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Exchange of carbonyl sulfide (COS) between the atmosphere and various soils in China

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Abstract. Using a dynamic enclosure, the exchange rates of carbonyl sulfide (COS) between the atmosphere and 18 soils from 12 provinces in China were investigated. The emission or uptake of COS from the soils was highly dependent on the soil type, soil temperature, soil moisture, and atmospheric COS mixing ratio. In general, with the only exception being paddy soils, the soils in this investigation acted as sinks for atmospheric COS under wide ranges of soil temperature and soil moisture. Two intensively investigated wheat soils and one forest soil had optimal soil temperatures for COS uptake of around 15 °C, and the optimal soil water content varied from 13% to 58%. COS emission rates from the two paddy soils increased exponentially with increment of the soil temperature, and decreased with increasing the soil water content. However, negligible emission was found when the paddy soils were under waterlogging status. The observed compensation points for various soils were different and increased significantly with soil temperature. The laboratory simulation agreed with the preliminary field measurements for the paddy soil in Jiaxing, Zhejiang province.

1 Introduction

Carbonyl sulfide (COS), the most abundant and long-lived reduced sulfur gas 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 ozone destruction (Turco et al., 1980; Solomon et al., 1993; Roche et al., 1994; Andreae and Crutzen, 1997). Atmospheric sinks and sources of COS have aroused widely attention, and many studies have examined for atmospheric COS sinks and sources (Bartell, et al., 1993; Kesselmeier and Merk, 1993; Kesselmeier, et al., 1993; de Mello and Hines, 1994; Gries et al., 1994; Kuhn et al., 1999, 2000; Kettle et al., 2002; Xu et al., 2002; Geng and Mu, 2004; Sandoval-Soto et al., 2005; Yi et al., 2007, 2008; Van Diest and Kesselmeier, 2008).

Soils were previously considered to represent one of the dominant sources for atmospheric COS (Khalil and Rasmussen, 1984; Chin and Davis, 1993). However, recently, field studies and laboratory simulations have presented convincing evidence that soils act more as a sink than as a source for COS (Castro and Galloway, 1991; Fried et al., 1993; de Mello and Hines, 1994; Kesselmeier et al., 1999; Kuhn et al., 1999; Kettle et al., 2002; Geng and Mu, 2004; Yi et al., 2007, 2008; Van Diest and Kesselmeier, 2008). Earlier researchers investigating COS exchange usually used enclosure methods with COS-free sweep air (Aneja et al., 1979; Adams et al., 1981; Goldan et al., 1987; Lamb, et al., 1987; MacTaggart et al., 1987), which masked the potential of soils to act as a sink for sulfur compounds. In contrast, some other researchers used very high concentration of COS to study the potential of soils to take up COS (Bremner and Banwart, 1976; Kluczewski et al., 1985; Lehmann and Conrad, 1996), which also generated artificial COS concentration gradients. Therefore, earlier data should be checked for artifacts due to the use of inappropriate air mixtures for flushing enclosures.

Watts (2000) estimated COS deposition and emission rates for two different types of soils as $0.92\pm0.78\,\mathrm{Tg\,a^{-1}}$ (sink, "oxic" soils) and $0.02\pm0.01\,\mathrm{Tg\,a^{-1}}$ (source, "anoxic" soils). However, the estimate was only based on a few studies with limited soil types, especially in the case of "oxic" soils (only

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two results from two types of soils were used as the basis for the estimation) and contained considerable uncertainty. Kesselmeier et al. (1999) were the first to parameterize the influencing factors of COS uptake by soil taken from arable land. Van Diest and Kesselmeier (2008) investigated COS exchanges between four kinds of soils (three arable soils from Germany, China, and Finland and one forest soil from Siberia) and the atmosphere for parameterization in relation to ambient COS concentration, soil water content, and temperature. They suggested that the uptake of COS depended on diffusivity, which was controlled by water-filled pore space (WFPS). The parameterization of COS uptake gave a clear clue as to how to reduce existing uncertainties in estimating COS uptake by different soils. Because COS exchange between soils and the atmosphere is largely dependent upon soil type, additional study is needed to reassess the parameterization of different soil types using the enclosure method with ambient air (Kesselmeier et al., 1999; Watts, 2000; Kettle et al., 2002; Sandoval-Soto et al., 2005; Van Diest and Kesselmeier, 2008).

