

Controlling variables for the uptake of atmospheric carbonyl sulfide by soil

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Abstract. Soil samples from arable land were investigated for their exchange of carbonyl sulfide (COS) with the atmosphere under controlled conditions using dynamic cuvettes in a climate chamber. The investigated soil type acted as a significant sink for the trace gas COS. Atmospheric COS mixing ratios, temperature, and soil water content were found to be the physicochemical parameters controlling the uptake. Emission was never observed under conditions representative of a natural environment. The observed compensation point (i.e., an ambient concentration where the consumption and production balance each other and the net flux is zero) for the uptake was about 53 parts per trillion. Uptake rates ranged between 1.5 and 10.3 $\text{pmol m}^{-2} \text{s}^{-1}$. The consumption of COS by the soil sample depended on the physiological activity of the microorganisms in the soil, as indicated by a clear optimum temperature and by a drastic inhibition in the presence of the enzyme inhibitor 6-ethoxy-2-benzothiazole-2-sulfonamide (EZ), a specific inhibitor for carbonic anhydrase.

1. Introduction

Carbonyl sulfide (COS), the most abundant volatile reduced sulfur compound and nearly inert to photochemical decomposition in the troposphere, is an important precursor for the stratospheric sulfate aerosol layer [Crutzen, 1976; Hofmann, 1990; Engel and Schmidt, 1994] and thus has an impact on the Earth's radiation budget as well as on heterogeneous reaction chemistry leading to ozone destruction [Turco *et al.*, 1980; Roche *et al.*, 1994; Fahey *et al.*, 1993; Solomon *et al.*, 1993]. Our understanding of the sink and source relationships of this trace gas is still poor as reflected in imbalanced budget estimates [Chin and Davis, 1993; Johnson *et al.*, 1993], which were proposed to be corrected recently by exchanging the soil source strength into a soil sink strength [Andreae and Crutzen, 1997].

Vegetation with a sink strength of 0.16–0.91 Tg COS yr^{-1} is the major tropospheric sink of COS [Andreae and Jaeschke, 1992; Chin and Davis, 1993; Kesselmeier and Merk, 1993; Kesselmeier *et al.*, 1997]. Soils were previously considered to represent one of the dominant sources of COS [Khalil and Rasmussen, 1984; Andreae and Jaeschke, 1992; Chin and Davis, 1993; Johnson *et al.*, 1993], in addition to photochemical production in oceanic surface layers and CS_2 oxidation. However, recently published field studies present convincing evidence that soils act more as a sink than as a source for COS [Castro and Galloway, 1991; Fried *et al.*, 1993; DeMello and Hines, 1994; Kuhn *et al.*, 1999], which suggests that earlier data should be checked for artifacts due to the use of inappropriate air mixtures for flushing enclosures. As the ambient concentration of a given trace gas controls the direction as well as the magnitude of its flux between biosphere and atmosphere [Kesselmeier and Merk, 1993; Kesselmeier *et al.*, 1993; Conrad, 1994], earlier studies using COS-free air for purging the soil enclosures masked the uptake capability of soils, as clearly shown by Castro and Galloway [1991] under field conditions. With this

background, Andreae and Crutzen [1997] recently proposed to regard soils globally as a COS sink instead of as a source, which leads to an obviously more balanced global budget of sinks and sources. However, it should be kept in mind that the tropospheric oxidation of dimethyl sulfide (DMS) is regarded to act as an additional source for atmospheric COS within a range of 0.1–0.28 Tg COS yr^{-1} [Barnes *et al.*, 1994, 1996]. Furthermore, the anthropogenic input of reduced sulfur compounds, including COS, may be underestimated [Dippell and Jaeschke, 1996]. Both examples would introduce a new significant imbalance into the global budget estimates.

As outlined above, there is a clear need for a better understanding of the role of soils as an important sink for COS and the consequent impact on the global COS budget. Investigations of the uptake of COS by soils under controlled laboratory conditions are a useful approach to examining the uptake processes. Some earlier studies have already shown the general uptake capability of soils. However, within these studies [Bremner and Banwart, 1976; Kluczewski *et al.*, 1985; Lehmann and Conrad, 1996], very high concentrations of COS were used for flushing the enclosures, which also generated artificial COS concentration gradients and leads to similar problems in interpretation as in the cases of flushing with COS-free air. Within our studies we therefore investigated the exchange of COS between a soil and the atmosphere under more realistic conditions in the range of natural atmospheric COS mixing ratios. We studied the controlling variables such as atmospheric mixing ratios, temperature, and soil moisture content. Additionally, we included enzymatic investigations in order to verify the biological control of the uptake.

