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Uptake of Carbonyl Sulfide (COS) and Emission of Dimethyl Sulfide (DMS) by Plants

By

S. YONEMURA^{1,2)}, L. SANDOVAL-SOTO²⁾, J. KESSELMEIER²⁾, U. KUHN²⁾, M. VON HOBE^{2,3)}, D. YAKIR⁴⁾ & S. KAWASHIMA¹⁾

Key words: Carbonyl sulfide, dimethyl sulfide, leaf, carbonic anhydrase.

S u m m a r y

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Higher plants represent a significant sink for atmospheric carbonyl sulfide (COS) and a potential source of dimethyl sulfide (DMS). In the present work, COS uptake was investigated on various plant species (*Quercus robur*, *Juniperus excelsa*, *Hibiscus spec.*, *Sorghum bicolor*) differing in the activities of carbonic anhydrase (CA), the enzyme recognized responsible for COS consumption. COS uptake was observed for all plant species, and the range of COS consumption was 1.5-25 pmol m⁻² s⁻¹ (deposition velocity 1.2-10.6 mm s⁻¹). The COS uptake was found to be light-independent, but was strongly under stomatal control. For the C₃ plant species the uptake rates were well correlated with the inherent capacity of CA, a fact that may confer a comfortable tool to model COS uptake by plants, and ultimately may help to decrease the uncertainty in estimates of the global COS sink strength of vegetation. *S. bicolor*, owing a C₄ metabolism and respective low CA activity, exhibited a relatively high COS uptake rate as compared to the C₃ plants. Potential reasons for this deviation are discussed. Emission of DMS was species-specific and was only observed in case of *Hibiscus spec.* under light conditions.

¹⁾ Air Quality Conservation Unit, National Institute for Agro-Environmental Sciences, 3-1-3 Kannondai, Tsukuba, Ibaraki, .305-8604 Japan. Fax: +81-298-838-8199, e-mail: yone@affrc.go.jp

²⁾ Biogeochemistry Department, Max Planck Institute for Chemistry, Joh.-J.-Becher-Weg 27, 55128 Mainz, Germany

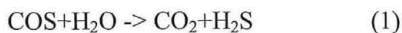
³⁾ now at ICG-I-Stratosphere, Forschungszentrum GmbH, D52425 Jülich, Germany.

⁴⁾ Environmental Sciences & Energy Research, Weizmann Institute of Science, Rehovot 76100, Israel.

Introduction

Reduced sulfur compounds in the atmosphere, among them carbonyl sulfide (COS) and dimethyl sulfide (DMS) play important roles in atmospheric chemistry and physics. COS, with 500 ppt the most abundant reduced sulfur compound in the atmosphere is quite stable under tropospheric conditions with a lifetime of several years. It can be transported into the stratosphere where it underlies photochemical decomposition, and is thus involved in stratospheric ozone destruction and contributes to stratospheric aerosols (CRUTZEN 1976). Within a recent paper KETTLE & al. 2002 concluded that COS sources and sinks are largely balanced. COS is considered to be predominantly released by oceans and by photochemical decomposition of atmospheric CS₂ and DMS. The most important sinks are represented by vegetation (PROTOSCHILL-KREBS & KESSELMEIER 1992, KESSELMEIER & MERK 1993, PROTOSCHILL-KREBS & al. 1996) as well as soil (LEHMANN & CONRAD 1996, KESSELMEIER & al. 1999, KUHN & al. 1999) and oxidation in the stratosphere.

The biological uptake of COS by algae, lichens, higher plants and soil is ultimately attributed to the enzymatic consumption by carbonic anhydrase (CA, EC 4.2.1.1) (e.g., PROTOSCHILL-KREBS & KESSELMEIER 1992, PROTOSCHILL-KREBS & al. 1995, 1996, KESSELMEIER & al. 1999, KUHN & KESSELMEIER 2000, BLEZINGER & al. 2000). The enzyme converts atmospheric CO₂ to bicarbonate and thus plays a crucial role in the CO₂ exchange and is found ubiquitously in all living organisms. In the presence of CA, COS is irreversibly decomposed:



The enzyme can take up COS much more efficient than CO₂ (PROTOSCHILL-KREBS & al. 1995, 1996, KESSELMEIER & MERK 1993) and metabolizes this compound at even low atmospheric concentrations (low enzymatic K_m value). Recently, GILLON & YAKIR 2001 investigated activities of CA over a wide variety of plant species in relation to isotope fractionation. They studied the influence of CA on the ¹⁸O discrimination during the assimilation of atmospheric CO₂ by terrestrial vegetation. The authors were able to rank a large number of plant species according to their CA activities and illustrated the global distribution of CA.