The objective of this study was to compare the exchange rates of COS between the atmosphere and different types of soils in China. The factors affecting the exchange rates, i.e., temperature, soil moisture, and COS mixing ratio, were also investigated for five soils. Our results extend the data set and yield better insight into the role of different soils in the atmospheric COS budget.

2 Materials and methods

2.1 Sampling sites

Eighteen types of soil were sampled from 12 provinces in China (Fig. 1) covering about half of China's agricultural regions. Samples were taken from the top 5 cm of the soil profile and sieved to <2 mm using a stainless steel sieve.

The characteristics of the five most intensively investigated soils were determined, and these are listed in Table 1. Soil characteristics were determined at the Beijing Academy of Agriculture & Forestry Sciences using standard protocols (Liu, 1996). Samples were stored at 3 °C prior to investigation.

2.2 Construction and performance of exchange enclosure

A dynamic enclosure was used to measure the COS exchange rate from the different soils. The enclosure consisted of a stainless steel cylinder (20 cm high(H), 18 cm inner diameter (ID) and with a 5-L volume) with an inner surface covered by a Teflon film to prevent any effects from contamination or adsorption. An inlet (perforated stainless steel ring) that allowed gas with fixed COS concentration into the enclosure was located near the bottom of the cylinder. The investigated soil was put into a glass dish (ID, 15 cm) at the bottom of the enclosure. Soil temperature was controlled by putting the enclosure in a super-constant-temperature water boiler (CS501, Chongqing Testing Equipment Corporation, Chongqing, China). COS concentrations within the desired range for flushing the enclosure were obtained by mixing a purified compressed air (50 ppt COS) with high-concentration COS gas (5–50 ppb COS) from a glass flask (10 L). The flow rates of the purified compressed air and the high-concentration COS gas was controlled by two mass flow meters (SY-9506, Beijing Shengye Technologic Development Corporation, Beijing, China) with ranges of 0–5 L min^{-1} and 0–100 mL min^{-1}, respectively. Before being introduced into the enclosure, the mixed air was humidified by a water bubbler which was also placed inside the water boiler to prevent the soil samples from drying during the experiments. COS concentration from the exhaust of the water bubbler was analyzed by the GC-FPD every 10 min, could achieve steady value (maximum 10% variation) after 30 min. Then, all exchange rate measurements were conducted under the condition of the dynamic equilibrium. The total airflow rate through the enclosure was normally kept at 0.7–0.8 L min^{-1}.

The COS exchange rate (ER, pmol m^{-2} s^{-1} or pmol g $(DW)^{-1}$ h^{-1}) in the enclosure was calculated using the following equation:

$$\mathrm{ER}=(V/A)\times(C_{\mathrm{out}}-C_{\mathrm{in}}) \text{ or } \mathrm{ER}=(V/W)\times(C_{\mathrm{out}}-C_{\mathrm{in}}), \quad (1)$$

where V (m^3 h^{-1}) is the steady flow rate of the flushing gas through the enclosure and A (m^2) is the surface area of soil spread on the glass dish. W (g) is the dry weight of the applied soil, and C_{in} and C_{out} (pmol m^{-3}) are the COS concentrations in the inlet and outlet of the enclosure, respectively.

The influence of the soil mass relative to surface area (i.e., soil column height inside the enclosure) on the COS exchange was tested incrementally up to 200 g of fresh soil (two soils of lawn and winter wheat from Beijing, and one paddy soil from Jiaxing). We found a linear correlation between the COS exchange rate and soil mass up to 100 g. This correlation shifted to a saturation-like exchange behavior with increased soil mass between 100 g and 200 g. Therefore, all experiments were performed using only 100 g of soil. Soil water content was varied by air-drying soils and re-moistening them with deionization water.