2. Material and Methods

2.1. Soil Samples

Soil samples, consisting of sandy clay with a low loess content, were obtained from an agricultural site near Mainz, Germany. Samples were taken from the top 5 cm after removing winter barley plants. The samples were sieved with a stainless

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Table 1. Data on Soil Characteristics Made Available by the Landesamt für Pflanzenschutz (District Office for Plant Protection), Mainz, Germany

	Value
pH	7.3
Calcium carbonate, wt %	8.8
Humus, wt %	2.22
C _{total} , wt %	1.94
C _{organic} , wt %	1.36
S _{total} , wt %	0.022
N _{total} , wt %	0.156
Field capacity, % H ₂ O g ⁻¹ DW	52

DW, dry weight.

steel sieve (mesh width 2 mm). Soil characteristics, based on soil analysis according to standard protocols, were determined by the University of Mainz and the Landesamt für Pflanzenschutz and are given in Table 1. Field capacity (potential water storing capacity given in % H₂O g⁻¹ dry weight (DW)), was determined according to conventional methods [Larcher, 1994; Kuntze *et al.*, 1994]. Samples were stored in polyethylene bottles at 3°C until the trace gas flux investigations. Soil water content was varied by air drying and by moistening with deionized water ($R > 18 \text{ M}\Omega \text{ cm}$).

2.2. Construction and Performance of Soil Enclosures

The measurements were performed with two enclosures (cuvettes): one enclosing the soil sample and the other serving as an empty reference. Both cuvettes were installed inside a climate chamber under controlled temperature and light conditions. Exchange data were calculated as the difference between the two cuvettes. The cuvettes were constructed of Teflon (FEP) film as principally described by Kesselmeier *et al.* [1996] and Kuhn and Kesselmeier [1997] and had the following dimensions: ID, 14.5 cm; length, 9 cm; volume, 1.5 L. Total airflow through each cuvette was 1 L min⁻¹. All gas lines downstream of the cuvettes were heated to 30°C to prevent water vapor condensation. Temperatures were measured with thermocouples (0.005", Chrom-Constantan, Omega, Manchester, England). Relative humidity and temperature at the cuvette inlet were determined with a Vaisala sensor (model 133Y, Vaisala, Malmö, Sweden). CO₂ exchange was measured with an infrared gas analyzer (Licor 6262, Licor, Lincoln, Nebraska) and allowed the calculation of soil respiration.

The influence of the soil mass per surface area (i.e., the soil column height inside the cuvette) on the exchange of COS was tested up to 400 g fresh soil weight per cuvette ground area. This corresponds to 2.42 g cm⁻² and 2.6–3.1 cm soil column height. We found a linear correlation of COS exchange and soil mass up to 200 g soil per cuvette (1.21 g cm⁻² and 1.6–2.1 cm soil height), which shifted to a saturation-like exchange behavior with increasing soil masses between 200 and 400 g. All further experiments were performed with 200 g of soil per cuvette. All results are generally related to the applied mass of soil. For comparison of the obtained values with surface area-related field data, the laboratory data were adjusted to a soil mass of 400 g, exhibiting an exchange saturation comparable to natural soil surfaces.

2.3. Configuration of Gas Mixtures

Compressed air was purified by passing it through a three-stage gas purification system consisting of three columns with

(1) silicagel (Merck, Darmstadt, Germany), (2) molecular sieve (0.5 nm, Merck, Darmstadt), and (3) charcoal (Merck, Darmstadt), 3 L each. COS concentration at the outlet of the gas purification system was found to be near zero (<5 parts per trillion (ppt)). COS mixing ratios in the desired ranges were obtained by mixing the purified compressed air with known gas mixtures produced from a permeation device (Haunold, Frankfurt, Germany) with COS permeation tubes (VICI Metronics, Santa Clara, California). All flows were regulated by mass flow controllers (MKS, Andover, Massachusetts). After adjustment of the mixing ratios, the air was humidified by bubbling through a water bottle placed inside the climate chamber at the same temperature as the cuvettes. The relative humidities obtained were in the range of 95% and prevented the soil samples from drying during the experiments.

