CO_2 assimilation over COS uptake, demonstrated by values for R_{ass}/R_{amb} greater than one. However, the preference for COS may vary with varying CO_2 assimilation rates (Fig. 4). Clearly, R_{ass}/R_{amb} increases with the CO_2 assimilation, thus demonstrating that the COS

Table 2. Uptake of $COS(COS_{upt})$ from ambient air in relation to the photosynthetic CO_2 assimilation (CO_{2ass}).

	Ranges of CO_2/COS ratios [mmol/nmol]		R_{ass}/R_{amb}
	(R_{ass}) $[CO_{2ass}/COS_{upt}]$	(R_{amb}) $[CO_{2amb}/COS_{amb}]$	
Pea, nf	0.24—3.1	0.29—1.0	2.50 ± 1.7 (n = 10)
Pea, f	0.08—0.73	0.63—1.0	0.26 ± 0.2 (n = 9)
Rapeseed, f	0.71—1.13	1.05—1.26	0.80 ± 0.1 (n = 4)
Corn, f	0.06—0.53	0.57—0.79	0.35 ± 0.2 (n = 33)

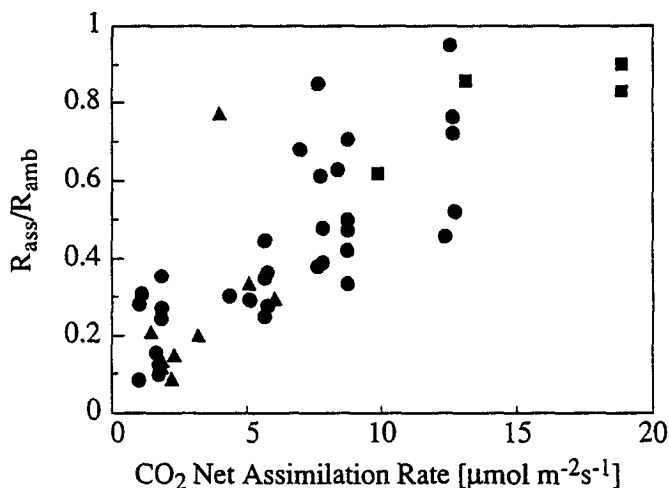nf: non-fertilized (tap water); f: fertilized (Hoagland solution).

Fig. 4. Assimilation ratios versus atmospheric ratios of CO_2 and COS in correlation with the CO_2 net assimilation rate leaves from fertilized plants (watered with Hoagland solution). Note that the quotient of assimilation ratios/ambient ratios is always less than one, indicating preference for COS. Circles, corn; squares, rapeseed; triangles, peas.

uptake by corn leaves is less favoured if photosynthetic activity increases, but never exceeds a value of 1. An increase in R_{ass}/R_{amb} with CO_2 assimilation was barely observable with non nutrient supported pea leaves (data not shown).

Conclusions

Though we used only young plants for the studies described in this paper, the work confirms results and interpretations obtained during field work (growing and mature plants) which showed that deposition of COS to plants and vegetated land correlated closely with CO_2 assimilation (Hofmann et al. 1992a). This close correlation to photosynthetic CO_2 assimilation and the observed compensation points around 150 pptv indicate that terrestrial plants might always consume COS especially when they are photosynthetically active. Furthermore, we know about the physiological background of the coupling of the assimilation of CO_2 and COS via carbonic anhydrase (see Protoschill-Krebs & Kesselmeier 1992). When CO_2/COS-uptake ratios are compared to atmospheric ratios, the plants investigated even demonstrate a preference for COS cover CO_2. The amount of CO_2 fixation and the COS/CO_2 ratio can be used to calculate global COS deposition to vegetation. Using a figure of $100-120 \times 10^{15}$ g

(C) as CO_2 fixed per year by terrestrial vegetation on a global scale (see Solomon et al. 1985; Bolin 1983; Warneck 1988; Degens 1989) and assuming that the uptake ratio COS/CO_2 is just similar to that in the atmosphere, we calculate 0.86—1.0 Tg (COS) consumed globally by terrestrial vegetation. This value is in the range of the sink strength of 0.16—0.91 Tg (COS) found by Chin & Davis (1993) calculated in a similar way. However, the sink might be larger if all plants really prefer COS over CO_2 and thus might balance the known sources. However, in contrast, COS emissions in ambient air, as sometimes observed (Kesselmeier et al. 1992; Berresheim & Vulcan 1992; c.f. Chin & Davis 1993), are not understood. Therefore, the biogenic production of COS by plants should be intensively investigated to further understanding of the exchange behaviour of this important trace gas. Until deposition and emission of COS are both understood, we will have severe problems in determining on which basis to calculate global fluxes.

Acknowledgements

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