The control experiments for the dynamic enclosure, in which the steel cylinder containing no soil sample, were conducted between 10 and 40 °C. Weak emissions of COS were found from the blank enclosure, especially when temperature was higher than 20 °C (Fig. 2). To eliminate the background COS contribution, the blank COS exchange rate was subtracted from the total exchange rates measured from the soil samples. To verify our laboratory simulation for paddy field soil, we carried out a brief set of field measurements in Jiaxing, Zhejiang province, the collection site for our paddy soil sample. Two dynamic chambers were adopted for exchange rate measurements. Each dynamic chamber consists

Table 1. The characteristics of five soil samples (W1: wheat soil in Beijing; W2: wheat soil in Zibo (Shandong Province); P1: Paddy soil in Jiaxing (Zhejiang Province); P2: Paddy soil in Guangzhou (Guangdong Province); F: forest soil in Beijing).

Soil	pH	$C_{organic}$ g/kg	N_{total} g/kg	P_{total} g/kg	S_{total} g/kg	S^{a}_{effect} mg/kg
W1	6.31	8.24	0.92	0.618	0.12	25.0
W2	7.74	15.1	1.13	0.783	0.40	94.8
P1	6.14	24.5	2.26	0.579	0.45	31.5
P2	6.42	29.1	2.42	0.860	0.65	56.2
F	6.44	61.5	4.94	0.967	0.90	21.2

[a] S_{effect}: soil available sulfur (S_{effect}) means the sulfur in the soil can be used for crops assimilation, including soluble sulfur and part of the adsorption sulfur and organic sulfur. It was measured by turbidimetry method after extraction from soils with 0.5 mol L^{-1} $NaHCO_3$ (Liu, 1996).

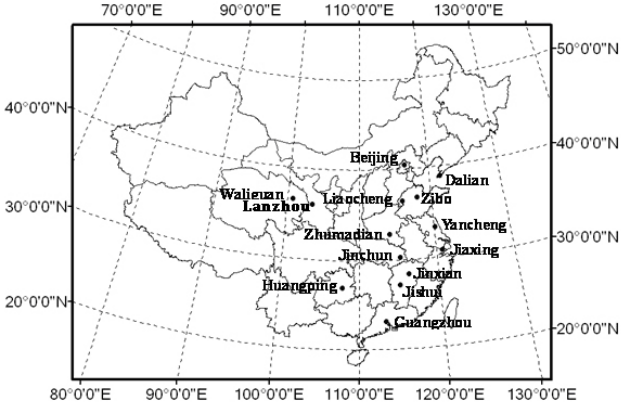

Fig. 1. Locations of sampling sites in this study.

of a Polyvinylchlorid tube (30 cm (H)×20 cm (ID)) that has an inner surface covered by Teflon film (0.1 mm). Four inlets of Teflon tubes were evenly connected to each chamber at the outside with heights of 5 cm above the bottom, and the other ends of the four tubes rose to 50 cm above ground. A mini-pump connected with an outlet at the top of the chamber was used to drive ambient air into the chamber. The flow rate was kept at 3.27 L min^{-1}. During COS exchange rates measurements, one chamber was mounted on a pedestal (15 cm (H)×20 cm (ID) with bottom open, the other one was also mounted on the same pedestal, but with bottom covered by Teflon film. The pedestal had a gutter around the outside of its upper rim that could be filled with water to make an air-tight seal with the chamber. The pedestals for the chambers other than the reference one was inserted 10 cm into the investigated soil for one day before the exchange rate measurements. After flushing the chamber for 30 min with outside ambient air, air samples were collected into 2-L Teflon bags (0.1 mm film) and analyzed within 3 days after collection.