2.4. Sampling and Analysis of Carbonyl Sulfide and Error Estimation

COS was sampled by cryogenic trapping with an efficiency of 100% and analyzed on a gas chromatograph equipped with a flame photometric detector according to Hofmann *et al.* [1992]. The relative precision of the measurements was 6%, based on the reproducibility of consecutive samples over a 2-day period with 90 ppt (number of replicates $n = 26$) and 710 ppt ($n = 25$) COS standards. The overall, absolute accuracy is estimated to be ~10%, based on the variability of permeation device samples injected on a daily basis ($n = 60$). The following assumptions were made to calculate the errors of the COS exchange rates: 6% error for the measurements of the COS concentrations c at the cuvette inlet σ_{in} and cuvette outlet σ_{out} , 5% error in the cuvette flow measurement σ_Q , and 0.5% in the dry weight estimation σ_A . On the basis of these values we calculated the total error σ_F of the COS exchange rates according to the law of error propagation [Doerffel, 1984]:

$$\sigma_F = \sqrt{\frac{[(c_{in}\sigma_{in})^2 + (c_{out}\sigma_{out})^2]}{(c_{out} - c_{in})^2} + \sigma_Q^2 + \sigma_A^2} \quad (1)$$

2.5. Data Storage and Handling

All continuously measured parameters were stored as 5-min averages on a data logger (model 21X, Campbell Scientific Inc., Shepshed, England).

2.6. Enzyme Inhibition

The enzyme carbonic anhydrase (CA) was inhibited by 6-ethoxy-2-benzothiazole-2-sulfonamide (EZ). Owing to its ability to penetrate biological membranes, this specific inhibitor is able to inhibit extracellular as well as intracellular CA [Moroney *et al.*, 1985]. According to Anderson and Domsch [1975], EZ was mixed thoroughly with the soil sample (0.5 g/100 g soil) and kept at room temperature for 2 hours before measurements were taken.

2.7. Algorithmic Description of the COS Uptake

An algorithm taking into account an enzymatic behavior for process description [Sharpe and de Michelle, 1977], simplified by Guenther *et al.* [1991, 1993] to describe isoprene emission from higher plants, was in this case empirically adapted to outline the COS exchange dependence on temperature as well as soil water content. Thus the exchange at a given temperature F_T or given soil water content F_W is described as a function of a standard exchange factor F_0 multiplied by a temperature $\varphi(T)$ or soil water content $\varphi(W)$ correction factor,

respectively (equations (2) and (3)). Empirical coefficients were fitted by iterative adaptation of the least squared errors. Standard temperature was defined as 25°C, and standard soil water content was defined as 13.5%.

$$F_T = F_0 \varphi(T) \quad (2)$$

with F_T , COS exchange rate at temperature T (pmol g DW⁻¹ h⁻¹); F_0 , COS exchange rate at standard temperature T_s (pmol g DW⁻¹ h⁻¹); and $\varphi(T)$, empirical correction factor for temperature.

$$F_W = F_0 \varphi(W) \quad (3)$$

with F_W , COS exchange rate at water content W (pmol g DW⁻¹ h⁻¹); F_0 , COS exchange rate at standard water content W_s (pmol g DW⁻¹ h⁻¹); and $\varphi(W)$, empirical correction factor for water content. The parameter $\varphi(T)$ is defined by

$$\varphi(T) = \frac{\exp \frac{k_{T1}(T(^{\circ}\text{C}) - T_s(^{\circ}\text{C}))}{RT_s(^{\circ}\text{C})T(^{\circ}\text{C})}}{1 + \exp \frac{k_{T2}(T(^{\circ}\text{C}) - k_{T3})}{RT_s(^{\circ}\text{C})T(^{\circ}\text{C})}} \quad (4)$$

with $T(^{\circ}\text{C})$ or $T(\text{K})$, actual temperature ($^{\circ}\text{C}$ or K); $T_s(^{\circ}\text{C})$ or $T_s(\text{K})$, standard temperature ($^{\circ}\text{C}$ or K); R , molar gas constant (8.314) (J K⁻¹ mol⁻¹); k_{T1} , empirical coefficient (116,781) (J K mol⁻¹ °C⁻¹); k_{T2} , empirical coefficient (312,219.8) (J K mol⁻¹ °C⁻¹); and k_{T3} , empirical coefficient (18.449) (°C). The parameter $\varphi(W)$ is defined by

$$\varphi(W) = \frac{\exp \frac{k_{w1}(W - W_s)}{RW W_s}}{1 + \exp \frac{k_{w2}(W - k_{w3})}{RW_s W}} \quad (5)$$

with W , actual water content (%); W_s , standard water content (%); R , molar gas constant (8.314) (J K⁻¹ mol⁻¹); k_{w1} , empirical coefficient (165.627) (J (%) K⁻¹ mol⁻¹); k_{w2} , empirical coefficient (1,028.005) (J (%) K⁻¹ mol⁻¹); and k_{w3} , empirical coefficient (15.071) (%).

