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Global uptake of carbonyl sulfide (COS) by terrestrial vegetation: Estimates corrected by deposition velocities normalized to the uptake of carbon dioxide (CO_2)

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Abstract. COS uptake by trees, as observed under dark/light changes and under application of the plant hormone abscisic acid, exhibited a strong correlation with the CO_2 assimilation rate and the stomatal conductance. As the uptake of COS occurred exclusively through the stomata we compared experimentally derived and re-evaluated deposition velocities (V_d; related to stomatal conductance) for COS and CO_2. We show that V_d of COS is generally significantly larger than that of CO_2. We therefore introduced this attribute into a new global estimate of COS fluxes into vegetation. The new global estimate of the COS uptake based on available net primary productivity data (NPP) ranges between 0.69–1.40 $\mathrm{Tg\,a^{-1}}$. However, as a COS molecule is irreversibly split in contrast to CO_2 which is released again by respiration processes, we took into account the Gross Primary Productivity (GPP) representing the true CO_2 leaf flux the COS uptake has to be related to. Such a GPP based deposition estimate ranged between 1.4-2.8 $\mathrm{Tg\,a^{-1}}$ (0.73–1.50 $\mathrm{Tg\,S\,a^{-1}}$). We believe that in order to obtain accurate global COS sink estimates such a GPP-based estimate corrected by the different deposition velocities of COS and CO_2 must be taken into account.

1 Introduction

Carbonyl sulfide (COS) is a substantial source for stratospheric sulfate aerosol and plays an important role in stratospheric ozone chemistry (Crutzen, 1976; Andreae and Crutzen, 1997). According to Watts (2000) and Kettle et al. (2002) total global sources and sinks are balanced within the uncertainties of the estimates. Deposition to vegetation and soils represents the main sink for this trace gas (Logan et al., 1979; Brown and Bell, 1986; Chin and Davis, 1993, 1995; Geng and Mu, 2004). Soils have been recognized as a global sink for COS only recently and the uncertainty is rather large as parameterization of the uptake has been performed with only one soil type to date (Kesselmeier et al., 1999), which clearly warrants further studies. The role of vegetation as a major global tropospheric sink for COS has been studied for 20 years and is undisputed, but the uncertainty in the quantitative estimates of this sink is still large. Two common methods for the estimate of the global COS sink strength were reported. The estimate by Brown and Bell (1986) is based on the deposition velocity of COS and its atmospheric concentration. Another approach is described by Chin and Davis (1993) who used the correlation between the COS deposition and the CO_2 assimilation, assuming the same deposition velocities for CO_2 and COS. Recent estimates refer to this method (Kesselmeier and Merk, 1993; Andreae and Crutzen, 1997; Watts, 2000; Kettle et al., 2002). However, a simple 1:1 relation for the uptake ratio of COS/CO_2 appears insufficient as a preferential uptake of COS on a leaf as well enzymatic basis has been reported (Kesselmeier and Merk, 1993; Protoschill-Krebs et al., 1996). Therefore, we studied the stomatal uptake of COS separately. Moreover we investigated the close correlation between the rate of photosynthesis and the COS uptake for several European tree species and considered the differences in deposition velocities for CO_2 and COS. The observed ratios of the deposition velocities were used to improve global estimates of the COS vegetation sink based on Net Primary Production.

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2 Materials and methods

2.1 Plant material and growth

For all experiments young trees (3–4 years old) from German and English tree nurseries were used. Tree species investigated were Holm oak (*Quercus ilex* L.), European beech (*Fagus sylvatica* L.), Norwegian spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). The trees were kept in 20 l pots with gardener's compost for the years 1997–2000 and fertilized with commercially available fertilizer (Baumfit, Spiess-Urania, Germany). For the Mediterranean tree species *Quercus ilex* sand was mixed with the soil in a 1 to 2 ratio. The trees were grown in a greenhouse at 25°C under a 12/12 h light-dark regime with a light intensity of 600 μmol m^{-2} s^{-1} of photons (PAR) and a relative humidity of 70% under 350 ppm CO_2.

2.2 Purification of ambient air

Compressed air was purified by passing it (6 l min^{-1}) through a multistage gas purification system consisting of (1) silica gel (Merck, Germany), (2) molecular sieve (0.5 nm, Merck, Darmstadt), (3) charcoal (Merck,Germany), and soda lime (Merck, Germany), 3 l each. COS and CO_2 mixing ratios were adjusted to desired values by mixing the purified compressed air with known gas mixtures produced from a permeation device (Haunold, Germany) with COS permeation tubes (VICI Metronics, Santa Clara, California) and CO_2 from a pressurized bottle (Messer-Griesheim, Germany). All flows were regulated by mass flow controllers (MKS, Massachusetts, USA).