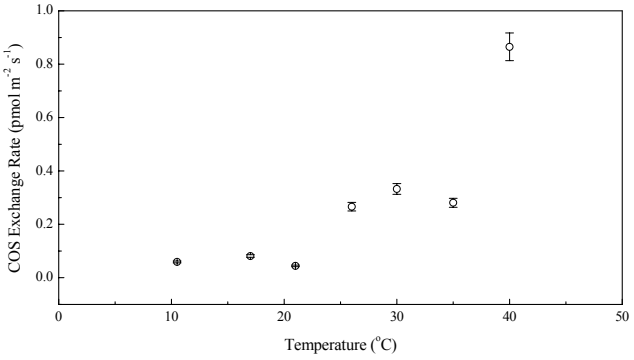

Fig. 2. COS exchange rates of the blank enclosure system (with glass dish) in relation to the temperature. The error bars are calculated from formula (2); each exchange rate measurement was conducted twice.

2.3 COS analysis

COS was sampled by cryogenic trapping and analyzed by means of a gas chromatograph (GC) equipped with a flame photometric detector (FPD) according to Hofmann et al. (1992). Detailed description of the method can be found in Mu et al. (2002, 2004). The detection limit for COS was approximately 0.88 pmol L^{-1} (800 mL gas sample). The relative precision of the method for COS was less than 6%, and the recovery efficiency of COS was about 94% (Mu et al., 2002, 2004).

The following assumptions were made in calculating the errors of the exchange rates: 10% error for the COS measurements at the enclosure inlet (σ_{in}) and the enclosure outlet (σ_{out}), 5% error in the enclosure flow measurement (σ_Q), and 1% error in the surface area determination or the soil mass determination($\sigma_{A/W}$). The total exchange rate error (σ_F) can be obtained by using the error propagation method according to Doerffel (1984):

$$\sigma_F = \sqrt{\frac{[(C_{in}\sigma_{in})^2 + (C_{out}\sigma_{out})^2]}{(C_{out} - C_{in})^2} + \sigma_Q^2 + \sigma_{A/W}^2} \quad (2)$$

3 Results

For all soil samples, we investigated COS exchange rates at the original moisture level and at two different temperature: 17 °C and 25 °C. COS concentration was kept at around 500±80 ppt. We derived COS deposition velocities for each soil sample using the measured exchange rates and the COS concentration.

Table 2 gives an overview of the exchange rate and deposition velocity measured at 17 °C and 25 °C at original moisture levels for each of the investigated soils. It is evident that large difference in COS exchange rate and deposition velocity exist among the different soil types. The maximal

Table 2. COS exchange rates (ER) and deposition velocities of various soils in China.