3. Results

3.1. Uptake of COS Under Varying COS Mixing Ratios

According to a simple empirical concept proposed by Conrad [1994] and Lehmann and Conrad [1996] to describe the dependence of the COS flux rate on the ambient concentration, the net exchange within a certain biotic system is interpreted as the result of simultaneously operating production and consumption processes. The consumption rate is assumed to be a function of trace gas concentration, whereas the production rate is not. This implies the existence of a so-called compensation point, that is, an ambient concentration where the consumption and production balance each other and the net flux is zero. The production rate, the deposition velocity, and the compensation point concentration are determined by the linear regression of observed fluxes versus concentrations, and are found as the ordinate intercept, the slope, and the abscissa intercept of the regression line, respectively. At ambient concentrations below the compensation point, net emission is observed, while concentrations above the compensation point are associated with net deposition. Within our experiments we varied the COS mixing ratios in the air flushing the cuvette between 0 and 2700 ppt. Owing to the uptake of COS

by the enclosed soil in the well-mixed cuvette atmosphere, the mixing ratio measured at the outlet dropped to lower values. According to Winner and Greutner [1989] these outlet values represent the effective mixing ratios for the incubated soil samples. Therefore we related all exchange data to the COS concentrations at the cuvette outlet. The data are compiled in Figure 1 and show an increase of COS uptake with increasing ambient COS mixing ratios. This increase appears linear for the range between 0 and 1200 ppt. Under higher concentrations a saturation-like uptake behavior is visible (upper inset). Only below mixing ratios of 50 ppt was a significant (confidence level equal to 95%) emission of COS found. The observed linear correlation between the uptake of COS and the ambient concentrations in the range of 0–1200 ppt made it possible to normalize all other data obtained in the course of this study to virtual fumigation conditions of 500 ppt COS (see equation (6) below).

3.2. Uptake of COS Under Varying Temperatures

Temperature has a significant influence on chemical as well as biological reactions. We therefore determined the COS uptake by the soil under varying temperatures (0° to 30°C) as a function of COS mixing ratios between 0 and 1400 ppt. In accordance with the uptake of COS under varying mixing ratios at 17°C as described in the previous section, a linear response was also found between the exchange rates and COS mixing ratios under all investigated temperature regimes (Figure 2).

The data obtained from the experiments with COS concentrations around 600 (±130 ppt), and hence close to natural ambient conditions (500 ± 100 ppt), were used to describe the dependence of COS uptake on temperature. The linear response curves allowed a normalization of the COS exchange rates to a uniform COS mixing ratio of 500 ppt according to (6) and thus allowed a comparison and discussion of the temperature dependency.

$$F_n = \frac{(F_{\text{exp}} - F_p)}{\text{COS}_{\text{exp}}} \text{COS}_{\text{norm}} + F_p \quad (6)$$

with F_n , normalized net flux of COS (mol g DW⁻¹ h⁻¹); F_{exp} , measured net flux under experimental conditions (mol g DW⁻¹ h⁻¹); COS_{exp} , COS mixing ratio under experimental conditions (parts per trillion, ppt); COS_{norm} , COS mixing ratio under normalized conditions (ppt); and F_p , y axis intersection of regression line (e.g., Figure 2) representing the production rate of COS in the soil at the given temperature [Lehmann and Conrad, 1996] (mol g DW⁻¹ h⁻¹).

Figure 3 shows the normalized COS exchange data in relation to the temperature regimes. The uptake increases with temperature up to an optimum between 16 and 20°C, followed by a sharp decrease at higher temperatures. Using the empirical model of Conrad [1994] and Lehmann and Conrad [1996] and the data presented in Figure 2, the COS deposition velocity and the production rate can also be described as a function of the incubation temperature (Figure 4). The temperature dependency of the deposition velocity, derived from the slopes of the regression lines, showed a similar pattern as compared to the flux data of the natural COS concentrations range (Figure 3). The production rates, which were derived from the ordinate intercepts of Figure 2, were very low and resulted in high relative errors. Thus, although a similar pattern for the production rate is expected, it is not as obvious in Figure 4.