In contrast to COS, dimethyl sulfide (DMS) is photochemically destroyed in the troposphere, contributing to sulfate aerosol production which acts as cloud condensation nuclei (CCN) in the remote marine atmosphere, thus contributing to direct and indirect radiative forcing (ANDREAE & CRUTZEN 1997). The production of dimethylsulfoniopropionate (DMSP) by marine algae is considered to be the most predominant source of DMS (TROSSAT & al. 1998, STEFELS 2000). Only a limited number of papers about emission from higher plants have been published until now and its impact on global scale is not yet known (KANDA & TSURUTA 1995a,b, KANDA & al. 1995, WATTS 2000). In order to contribute to the understanding of the sulfur budget of higher plants, we examined different plant species

on (i) their COS uptake capacity and its dependence on the activity of CA and (ii) the ability of the plants to emit DMS.

Material and Methods

Trace gas exchange was investigated by use of a dynamic (flow-through) enclosure system, consisting of two Teflon-film cuvettes, one used as the measurement chamber enclosing leaves or a branch, and the other as an empty reference. The whole system was placed in a climatically controlled growth-chamber. All experiments included monitoring of the exchange of CO_2 and water vapor by an infrared gas analyzer. For details of the complete cuvette system see KUHN & KESSELMEIER 2000. Sulfur gas exchange was investigated using an automatically working sampling and analysis system according to Von HOBE & al. 2000. Precision and accuracy of the analytical system at typical concentration ranges of COS and DMS in this study were both better than 2%.

Plant species were selected according to their CA activity within leaves as given by GILLON & YAKIR 2001. The selected plant species were *Sorghum bicolor* (C_4 ; CA assay activity of $51.9 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$), *Juniperus excelsa* (C_3 ; CA assay activity of $163 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$), *Hibiscus spec.* (C_3 ; CA assay activity of $1183 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$), and *Quercus robur* (C_3 ; CA assay activity of $3516 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$). Whole individuals of young potted plants were placed into the climate chamber and one branch was enclosed by the cuvette system.

Results and Discussion

Diel courses of COS exchange were investigated under light and dark conditions in a controlled environment of a climatic chamber. Similar findings were observed for all plant species measured. The exchange of COS was found to be a function of ambient COS concentration, and observed COS uptake rates could be normalized to an atmospheric mixing ratio of 500 ppt (see KESSELMEIER & al. 1999, KUHN & KESSELMEIER 2000, SANDOVAL-SOTO & al. 2005). Furthermore the uptake of COS was found to be strictly under stomatal control, normally leading to decline of COS during nighttime. Interestingly, *Q. robur* was the only plant showing significant COS uptake in the dark. As this uptake by the oak tree under dark conditions was accompanied by a concurrent incomplete closure of stomata, the nighttime consumption of COS was indicative of the light-independent activity of CA. Light-independent COS uptake has also been reported for soil (KESSELMEIER & al. 1999) and for lichens, which exchange gases over their entire surface and hence lack stomatal control (KUHN & KESSELMEIER 2000). Lawn has also been shown to act as a significant sink for COS during nighttime (GENG & MU 2004), though it is difficult to extract the different contributions of soil and plant surface on the net COS uptake. All investigated plant species showed COS uptake during daytime conditions. A summary of the results is given in Table 1. The range of obtained COS uptake rates is in reasonable agreement with field results of previous studies on higher plants (KANDA & al. 1995, KUHN & al. 1999, GENG & MU 2004). Of special interest are the results comparing the deposition velocities of CO_2 and COS. The ratios of these parameters demonstrate the privileged uptake of COS over CO_2 (KESSELMEIER & MERK 1993, PROTOSCHILL-KREBS & al. 1996, SANDOVAL-SOTO & al. 2005).

Table 1. COS uptake and plant physiological activities of the measured plant species. Values are average values $\pm$ standard deviation, observed under light conditions. COS uptake is calculated per unit leaf area and normalized to an atmospheric concentration of 500 ppt (see text). V_d is the deposition velocity of plant leaves calculated on the basis of exchange rates and the relevant atmospheric COS concentration in the enclosure. CO_2 concentrations were 377 ± 20 ppm in all experiments. Air temperatures in the cuvette were $26.6\pm 0.5^\circ C$. PAR was $424\pm 10 \mu mol m^{-2} s^{-1}$. Number of samples for COS data > 5 (15 minutes time resolution), for assimilation and transpiration data > 15 (5 minutes time resolution).