Site	Plant type	Parent material	Soil moisture %[a]	ER (17 °C) pmol m^{-2} s^{-1}	ER (25 °C) pmol m^{-2} s^{-1}	ER (17 °C) pmol g^{-1} h^{-1}	ER (25 °C) pmol g^{-1} h^{-1}	Deposition velocity[b] mm s^{-1} (17 °C)	Deposition velocity mm s^{-1} (25 °C)
Jinxian, Jiangxi	badlands	Red earth	19.0	0.061	−2.84	0.049	-1.84	–	0.12
Liaocheng, Shandong	cotton	Fluvo-aquic soil	16.5	−1.32	−1.10	−0.84	−0.69	0.075	0.056
Yancheng, Jiangsu	cotton	Solonchak soil	17.8	−0.49	−0.11	−0.31	−0.05	0.02	0.0051
Beijing	forest	Drab soil	43.9	−4.05	−0.83	−3.21	−0.81	0.17	0.041
Waliguan, Qinghai	grass	Chestnut soil	9.77	−3.76	−2.69	−2.28	−1.62	0.22	0.15
Beijing	lawn	Drab soil	8.35	−4.90	−4.83	−3.00	−3.08	0.23	0.26
Liaocheng, Shandong	maize	Fluvo-aquic soil	18.9	−2.17	−1.41	−1.42	−0.90	0.10	0.075
Jiaxing, Zhejiang	paddy	Drab soil	20.7	0.44	1.19	0.27	0.63	–	–
Guangzhou, Guangdong	paddy	Paddy soil	19.4	0.69	12.9	0.46	8.56	–	–
Jinchun, Hubei	paddy	Red earth	23.2	0.57	2.00	0.40	1.34	–	–
Jishui, Jiangxi	paddy	Red earth	18.8	−2.04	0.29	−1.33	0.22	0.077	–
Yancheng, Jiangsu	paddy	Solonchak soil	19.7	−0.41	−0.10	−0.27	−0.04	0.018	0.0044
Huangping, Guizhou	paddy	Yellow earth	27.8	−3.20	−3.56	−2.25	−2.15	0.15	0.19
Lanzhou, Gansu	plum blossom	Grey-drab soil	10.7	−2.46	−2.18	−1.51	−1.32	0.12	0.096
Dalian, Liaoning	wheat	Burozem	9.13	−2.10	−2.76	−1.26	−1.66	0.096	0.17
Zibo, Shandong	wheat	Burozem	17.2	−4.32	−2.73	−2.80	−1.66	0.18	0.13
Beijing	wheat	Drab soil	8.00	−1.04	−0.73	−0.69	−0.44	0.052	0.031
Zhumadian, Henan	wheat/paddy	Yellow-brown	13.1	−0.77	0.02	−0.48	0.032	0.039	–

[a] Soil moisture %=water (g)/soil (dry weight, g) × 100%; [b] Deposition velocity=COS exchange rate/the outlet concentration of COS.

emission and uptake rates were 12.9 pmol m^{-2} s^{-1} at 25 °C (paddy soil) and −4.90 pmol m^{-2} s^{-1} at 17 °C (lawn soil).

Three of the paddy soil samples acted as COS sources at both 17 °C and 25 °C, whereas two acted as COS sinks. COS uptake (sink) was observed at 17 °C for the paddy soil from Jishui (Jiangxi province), although a weak emission (source) was observed at 25 °C. The same behavior was observed for the paddy soil from Zhumadian (Henan province), where wheat and rice are cultivated in rotation. In contrast to the paddy soils, all other soils acted as COS sinks.

To investigate the influence of COS concentration, soil temperature, and moisture on COS exchange, we focused on five soil samples. Two of these were from northern wheat land soils: Beijing (W1) and Zibo (Shandong province) (W2); two were from southern paddy-field soils: Jiaxing (Zhejiang province) (P1) and Guangzhou (Guangdong province) (P2); and one was from northern forest (larch)-land soil: Beijing (Lingshan) (F).

3.1 COS exchange rates under varying COS concentrations

The exchange rate of COS and its dominant direction are recognized to strongly depend upon ambient COS concentration (Conrad, 1994; Lehmann and Conrad, 1996; Kesselmeier et al., 1999) and a so-called compensation point (under a typical ambient concentration, the consumption and production balance each other, and the net exchange rate is zero; Kesselmeier et al., 1999). When the ambient concentration is above the compensation point, net deposition occurs. Whereas when concentrations are below the compensation point, net emission occurs. The compensation point, therefore, is an important parameter in judging exchange direction. To obtain the compensation points for the different soils in this study, the exchange rates from the investigated soils were measured under varying COS concentrations, from 50 ppt to 1400 ppt, at 17 °C and 25 °C (Fig. 3). Linear correlations between COS exchange rate and COS concentration were found for all investigated soil samples. The compensation points for the five soils were determined by the linear regression as the abscissa intercept of the regression line (Kesselmeier et al., 1999). The compensation points, ordinate intercepts, slopes and correlation coefficients of the linear correlation analysis are listed in Table 3, together with the values reported in the literature for other soils.

For the paddy soils, P1 and P2, the compensation points were around the global average concentration of 500 ppt at 17 °C, but were much greater at 25 °C. These soils can be considered as COS sources, especially when their temperature is above 17 °C.