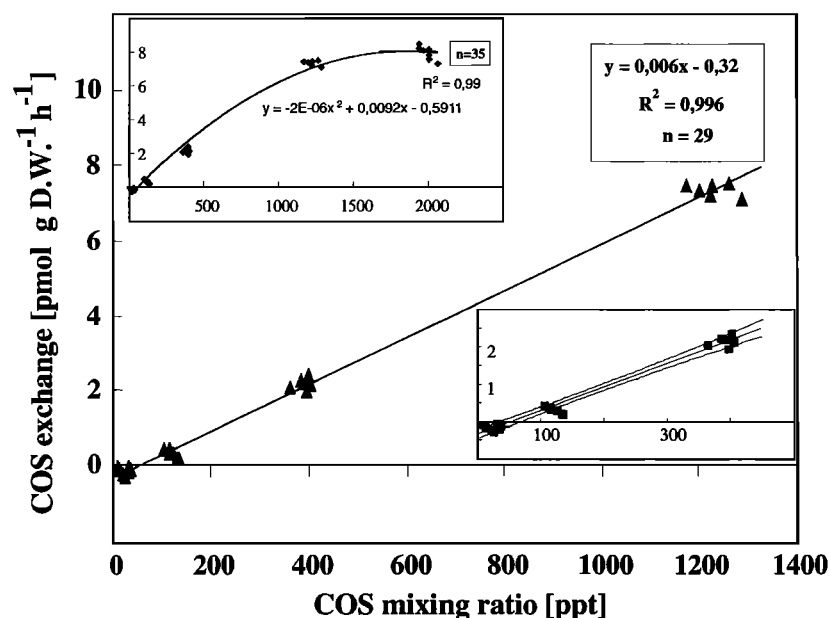


Figure 1. COS exchange correlated to the ambient mixing ratio inside the cuvette (positive sign is uptake). For each condition, two different soil samples were measured at least four times. Air temperature within the cuvettes was held constant at $17 \pm 1^\circ\text{C}$. The left, upper inset gives the exchange data over all ambient concentration ranges. The right, lower inset exhibits the range between 0 and 400 ppt including the 95% confidence level. The compensation point, reflecting the compensation between simultaneously operating production and consumption processes, was calculated to be about 53 ppt COS.

3.3. Uptake of COS Under Varying Soil Water Content

The water content of soils is a critical parameter for the exchange of trace gases [Conrad, 1995; Meixner *et al.*, 1997], as it influences chemical, physical, and biological processes. Therefore we investigated the exchange of COS by varying the soil water content between 5 and 42% (dry weight). Temperature was held constant near the temperature optimum (see Figure 3) at 15°C (± 0.6). This cool environment allowed several repetitions of the measurements with a negligible water loss of 0.2–0.5% during the experiment. Figure 5 shows the COS exchange normalized to an ambient mixing ratio of 500 ppt COS (see section 3.1) in relation to the soil water content.

The data show a zero exchange at a water content below 6%. Higher water contents between 10 and 15% resulted in a maximum of COS uptake, but further increases in the water content led to a decrease of exchange.

3.4. Physiological Background for the Uptake of COS

Both biological and physicochemical parameters can potentially explain the revealed COS exchange behavior in relation to the soil water content and ambient COS concentration. The observed optimum in relation to temperature, however, points to an enzymatically catalyzed process [Radmer and Kok, 1979]. An enzyme increases the turnover with increasing temperature, but this trend is superimposed by a decrease of activity if

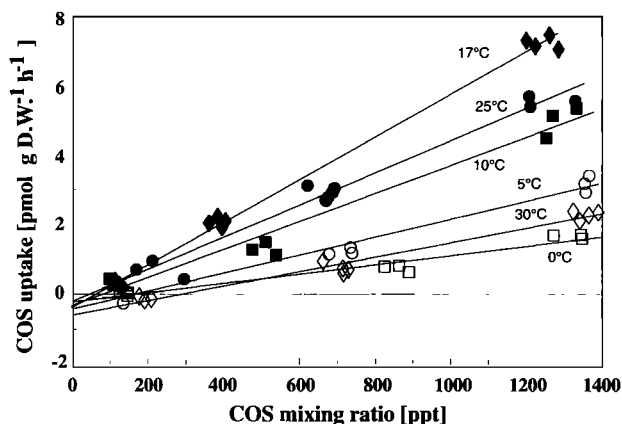


Figure 2. Relation between COS uptake and ambient mixing ratios at different temperatures. Three groups of three to four samples each were taken for every temperature range. All regression lines calculated showed $r^2 > 0.95$.