2.3 Enclosure system (cuvettes) and exchange measurements

Gas exchange of enclosed tree branches was investigated using a dynamic (flow-through) Teflon-film-cuvette system consisting of a plant measuring and an empty reference cuvette with all inner surfaces made of Teflon to avoid interference with the investigated trace gases. All experiments were performed in a climate chamber with identical conditions as compared to the growth chamber. Trace gas sampling was accompanied by measurements of ambient CO_2, CO_2 exchange and transpiration by an infra-red gas analyzer. For details see Kuhn et al. (1999, 2000) and Kuhn and Kesselmeier (2000). Leaf area was determined by copying leaf contours onto paper in order not to destroy the leaves. The area was measured by a calibrated scanner system (ScanJET IICX with DeskSCAN II; both Hewlett-Packard, USA), and SIZE 1.10 (Müller, Germany). The enclosures were constantly flushed with 1 l min^{-1} of purified and conditioned ambient air (see above) which was artificially moistened (r.H. >70%) before entering the cuvettes. COS was quantified in the ppt range by an automated analytical system according to Von Hobe et al. (2000) by consecutive sampling at both cuvettes. The gas exchange rates (F) were calculated from the measured concentration difference (δ_c=c_{sample}-c_{ref}), the chamber flush rate (Q) and the enclosed leaf area (A).

$$F = \delta c * (Q/A) .$$

Deposition velocities (V_d) related to stomatal conductance were calculated in relation to the ambient air concentration of the reference cuvette (c_{ref}).

$$V_d = F/c_{ref} .$$

Accuracy and precision of the analytical system were better than 2% plus any uncertainties introduced by the cuvette sampling, mainly by the accuracy of mass flow controllers. The stomatal conductance for water vapor was determined according to Pearcy et al. (1989).

2.4 Induction of stomatal closure

Stomatal closure was induced by infiltration of abscisic acid (ABA) to an oak branch cut from the tree two days before this application. The ABA treatment was performed by cutting a small branch of *Quercus ilex* under water (to prevent air from penetrating into the water-conducting elements) and dipping it into a nutrient solution of 1.0 mM KCl, 0.1 mM NaCl , 0.1 mM $CaCl_2$. Measurements of CO_2 exchange and water vapor transpiration proved the unrestricted viability of this sample branch. ABA was applied by exchanging the nutrient solution against a fresh one containing additional 0.1 mM ABA, which was transported into the leaves by the transpiration stream. For details see Gabriel et al. (1999).

3 Results

3.1 Stomatal uptake

The automated analytical COS analyzer allowed a dense protocol to follow the exchange behavior with high time resolution. Figure 1 shows the COS uptake by an enclosed branch of *Fagus sylvatica* (European beech) in relation to assimilation and stomatal conductance over nearly three days of measurements. The COS-uptake closely followed the light/dark cycle. This behavior can be related to the calculated stomatal aperture and consequently directly compared to the exchange of CO_2, i.e. net photosynthetic assimilation rate. Low uptake rates were found under dark conditions. As the stomata did not completely close in the dark and a respiration activity was detectable, the low COS exchange may be understood as a physiological consumption at a lower rate. On the other hand we do not exclude fluctuations and scatter caused by the non-simultaneous COS sampling at the sample and reference cuvette due to switching of the automated system from one cuvette to the other. Nevertheless, a clear relation to light and stomatal aperture is obvious, though the enzymatic pathway of COS consumption by carbonic anhydrase itself is generally light independent (Protoschill-Krebs et al., 1996).

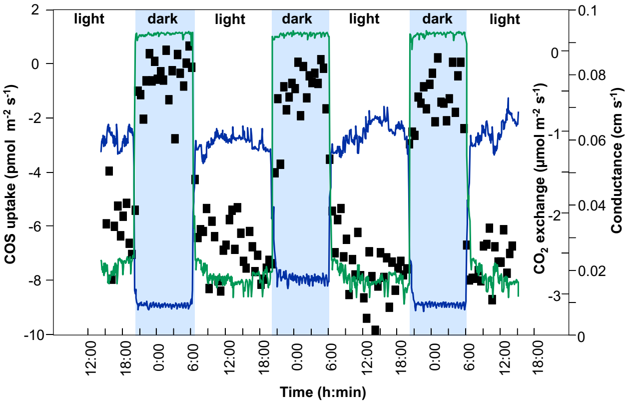

Fig. 1. Exchange (negative=uptake) of carbonyl sulfide (COS, filled squares) in relation to branch (leaf) conductance (blue line) as a measure of stomatal pore width and CO_2 exchange (green line) with negative values for uptake (assimilation) and positive values for emission (respiration) for European beech (*Fagus sylvatica* L.).