Plant species	Leaf area cm ²	Dry weight g	COS in cuvette ppt	COS uptake pmol m ⁻² s ⁻¹	$V_{d\ COS}$ m s ⁻¹	Assimilation $\mu mol m^{-2} s^{-1}$	Transpiration mmol m ⁻² s ⁻¹	Stomatal cond. mol m ⁻² s ⁻¹	$V_{d\ COS} / V_{d\ CO_2}$
<i>Sorghum bicolor 1</i>	87	0.53	460 $\pm$ 10	8.9 $\pm$ 3.2	4.8 $\pm$ 1.9	7.1	0.56	0.053	1.34 $\pm$ 0.4
<i>Sorghum bicolor 2</i>	48	0.27	461 $\pm$ 8	6.1 $\pm$ 2.7	3.1 $\pm$ 1.4	7.8	0.75	0.065	0.77 $\pm$ 0.3
<i>Quercus robur</i>	87	0.74	530 $\pm$ 21	20.4 $\pm$ 3.2	10.6 $\pm$ 1.6	5.6	1.27	0.709	3.56 $\pm$ 0.6
<i>Juniperus excelsa</i>	310	4.04	422 $\pm$ 20	2.1 $\pm$ 0.6	1.2 $\pm$ 0.4	0.8	0.18	0.015	2.81 $\pm$ 0.9
<i>Hibiscus spec.</i>	111	2.22	427 $\pm$ 14	10.5 $\pm$ 3.4	6.6 $\pm$ 2.6	1.8	0.46	0.182	1.74 $\pm$ 0.4

As the uptake and consumption of COS has been demonstrated to be based on the enzyme carbonic anhydrase (PROTOSCHILL-KREBS & KESSELMEIER 1992, PROTOSCHILL-KREBS & al. 1995, 1996, KESSELMEIER & al. 1999, KUHN & KESSELMEIER 2000, BLEZINGER & al. 2000), we correlated the normalized COS uptake rates with data of plant species-specific CA activity as recently published by GILLON & YAKIR 2001. The COS uptake of all investigated C_3 plants showed a strong linear correlation (Fig. 1, solid symbols), indicating that the capacity for COS consumption is based on the inherent capacity of CA. By means of data on the global geographic distribution of CA (GILLON & YAKIR 2001), a strong dependence of COS uptake on the CA activity as found here may confer a comfortable tool to estimate the global sink strength for COS by vegetation. Although our dataset is very small and confirmation of our data by replication on these and other tree species is crucial, our findings may ultimately help to decrease the uncertainty in current estimates of the global COS budget.