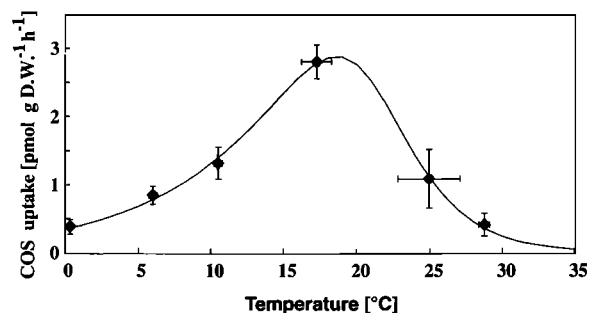


Figure 3. COS uptake normalized to ambient mixing ratios of 500 ppt in relation to the temperature regimes ($n = 4$; error bars are 1σ). Only measurements applying COS concentrations close to natural ambient conditions (600 ± 130 ppt) were used. The plotted line gives the mathematical approximation according to the algorithm $F_T = F_0\varphi(T)$ as described in section 2.7. Some error bars are smaller than the symbol width.

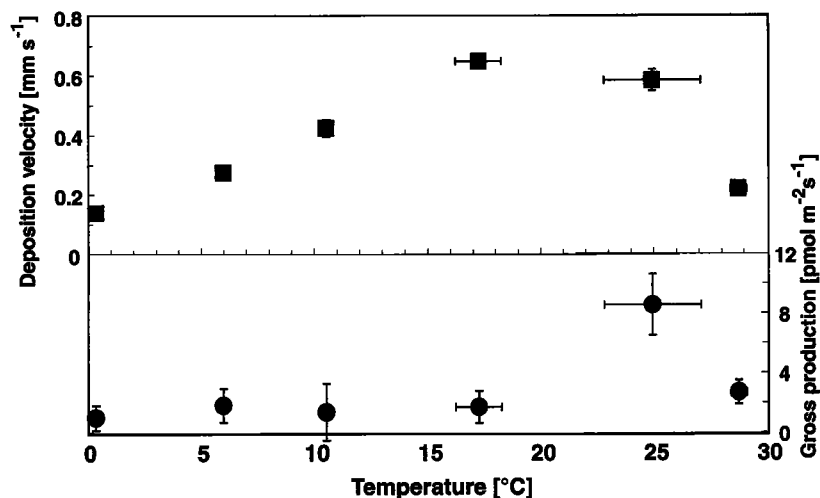


Figure 4. COS deposition velocities (mm s^{-1}) and gross production rates per surface area ($\text{pmol m}^{-2} \text{s}^{-1}$) as a function of the incubation temperature determined by the slopes and the ordinate intercepts, respectively, of the regression lines in Figure 2 (normalized to ambient mixing ratios of 500 ppt). Some error bars are smaller than the symbol width. Dry weight-based production rates were transformed into surface-based rates. For comparison of the obtained values with surface area-related field data, the laboratory data were adjusted to a soil mass of 400 g, exhibiting an exchange saturation comparable to natural soil surfaces (for details, see section 2.2).

the temperature range exceeds a certain value owing to reorganization and/or denaturation of the enzyme structures. The key enzyme for the uptake of COS by different biological organisms has been identified to be carbonic anhydrase (CA) [Chengelis and Neal, 1979, 1980; Miller et al., 1989; Badger and Price, 1990; Protoschill-Krebs and Kesselmeier, 1992; Protoschill-Krebs et al., 1995, 1996; Kuhn, 1997]. According to Moroney et al. [1985] this enzyme can be specifically inhibited by 6-ethoxy-2-benzothiazole-2-sulfonamide (EZ). We therefore compared the uptake of the soil sample with and without inhibition of the specific enzyme CA. Results are shown in Figure 6. The addition of the inhibitor EZ to the soil sample resulted in a highly

significant ($p < 0.001$) reduction of the COS uptake of more than 50%, showing CA to be the dominant factor for the consumption of COS by the investigated soil.