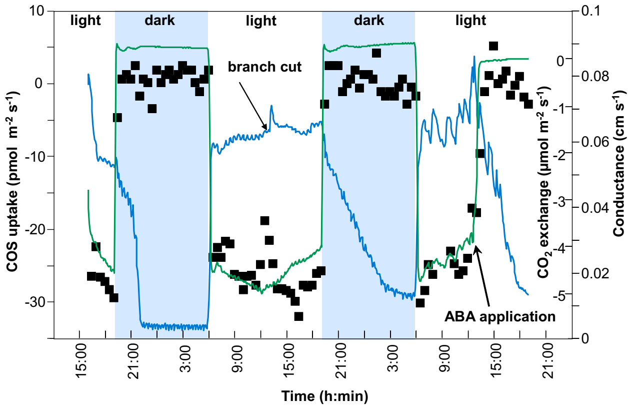

Fig. 2. Exchange (negative=uptake) of carbonyl sulfide (COS, filled squares) in relation to branch conductance (blue line) as a measure of stomatal pore width and CO_2 exchange (green line) for Holm oak (*Quercus ilex* L.) with negative values for uptake (assimilation) and positive values for emission (respiration). Note: Conductance calculated from climate chamber conditions (25°C; 70 % r.H.).

The close relation between light and COS uptake in contrast to the light independent consumption by the enzyme carbonic anhydrase supports the assumption of an exclusively stomatal uptake pathway, as light represents a considerable trigger of stomatal movement. The final proof for a stomatal related exchange was demonstrated by the application of abscisic acid (ABA), a plant hormone which causes stomatal closure. Treatment with ABA was performed by cutting a small branch of *Quercus ilex* and incubating the stem into a vial filled with a buffer solution. Under these conditions, the branch was performing a normal behavior of gas exchange and COS uptake (Fig. 2) as followed for two light/dark episodes. In the course of the third light phase we infiltrated ABA and observed a fast decline of CO_2 exchange down to zero (no respiration measurable) closely accompanied by the decrease of COS uptake (Fig. 2). Stomatal conductance also showed a decrease to night values under the influence of ABA under light conditions, though with some delay which may be understood as inhomogeneous stomatal apertures or slight water condensation on the cuvette walls interfering with the water vapor measurements. However, the prompt decline of assimilation to a zero-exchange of CO_2 under light is a most convincing argument for the strict regulation of this trace gas exchange by stomatal aperture.

3.2 Deposition velocities of COS and CO_2

As described above, an exclusive uptake of COS via the stomatal pathway in close relation to the CO_2 exchange could be demonstrated. The simultaneous measurements of the CO_2-exchange during all enclosure studies has the potential for a better quantification of the COS uptake. We could directly link the uptake rates of COS and CO_2 by comparing the deposition to the leaves after normalization by the ambient atmospheric concentration of each trace gas, i.e. by comparing deposition velocities (V_d). The obtained COS and CO_2 deposition velocities for *F. sylvatica*, *Q. ilex*, *P. sylvestris* and *P. abies* are summarized in Table 1. A clear preference for COS deposition is indicated by the uptake ratios of V_d COS versus V_d CO_2 and was found for all tree species investigated. The results reflect a significantly pronounced uptake of COS over CO_2 by a factor between 1.4 and 3.4.