For other soils (W1, W2, and F), the compensation points were found to be below the global average COS concentration at 17 °C and 25 °C. As for the forest soil (F), the compensation point was 80 ppt at 17 °C, similar to the data obtained during field measurements on an oak woodland soil in California (Kuhn et al., 1999). Consequently, these soils should act as COS sinks under natural conditions. Additionally, the compensation points for the five soil types were higher at 25 °C than they were at 17 °C, indicating that an increase in temperature may favor the production of COS.

3.2 COS exchange rates under varying temperatures

Temperature has been shown to be an important factor governing sulfur emission as microorganism activity is enhanced (Hill et al., 1978; Adams et al., 1981; MacTaggart et al., 1987; Kesselmeier et al., 1999). Therefore, we investigated COS exchange between the soil and atmosphere under

Table 3. COS compensation point (CP), the ordinate intercepct, slope and correlation coefficent (R) of the regression line of the observed COS exchange rates versus concentrations in this study compared with other studies (P1: Paddy soil in Jiaxing (Zhejiang Province); P2: Paddy soil in Guangzhou (Guangdong Province); W1: wheat soil in Beijing; W2: wheat soil in Zibo (Shandong Province); F: forest soil in Beijing).

Soil	Water content (%)[a]	CP (ppt)	Ordinate intercept (17 °C)	Slope (17 °C)	R (17 °C)	CP (ppt)	Ordinate intercept (25 °C)	Slope (25 °C)	R (25 °C)	Reference
W1	8.00	255	1.054	−0.0041	−0.997	267	1.454	−0.0055	−0.999	This study (laboratory)
W2	17.2	120	1.413	−0.0118	−0.997	149	2.260	−0.0152	−0.999	This study (laboratory)
P1	20.7	491	4.125	−0.0084	−0.995	765	5.292	−0.0069	−0.998	This study (laboratory)
P2	19.4	572	4.388	−0.0077	−0.995	780	10.048	−0.0129	−0.998	This study (laboratory)
F	43.9	80	0.775	−0.0097	−0.998	225	2.748	−0.0122	−0.997	This study (laboratory)
Oak woodland		< 100								Kuhn et al. (1999) (field)
Sandy clay soil		∼ 53								Kesselmeier et al. (1999) (laboratory)
Forest soil						785				Conrad and Meuser (2000) (laboratory)
Rape field soil						1470				Conrad and Meuser (2000) (laboratory)

[a] The water content of the soil is the original as found in the field.

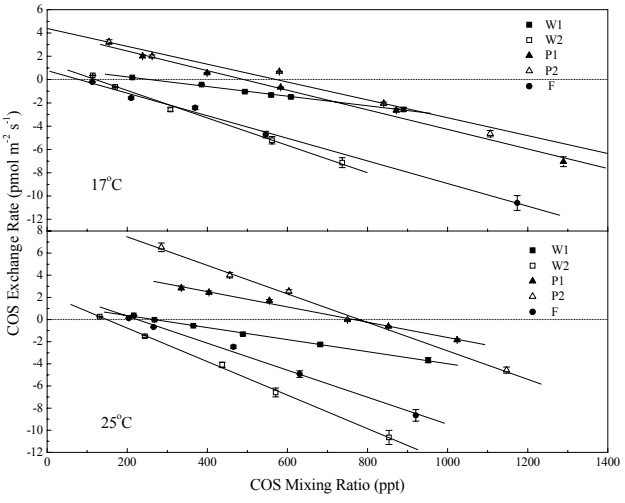

Fig. 3. COS exchange rates under different COS mixing ratios at 17 and 25 °C. (W1: wheat soil in Beijing, 8.00% moisture; W2: wheat soil in Zibo (Shandong Province), 17.2% moisture; P1: Paddy soil in Jiaxing (Zhejiang Province), 20.7% moisture; P2: Paddy soil in Guangzhou (Guangdong Province), 19.4% moisture; F: forest soil in Beijing, 43.9% moisture). The error bars are calculated from formula (2); each exchange rate measurement was conducted twice.