4. Discussion

The data show that the investigated soil type is a significant sink for the trace gas COS. The consumption of COS by this soil depends on physiologically active microorganisms, as indicated by the drastic inhibition in the presence of the enzyme inhibitor EZ. Physiologically active microorganisms, responsible for the consumption of COS by soils, were already indicated by experiments of Bremner and Banwart [1976]. However, even now there is still only rare information about these

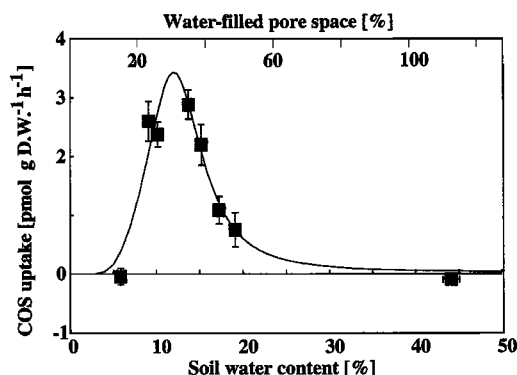


Figure 5. COS uptake in relation to the soil water content. COS uptake rates are normalized to ambient mixing ratios of 500 ppt COS ($n = 4$; error bars are 1σ). The plotted line gives the mathematical approximation according to the algorithm $F_w = F_0 \phi(W)$ as described in section 2.7. Some error bars are smaller than the symbol width. Soil water content was measured as described in section 2.1. Water-filled pore space (upper x axis) was estimated according to Hillel [1980], assuming a bulk density for clayey soils of 1.25 g cm^{-3} and a general particle density of 2.65 g cm^{-3} .

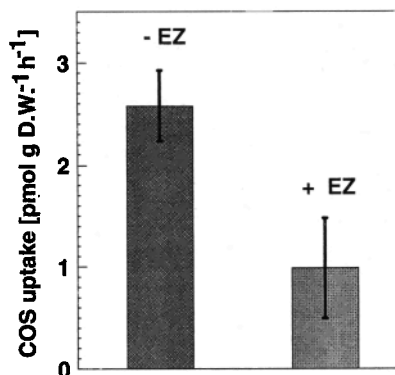


Figure 6. Inhibition of soil COS uptake by the carbonic anhydrase (CA) specific inhibitor 6-ethoxy-2-benzothiazole-2-sulfonamide (EZ); $n = 8$, $p < 0.001$. Inhibition by nucleophilic attack at the active center (Zn) of CA. Application is $0.5 \text{ g EZ}/100 \text{ g soil}$ with 2 hours of incubation before first measurements [Anderson and Domsch, 1975]. Standard deviation is $\pm 1 \sigma$.

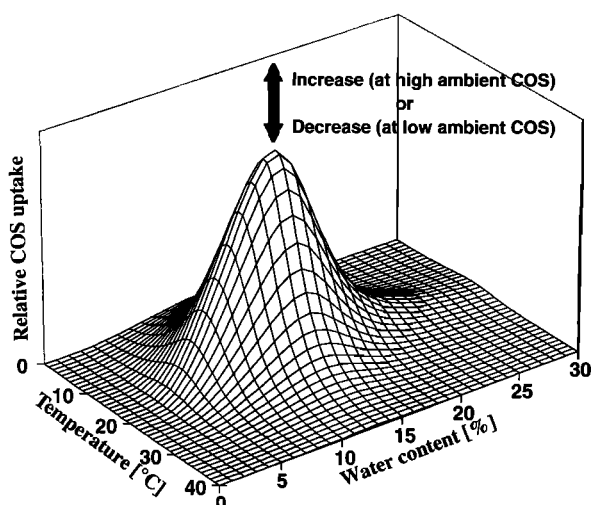


Figure 7. Modeling soil COS uptake in relation to temperature and soil water content. Atmospheric COS concentration influences the amplitude of the uptake.

COS-consuming soil microorganisms. To our knowledge, only Kelly *et al.* [1994] succeeded in showing *Thiobacillus* species consuming COS. It would be of great interest to expand the studies to more soil microorganisms, including fungi, in order to get a better understanding of the COS deposition to soils. Carbonic anhydrase (CA) activity responsible for the consumption of COS was shown in several microorganisms already [Chengelis and Neal, 1979, 1980; Miller *et al.*, 1989; Badger and Price, 1990; Protoschill-Krebs *et al.*, 1995]. According to our studies the enzyme carbonic anhydrase can be regarded as the dominant factor for the consumption of COS by the investigated soil. Atmospheric COS mixing ratios, temperature, and soil water content are the physicochemical parameters controlling the uptake. An existing algorithm was adapted to the temperature as well as soil water content dependencies (see Figures 3 and 4). Combining the environmental parameters, controlling the uptake of COS, we come up with an uptake algorithm where the actual flux F is achieved by multiplying a standard uptake rate F_0 by correction factors for water content $\varphi(W)$, ambient COS concentration $\varphi(C)$, and temperature $\varphi(T)$.