In order to widen our basis for further calculations, deposition velocities as reported in or calculated from published data sets were additionally taken into account. In some cases we were able to re-estimate data on the basis of the published figures and tables. For our own data sets published recently, we calculated on the basis of the original data. The results are shown in Table 2. The V_d-ratios are sensitive to the rate of CO_2 uptake taken into account. In case of enclosure measurements we used the net exchange as measured with the enclosed branch or leaf (Net Primary Productivity; $\mathrm{NPP_{cuvette}}$) in order to compare with other published data. However, in case of one data set (spruce forest, Xu et al. 2002) from flux studies above the forest, a correction might be necessary, as this flux value is representing the net exchange as a result of gross photosynthesis minus autotrophic (=NPP) and heterotrophic (soils) respiration. For the enclosure related data we found a range of $V_{d_{\mathrm{COS}}}/V_{d_{\mathrm{CO_2}}}$ between 1.3 and 5.5 with the exception of 0.4 for non fertilized pea plants (Kesselmeier and Merk, 1993), 7.0 for young corn plants (Hoffmann, 1993) and 8.7–10.3 for a spruce enclosure study (Huber, 1994). These extraordinary numbers may be subject of further speculation. Within this context, C_4 plants need some special discussion. As shown in table 2, *Zea mays* seems to fit quite well into the

Table 1. Leaf area based exchange and deposition velocities (V_d) of COS and CO_2 for *Fagus sylvatica* and *Quercus ilex*, growing under 350 ppm CO_2 over 2–3 years. Three tree individuals (T_1–T_3) were grown and investigated. COS-exchange data were obtained under an atmospheric COS mixing ratio of 600 ppt. *Pinus sylvestris* and *Picea abies* were only measured in one year.

Plant Species		COS Uptake (pmol m^{-2} s^{-1})	± SD	V_d COS (mm s^{-1})	± SD	(n)	CO_2 Uptake (μmol m^{-2} min^{-1})	± SD	V_d CO_2 (mm s^{-1})	± SD	(n)	V_d COS / V_d CO_2
F. sylvatica	T_1	13.8	4.8	0.551	0.211	19	171	12	0.199	0.022	> 57	2.77 (1.54–4.31)
Summer 1998	T_2	12.5	3.0	0.441	0.168	21	193	8	0.225	0.021	> 51	1.96 (1.11 – 2.99)
	T_3	12.3	4.7	0.429	0.226	36	238	7	0.277	0.025	> 69	1.55 (0.67–2.60)
F. sylvatica	T_1	21.7	4.8	0.873	0.217	28	317	29	0.370	0.046	> 84	2.36 (1.58–3.36)
Summer 1999	T_2	26.1	13.7	1.105	0.486	33	332	27	0.387	0.046	> 99	2.86 (1.43–4.67)
	T_3	19.1	8.5	0.994	0.268	43	354	25	0.290	0.078	> 129	3.43 (1.97–5.95)
F. sylvatica	T_1	11.3	5.1	0.460	0.221	54	204	6	0.238	0.022	> 162	1.93 (0.92–3.15)
Fall 1999	T_2	11.5	6.4	0.470	0.271	71	241	17	0.281	0.031	> 213	1.67 (0.64–2.96)
	T_3	14.1	0.5	0.575	0.094	99	201	5	0.234	0.021	> 297	2.46 (1.89–3.14)
Q. ilex	T_1	15.1	6.9	0.612	0.279	27	283	44	0.330	0.059	> 81	1.86 (0.86–3.29)
Summer 1998	T_2	12.9	4.9	0.542	0.210	50	197	14	0.229	0.026	> 150	2.37 (1.30–3.70)
	T_3	14.8	6.4	0.679	0.189	19	180	9	0.210	0.021	> 57	3.23 (2.12–4.59)
Q. ilex	T_1	16.4	4.6	0.751	0.166	33	347	25	0.404	0.045	> 99	1.86 (1.30–2.55)
Summer 1999	T_2	14.4	2.7	0.514	0.164	44	308	22	0.359	0.040	> 152	1.43 (0.88–2.13)
	T_3	15.4	3.4	0.700	0.113	29	318	17	0.371	0.037	> 87	1.89 (1.44–2.43)
Q. ilex	T_1	25.8	2.1	0.673	0.372	120	179	16	0.208	0.026	> 360	3.24 (1.29–5.74)
Winter 1999/2000	T_2	25.1	1.5	0.575	0.263	81	318	17	0.371	0.037	> 243	1.55 (0.76–2.51)
	T_3	23.1	2.5	0.733	0.219	94	289	23	0.336	0.039	> 282	2.18 (1.37–3.21)
P. sylvestris Fall 2002	T_1	21.1	1.7	0.743	0.035	23	298	22	0.427	0.021	> 69	1.74 (1.58–1.92)
P. abies Fall 2002	T_1	12.6	1.7	0.435	0.060	43	275	20	0.459	0.023	> 129	0.95 (0.78–1.14)