varying temperatures (1 °C to 40 °C). Figure 4 shows the result of COS exchange rates from the five soils under different temperatures at constant pressure and with a concentration of 500±80 ppt COS in the air used to flush the enclosure. The wheat (W1 and W2) and forest (F) soils showed increased uptake (sink) with increasing temperature to an optimum at 15–20 °C, followed by a sharp decrease at higher temperatures. These results support the data obtained by Kesselmeier et al. (1999), who found an optimum temperature between 16 and 20 °C for COS uptake. When the soil temperature was above 25 °C, weak emissions were measured from the W1 and F soils, whereas W2 remaned negative (uptake).

Carbonic anhydrase (CA) has been recognized as the key enzyme for the uptake of COS by different biological organisms (Chengelis and Neal, 1979; Chengelis and Neal, 1980; Miller et al., 1989; Badger and Price, 1990; Protoschill-Krebs and Kesselmeier, 1992; Protoschill-Krebs et al., 1995; Protoschill-Krebs et al., 1996; Kesselmeier et al., 1999). As mentioned by Kesselmeier et al. (1999), the activity of the enzyme should be responsible for the variation of COS exchange rates under different temperatures. de Mello (1992) found that the net consumption rate of COS in Sallie's Fen decreased from ∼50 to 15 nmol m^{-2} h^{-1} (13.9–4.17 pmol m^{-2} s^{-1}) as temperature increased from ∼16 to 30 °C.

For paddy soils (P1 and P2), the exchange rate of COS was around 0 at low temperatures (for P1 below 15 °C, for P2 below 10 °C), whereas at higher temperatures, the emission was obvious and increased exponentially with increasing temperature. The relationships between COS emission rate (F) and temperature (T, °C) for the paddy soils of P1 and P2 under the experimental soil moistures fitted the following equations:

$$F_{P1} = \exp(0.126 \times T - 2.26),\ R = 0.997 \quad (3)$$

$$F_{P2} = \exp(0.0884 \times T + 0.195),\ R = 0.995. \quad (4)$$

These relationships between COS exchange rate and soil temperature were inconsistent with the empirical algorithmic

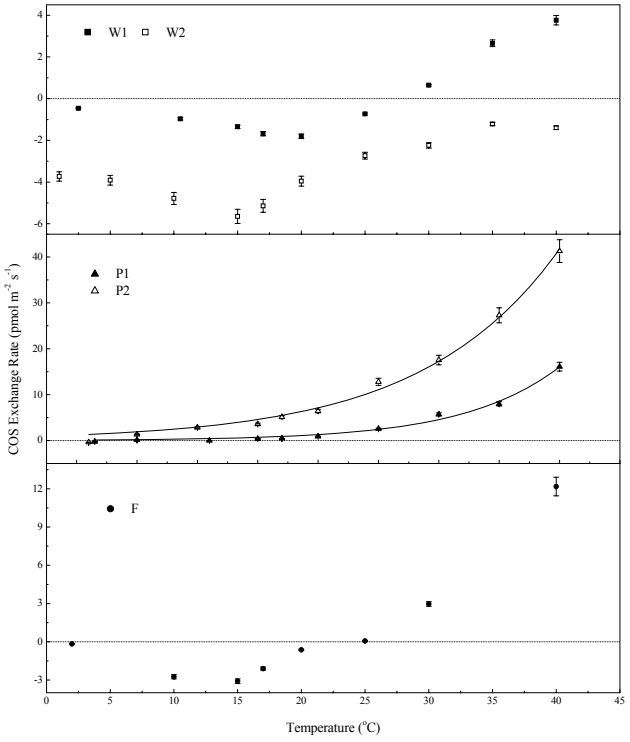

Fig. 4. COS exchange rates in relation to soil temperature. (W1: wheat soil in Beijing, 8.00% moisture; W2: wheat soil in Zibo (Shandong Province), 17.2% moisture; P1: Paddy soil in Jiaxing (Zhejiang Province), 20.7% moisture; P2: Paddy soil in Guangzhou (Guangdong Province), 19.4% moisture; F: forest soil in Beijing, 43.9% moisture). The error bars are calculated from formula (2); each exchange rate measurement was conducted twice.