$$F = F_0 \varphi(W) \varphi(C) \varphi(T) \quad (7)$$

The combined influences are illustrated by the three-dimensional plot in Figure 7. The observed temperature and soil water content dependencies result in a peak-shaped optimum whose amplitude is influenced by the applied atmospheric mixing ratio.

Emission of COS was not observed under a natural set of experimental conditions. According to Remde *et al.* [1989] and Conrad [1994] the gas exchange can be discussed as a result of simultaneously operating production and consumption processes. The applicability of this concept has been empirically confirmed for exchange of various biogenic trace gases with soils [Remde *et al.*, 1989; Conrad, 1994; Ludwig, 1994], for COS in plants [Goldan *et al.*, 1988; Kesselmeier and Merk, 1993; Kesselmeier *et al.*, 1993], and lichens [Kuhn and Kesselmeier, 1997; Kuhn, 1997]. However, the extremely low mixing ratios of COS leading to a measurable release of this gas from the soil samples (Figure 1) show that the production term of COS

within the investigated soil specimens is of minor importance. We calculated a COS production in the range of 0.33–1.8 pmol g DW⁻¹ h⁻¹, with a maximum at 25°C. These small numbers as compared to the measured COS uptake in combination with the compensation point observed around 50 ppt (95% confidence level, Figure 1) clearly show that the investigated soil type will hardly emit COS in nature. These results are in contrast to the investigations of Lehmann and Conrad [1996], who calculated a much higher compensation point, reflecting a higher probability of COS emission by soils. However, those studies were done with a different soil and a COS fumigation well above 500 ppt. Thus they may not reflect natural conditions and uptake behavior, as our studies point to a nonlinear pattern under fumigation with high COS concentrations. The observed compensation point of 53 ppt is very similar to data obtained during field measurements on a different soil type in California [Kuhn *et al.*, 1999] showing a compensation point below 100 ppt. Similar values of 90–150 ppt were also found for the exchange of COS between plants and the atmosphere [Kesselmeier and Merk, 1993].

The results of this study support data obtained within field experiments [Castro and Galloway, 1991; Fried *et al.*, 1993; DeMello and Hines, 1994; Kuhn *et al.*, 1999] which suggest that soils act as COS sinks instead of sources. The uptake rates reported here for the arable soil samples range between 1.5 and 10.3 (pmol m⁻² s⁻¹) and fit well into the range reported by Castro and Galloway [1991], who found a net COS deposition of 1.4–8.4 (pmol m⁻² s⁻¹) for unvegetated forest soils. Furthermore, the rates are similar to those observed with intact peat soil ranging between 1.25 and 4.2 (pmol m⁻² s⁻¹) [Fried *et al.*, 1993] and 1.0–15.3 (pmol m⁻² s⁻¹) [DeMello and Hines, 1994] or to those observed at the soil surface in an open Californian oak woodland ranging between 8.8 and 13.3 (pmol m⁻² s⁻¹), though these values may be slightly overestimated [Kuhn *et al.*, 1999]. Also, the calculated COS deposition velocities fit into the data sets as found in the literature for plant surfaces [Kluczewski *et al.*, 1985; Taylor *et al.*, 1983; Goldan *et al.*, 1988; Kesselmeier and Merk, 1993; Huber, 1994; Kuhn *et al.*, 1999] as well as soil surfaces [Kuhn *et al.*, 1999]. These similarities give reason to assume that soils in general should be considered as sinks and that an adaptation of the global budget by changing the source strength into a sink strength [Andreae and Crutzen, 1997] is justified, although soil types and soil redox conditions exist which will lead to a significant production and emission in some special cases such as salt marsh sediments [Devai and Delaune, 1995] or waterlogged paddy soils [Yang *et al.*, 1996]. In addition, those results have to be discussed in light of knowledge about the influence of atmospheric COS mixing ratios and compensation points. Further measurements of soil/atmosphere fluxes of COS under natural conditions are urgently needed and should be incorporated into future estimates of the global COS budget to reduce the existing uncertainties and imbalances.

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