scheme as obtained for the majority of C_3 plants. The V_d-ratios ranged near to 3, indicating a similar preference for COS. Very young plants even showed much higher ratios. In contrast, a recent study (Yonemura et al., 2005) reported a V_d-ratio for *Sorghum*, another C_4 grass, ranging around one, thus exhibiting no preferred uptake of COS. The authors related this behaviour to be caused by low carbonic anhydrase content which could not be balanced by the activity of the enzymes Phosphoenolpyruvate-Carboxylase (PEP-Co) and Ribulose-1,5-Bisphosphate-Carboxylase (Rubisco), both also principally capable to consume COS (Protoschill-Krebs and Kesselmeier 1992). Further studies on the enzymatic regulation of COS-uptake are crucially needed, especially for C_4 plants.

3.3 Corrected estimate of a global sink strength for COS

The data presented above on the uptake of COS normalized to the net assimilation or gross assimilation, respectively, allows a new global sink strength to be estimated for the vegetation (Table 3). Our calculations were based on deposition velocity (V_d) ratios of COS versus CO_2 fluxes according to Eq. (1).

$$J_{COS} = J_{CO_2} \times [COS]/[CO_2] \times V_{d_{COS}} / V_{d_{CO_2}} \qquad (1)$$

with

J_{COS}	global COS uptake (mol m^{-2} s^{-1})
J_{CO_2}	global CO_2 uptake (mol m^{-2} s^{-1})
[COS]	atmospheric COS mixing ratio (mol m^{-3})
[CO_2]	atmospheric CO_2 mixing ratio (mol m^{-3})
$V_{d_{COS}}$	COS deposition velocity (m s^{-1})
$V_{d_{CO_2}}$	CO_2 deposition velocity (m s^{-1}).

For global CO_2 fluxes we considered net primary productivity (NPP). NPP dry matter data according to Whittaker and Likens (1975) and Lieth (1975) were recalculated to NPP carbon according to Larcher (1994). Based on our observations of different deposition velocities we assigned ecotype related V_d-ratios and recalculated the COS sinks accordingly. For each ecotype we tried to take into account the exchange behavior of typical plant species. Based on our compilation in Table 2 we were able to assign a V_d-ratio for each ecotype except for "Extreme desert" and "Swamp and marsh". Instead a best guess was used. The results show that tropical and boreal forests, as well as savannas, are of highest significance for a global estimate of the vegetation sink strength. A ranking of ecotype-significance for the global budget shows that tropical rainforest contributes most, followed by tropical seasonal forest, savannah, boreal forest, cultivated land, temperate deciduous and evergreen forest, to an overall NPP based total COS sink strength of 0.69–1.4 Tg a^{-1}.

4 Discussion

The exchange of COS between the atmosphere and higher plants, algae, lichens, as well as soil has been reported to

Table 2. Carbonyl sulfide (COS) deposition velocities (V_d) and normalized net uptake as expressed in the V_d – ratio of COS and CO_2. Data as obtained in the course of this study by measurements and recalculations from published data compared to available literature values of measurements in the field, and laboratory (lab.) mainly with enclosures (encl.) or by relaxed eddy accumulation (REA) measurements.