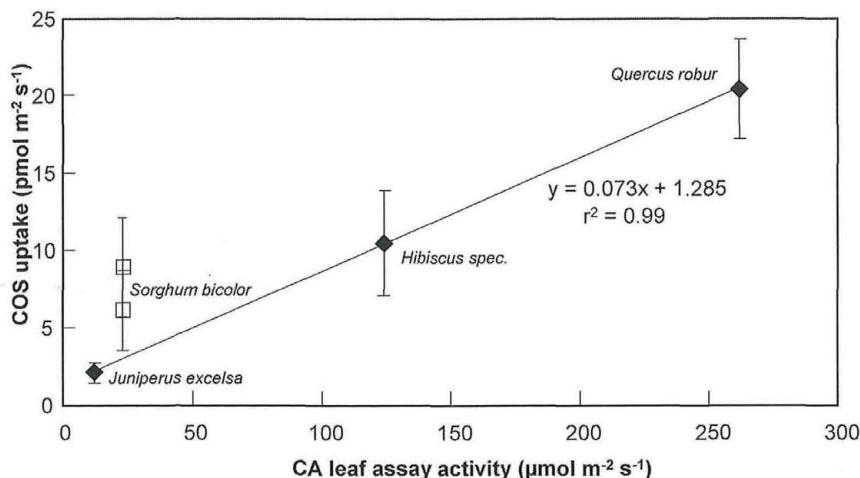


Fig. 1. Correlation between normalized COS uptake rates and CA activity for the investigated plant species. COS uptake rates were normalized to an atmospheric concentration of 500 ppt (see text). CA assay activity is given on leaf area basis in μM of CO_2 hydrated per m^2 and second, representing activity at 2°C and 17.5 mM CO_2 , as reported by GILLON & YAKIR 2001 (supplementary data). The latter authors corrected CA activity values for temperature and for CO_2 concentrations inside the leaf, which were estimated from gas exchange measurements, and assuming fixed K_m values of CO_2 conversion for the enzyme. Here we used CA activity values as measured directly in the assay, as we do not have information on internal COS concentrations. Furthermore, the location of the site of COS uptake, and differences in internal diffusion resistances, anatomy and physiology may impede direct comparison (see text). Hence, C_4 (*S. bicolor*; open symbols) were not incorporated into the linear correlation analysis of C_3 plants (solid symbols).

Interestingly, *Sorghum bicolor*, which belongs to the C_4 plants and contains low CA activity (GILLON & YAKIR 2001), revealed COS uptake rates higher than expected from the linear correlation of C_3 plants (Fig. 1, open symbols). This may be understood by the anatomical and physiological features of C_4 plants with their special adaptations to concentrate CO_2 within specialized cells grouped around the vascular bundle (bundle sheath cells). As summarized in recent reviews (VON CAEMMERER & FURBANK 2003, EDWARDS & al. 2004), anatomical and physiological (enzymatical) properties of C_4 plants lead to a concentration mechanism of CO_2 within the bundle sheath cells by way of the enzymes CA and phosphoenolpyruvate carboxylase (PEP-Co) located in the mesophyll cells. While in C_3 leaves, a chloroplast form of CA assists in the diffusion of CO_2 into the chloroplast stroma in all photosynthetic cells, in C_4 plants the CA is confined to the cytosol of the mesophyll cells, where PEP-Co is also located (BURNELL & HATCH 1988). Even though the total amount of CA in leaves of C_4 plants may be relatively small (GILLON & YAKIR 2001), the focused occurrence of CA in the cytosol of the mesophyll cells with large intercellular spaces may confer a reasonable explanation of a more efficient turnover of COS as compared to the C_3 plants, where COS must be

transported into the chloroplasts of photosynthetic cells to be processed. As shown in Table 1, also the assimilation rates of *S. bicolor* were very high as compared to the C_3 plants, indicative of the efficient turnover of CO_2 by CA. Thus, localization of CA in the leaves (i) in the cytosol of cells instead of the stroma of the chloroplast and (ii) in the well-ventilated mesophyll cells (low resistance for COS) may explain a more efficient COS uptake by this C_4 plant. On the other hand both RUBISCO and PEP-Co were shown to potentially contribute to the COS uptake of plants (PROTOSCHILL-KREBS & KESSELMEIER 1992). Hence PEP-Co, which is likewise located in the cytosol of the mesophyll cells in C_4 plants may additionally contribute to the over-proportional uptake rates observed for *S. bicolor*. RUBISCO, on the other hand, is not a likely candidate for COS consumption in C_4 plants, as it is confined to the bundle sheath cells in C_4 plants, owing high diffusion resistance for gases (WYRICH & al. 1998). Additional studies on the enzymatic regulation of COS uptake are crucially needed, especially for C_4 plants. It should be noted that in future studies, not only gas exchanges but also CA activities of the sample leaves should be measured to obtain precise relationship as in Fig. 1.

According to our results the ability of plants to emit DMS seems to be species-specific, and an emission of DMS was only found for *Hibiscus spec.* DMS emission from *H. spec.* with rates of $26 \pm 23 \text{ pmol m}^{-2} \text{ s}^{-1}$ was only observed under light condition and was negligible in the dark. The DMS emission under light condition is consistent with previous results of KANDA & TSURUTA 1995b, but contradicts small DMS emission in the dark reported by these authors. Flowers of *H. spec.* seemed not to be involved in the emission of DMS in our studies, as the DMS emission rates were not altered with or without a flower enclosed in the cuvette. Hence, our results do not support the role of flowers reported by JAMES & al. 1995. The pathways of primary enzymatic production of DMS in higher plants and its controlling functions are not yet known. In terms of the internal sulfur balance, the sulfur emission was much higher than the uptake by COS, pointing to additional sulfur sources within the plant. Accordingly, changing the COS mixing ratios from 0 to >1000 ppt did not show a significant effect on DMS emission. To fully understand mechanisms of DMS emission from higher plants, further systematic and comprehensive studies are necessary.

A c k n o w l e d g e m e n t s

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