Plant species	COS deposition velocity	Normalized relation COS/CO_2 net uptake ($V_{d\mathrm{COS}}/V_{d\mathrm{CO_2}}$)	Atmospheric concentration	Remarks	Reference
	(mm s^{-1})		(ppt)		
CROPS					
Allium cepa	0.29–0.35		4000	Lab., light, encl.	1
Brassica campestris ssp.	0.47–0.56		4000	Lab., light, encl.	1
Brassica napus	1.24	1.25	50–300	Lab., light, encl.	7
Brassica oleracea ssp.	0.46–0.52		4000	Lab., light, encl.	1
Glycine max	3.1		2000	Lab., light, encl.	2
Glycine max	0.71		500	Lab., light, encl.	3
Lactuca sativa	0.25–0.35		4000	Lab., light, encl.	1
Lolium perenne	0.78		4000	Lab., light, encl.	1
Lycopersicon esculentum	0.4		2000	Lab., light, encl.	2
Medicago sativa	1.6		500	Lab., light, encl.	3
Phaseolus vulgaris	1.4		2000	Lab., light, encl.	2
Pisum sativum. non fert.	0.2	0.4	300–900	Lab., light, encl.	7
Pisum sativum. fert.	1.1	3.8	300–900	Lab., light, encl.	7
Pisum sativum. fert.	$1.03^{\&}$	$3.1^{\&}$	820	Lab., light, encl	8
Raphanus sativus	0.57		4000	Lab., light, encl.	1
Spinacia oleracea	0.4		4000	Lab., light, encl.	1
Triticum aestivum	1.54		500	Lab., light, encl.	3
Triticum aestivum (10 d)	$1.08^{\&}$	$3.2^{\&}$	360	Lab., light, encl	8
Zea mays	1.14		500	Lab., light, encl.	3
Zea mays	0.69	2.85	100–900	Lab., light, encl.	7
Zea mays (9–12 d)	$2.36^{\&}$	$7.0^{\&}$	740	Lab., light, encl.	8
Grass, not specified	0.11–2.02		400–1500	Field, light & dark, encl.	10
TREES					
Fagus sylvatica	0.66±0.26	2.33±0.62	600	Lab., light, encl.	This work
Picea abies	0.4–1.8	$< 7^{\S}$	atmospheric	Field, light, REA	4
Picea abies	0.26 (0.5 max)	$8.7–10.3^{\&}$	300–650	Field, light, encl.	6
Picea abies	0.46±0.023	0.95	700	Lab., light, encl.	This work
Pinus sylvestris	0.43±0.021	1.74	700	Lab., light, encl.	This work
Porterandia cladantha	0.23 (max)	$2.37^{\S\S}$	400–600	Field, light, encl.	9
Quercus agrifolia	$0.44^{\S}$	$1.8^{\S}$	300–500	Field, light, encl.	5
Quercus ilex	0.64±0.09	2.18±0.66	600	Lab., light, encl.	This work
Sacoglottis gabonensis	$0.04^{\S\S}$	$1.74^{\S\S}$	400–600	Field, light, encl.	9
Sacoglottis gabonensis	$0.09^{\S\S}$	$5.49^{\S\S}$	400–600	Field, light, encl.	9

Note: No correction was applied to take into account the decrease of the measured net CO_2 exchange by respiration (Net uptake). Hence, considering a gross photosynthetic uptake by increasing the CO_2 uptake can lead to significantly reduced values for the normalized COS/CO_2-uptake in case of data obtained by flux studies above the forest with the influence of stem and soil respiration.

§ recalculated based on published fluxes and atmospheric mixing ratios of 500 ppt for COS and 350 ppm for CO_2.

§§ recalculated considering maximal V_d- values only.

$^{\&}$ calculated on actual data as given in the paper.

Literature cited: [1] Kluczewski et al. (1985); [2] Taylor et al. (1983); [3] Goldan et al. (1988); [4] Xu et al. (2002); [5] Kuhn et al. (1999); [6] Huber (1994); [7] Kesselmeier and Merk (1993); [8] Hofmann (1993); [9] Kesselmeier et al. (1993); [10] Geng and Mu (2004).

be governed by the actual ambient concentrations and to exhibit a compensation point, i.e. describing the atmospheric concentration where uptake and emission are balanced and the net exchange is zero (Goldan et al., 1988; Kesselmeier and Merk, 1993; Conrad, 1994; Blezinger et al., 2000; Kesselmeier et al., 1999; Kuhn et al., 1999; Conrad and Meuser, 2000; Kuhn and Kesselmeier, 2000, Geng and Mu, 2004). However, in case of vegetation all reported com-

Table 3. Estimate of global sink strength for carbonyl sulfide (COS) based on deposition velocity (V_d) ratios of COS versus CO_2 of typical plant species and net primary productivity (NPP). NPP dry matter data according to Whittaker and Likens (1975) and Lieth (1975) recalculated to NPP carbon according to Larcher (1994).

Ecosystem type	Area (10^6 km^2)	NPP dry matter (g m^{-2} a^{-1})	NPP dry matter (10^9 t a^{-1})	NPP C (10^{15} g a^{-1})	NPP CO_2 (10^{15} g/a)	V_d ratios COS/CO_2 min–max	F_{COS} Tg /a min–max	Plant species related V_d assigned (see Table 2)
Tropical rain forest	17	2200	37.40	16.46	60.34	1.7–3.6	0.246–0.508	*S. gabonensis.* *P. cladantha*
Tropical seasonal forest	7.5	1600	12.00	5.28	19.36	1.7–3.6	0.079–0.163	*S. gabonensis.* *P. cladantha*
Temperate evergreen forest	5	1300	6.50	2.86	10.49	1.5–2.9	0.037–0.071	*Q. ilex, Q. agrifolia*
Temperate deciduous forest	7	1200	8.40	3.70	13.55	1.7–3.0	0.054–0.095	*F. sylvatica*
Boreal forest	12	800	9.60	4.22	15.49	1–1.7	0.036–0.063	*P. abies, P. sylvestris*
Woodland and scrubland	8.5	700	5.95	2.62	9.60	1.5–2.9	0.034–0.065	*Q. ilex, Q. agrifolia*
Savannah	15	900	13.50	5.94	21.78	1.5–2.9	0.076–0.148	*Q. ilex, Q. agrifolia*
Temperate grassland	9	600	5.40	2.38	8.71	2.0–3.0	0.041–0.061	*Z. mays, T. aestivum*
Tundra and alpine	8	140	1.12	0.49	1.81	2.0–3.0	0.008–0.013	*best guess*
Desert and semi desert scrub	18	90	1.62	0.71	2.61	1.5–2.9	0.009–0.018	*Q. ilex, Q. agrifolia*
Extreme desert. rock. sand. ice	24	3	0.07	0.03	0.12	1.0–3.0	0.000–0.001	best guess
Cultivated land	14	650	9.10	4.00	14.68	1.3–3.8	0.043–0.130	*Z. mays, T. aestivum,* *B. Napus, P. sativum*
Swamp and marsh	2	3000	6.00	2.64	9.68	1.0–3.0	0.023–0.068	best guess
						TOTAL	0.686–1.404	

Table 4. Estimates of the global COS sink strength for terrestrial vegetation.

Tg a^{-1}	Source	Parameters considered
2–5	Brown and Bell (1986)	V_d, LAI, Area, COS atmospheric conc.
5.6	Servant (1989)	V_d, LAI, Area, COS atmospheric conc.
0.2–0.6	Goldan et al. (1988)	$R_{COS}=R_{CO_2}$, atmospheric conc., CO_2 uptake
0.93± 0.07	Kesselmeier and Merk (1993)	V_d COS=V_d CO_2, atmospheric ratios, CO_2 uptake
0.16–0.91	Chin and Davis (1993)	V_d COS=V_d CO_2, atmospheric ratios, CO_2 uptake
0.32	Kjellstrøm (1998)	V_d COS=V_d CO_2, atmospheric ratios, CO_2 uptake
0.56±0.1	Watts (2000)	V_d COS=V_d CO_2, atmospheric ratios, CO_2 uptake
0.21–0.27	Kettle et al. (2002)	Surface flux model, V_d COS=V_d CO_2, atmospheric ratios, CO_2 uptake
2.3±0.5	Xu et al. (2002)	Uptake ratio COS/CO_2, CO_2 uptake
1.37–2.81	This work	V_d COS$>V_d$ CO_2, atmospheric ratios, CO_2 uptake

pensation points are much lower than the observed ambient concentration ranges. Furthermore, within our reported experiments we never observed any COS emission, even under COS-free air. Moreover, by incorporating the deposition velocities of COS and CO_2 instead of their uptake ratios we already considered the linear relationship between the exchange of a trace gas and its atmospheric concentration. Thus, we assume that neither a compensation point nor the relationship between uptake and atmospheric concentration will interfere with our interpretations and estimates.

The close relation of COS uptake to photosynthesis and the clear consumption pathway via stomatal uptake allowed a recalculation of the COS uptake by terrestrial vegetation. We regard this V_d-ratio-corrected estimate of the COS sink strength to be necessary when estimating a COS sink strength from NPP and regard earlier estimates not taking such a correction into account as to be too low. Furthermore, we have to consider that COS is taken up and consumed without being released by the vegetation. COS is irreversibly lost within the biochemical consumption. A production pathway is not known to our knowledge. In contrast, CO_2 is clearly produced by respiration processes and its release leads to a carbon loss. Hence, all data on net carbon uptake or net primary production do not consider the gross uptake rates of CO_2, which represent the real basis for the uptake relationship between COS and CO_2. As we used the net primary productivity (NPP) data from Whittaker and Likens (1975) for global ecotype depending estimations, the loss by heterotrophic respiration had to be taken into account in order to relate the uptake of COS to the real uptake of CO_2. This NPP value represents only around 50% of the total gross CO_2 uptake by vegetation. A 50% loss by autotrophic respiration, i.e. respiration by the photoautotrophic biological organism itself, has been subtracted from the Gross Primary Productivity (GPP). In contrast, the data resulting from the enclosure measurements represent a net exchange based on the gross uptake of CO_2 minus the respiration of the leaves and some branches only. We regarded the respiration in the light to be lower than the dark respiration as it may be inhibited in the light (see Shapiro et al., 2004 and literature cited therein). Therefore, we assumed the contribution of the branch respiration to the overall net exchange data to be small as compared to the overall respiration of a whole tree with stem and roots. Hence, in a first attempt we doubled the number for the COS sink in order to relate to the real gross CO_2 flux which was the basis for the NPP calculated by Whittaker and Likens (1975). This correction leads to an estimate of a COS sink strength between 1.4–2.8 $\mathrm{Tg\,a^{-1}}$, equivalent to 0.73–1.5 $\mathrm{Tg\,a^{-1}}$ on a sulfur basis.

Table 4 gives an overview, comparing the different estimates as reported within the last years. Different procedures have been used based on several parameters such as atmospheric COS concentration, deposition velocity, leaf and ground area as well as the relation of COS deposition to the uptake of CO_2. The highest estimates between 2 and 5.6 $\mathrm{Tg\,a^{-1}}$ were calculated not taking into account the close relation to CO_2 assimilation, thus excluding any diurnal and seasonal effect. Much lower values, between 0.2 and 1.0 $\mathrm{Tg\,a^{-1}}$, supported by a modeling study with similar low estimates (Kettle et al., 2002), were obtained by relating the deposition of COS to the CO_2 assimilation data bases. The latter group, however, did not take into account the preferred uptake and enzymatic consumption of COS as related to the CO_2 assimilation. In contrast, the results of Xu et al. (2002), based on flux measurements over a coniferous forest, fit well into such an estimation by taking into account a preferential uptake ratio of COS/CO_2. Including such a preference by correction with the deposition velocity ratios, the new data presented here show that this new procedure results in a significant increase of the COS sink strength calculation again, as productivity, seasonality as well as the preferred uptake is taken into account.

Nevertheless, uncertainties remain large and depend on a still limited data set. A systematic error may be caused by the calculation procedure of the deposition velocity. According to Winner and Greitner (1989), the actual relevant atmospheric conditions for the incubated samples are represented by the concentrations inside the branch cuvette. We agree with the aforementioned authors. However, plotting exchange data against the atmospheric concentrations inside the branch cuvette lead to an increased scatter of the linearization. Therefore, we decided to take the concentrations inside the reference cuvette into account. Hence, as the branch cuvette air exhibited 20–40% lower COS values due to the consumption by the leaves, our actual result may underestimate V_d for COS. Therefore, the final number of the global uptake might also be underestimated by roughly 20–40%. Influences of climatic factors are minimized as long as the available NPP data are accurate. Closely relating the COS consumption to the NPP means to transfer automatically all environmental parameters affecting CO_2 exchange to the COS uptake. Based on a set of enclosure studies we report the net uptake of CO_2 in relation to the net uptake of COS. However, in contrast to the net exchange of CO_2, which is based on assimilation and respiration, the COS uptake seems to be irreversible under normal atmospheric concentrations. Hence, in case of CO_2 we have to add estimates of night- and daytime respiration rates in order to obtain the real Gross Primary Productivity (GPP) which can be regarded as the best basis for any CO_2 related estimation of the COS sink strength, as it includes all environmental parameters best. To achieve this goal we need exchange studies covering longer episodes and day/night studies in order to estimate autotrophic respiration for enclosure studies and autotrophic plus heterotrophic respiration for flux studies. Furthermore, we need a better experimental data set especially for tropical and boreal forest trees, as both ecotypes may represent a dominant contribution to the global terrestrial sink strength for COS.

5 Conclusions

Taking into account the deposition velocities for the uptake of COS in relation to CO_2 leads to a significant increase of the COS sink strength estimate for terrestrial vegetation in the range of 1.4–2.8 $\mathrm{Tg\,a^{-1}}$. As the calculation depends on GPP estimates it includes all environmental and seasonal effects. Such an estimate suggests that the vegetation sink strength may have been underestimated in earlier COS budget calculations. This result questions the balance of known sinks and sources. We need to investigate again well known COS sources in order to check their validity. It is beyond our capabilities to state errors, but we seem to have substantial gaps in our knowledge of the COS production and consumption. Undescribed sources may be detected by careful measurements. Within this context the recent report by Mu et al. (2004) for example about abiotic COS production within rain water is of high interest.

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