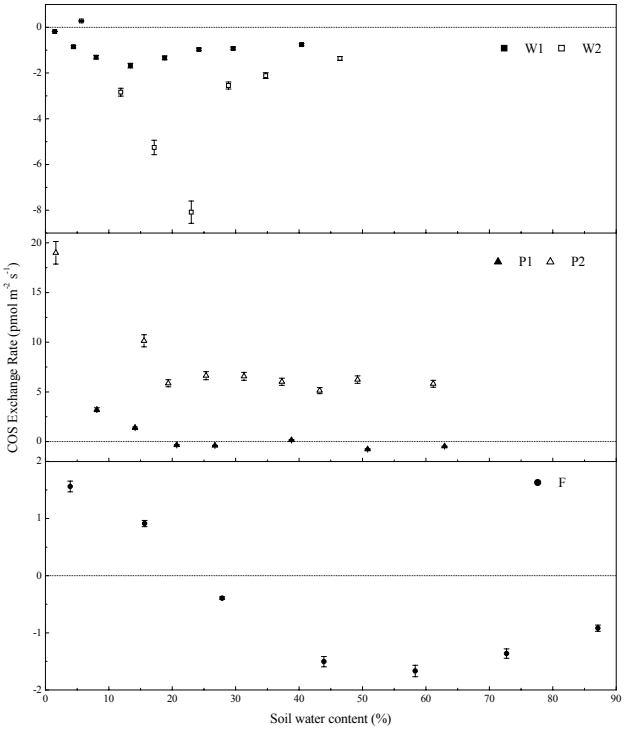

Fig. 5. COS exchange rates in relation to soil water content at 17 °C. (W1: wheat soil in Beijing; W2: wheat soil in Zibo (Shandong Province); P1: Paddy soil in Jiaxing (Zhejiang Province); P2: Paddy soil in Guangzhou (Guangdong Province); F: forest soil in Beijing). The error bars are calculated from formula (2); each exchange rate measurement was conducted twice.

model developed by Conrad (1994) and Kesselmeier et al. (1999) for several kinds of soils.

3.3 COS exchange rates under varying soil moistures

Soil water content is also a critical parameter controlling the exchange of trace gases (Conrad, 1995; Meixner et al., 1997; Kesselmeier et al., 1999), because it influences chemical, physical, and biological processes. The exchange rates of COS under varying soil water contents were also determined in this study under the optimal temperature at 17 °C. A cool environment allowed for several repetitions of the measurements with negligible water loss (0.3–0.8%). Again, we used air with a COS concentration of 500±80 ppt, and the results are shown in Fig. 5.

With only one exception for W2 at low moisture content of 5.66%, both W1 and W2 acted as a sink for atmospheric COS with varying the soil water content from 1.46% to 46.5%. The optimum water contents for W1 and W2 were found to be 13.4% and 23.0%, respectively. The maximum uptake rate for W2 was higher by a factor of 5 than that for W1. As for the forest soil (F), net emission was observed when soil water content was below 20%, whereas uptake increased with increasing soil water content, up to optimum at 58.3% water content.

The two paddy soils (P1 and P2) showed decreasing COS emission with increasing soil water content until the exchange rates reached a steady state when soil water content was above 20%. For P1, the steady exchange rate was about 0 pmol m^{-2} s^{-1}, and for P2, the steady exchange rate was about 6 pmol m^{-2} s^{-1}. Paddy soils are constantly waterlogged during rice growing season, the effects of waterlogging on COS exchange rates from the paddy soils were also investigated. No evident COS exchange was found after watering the paddy soils of P1 and P2 with de-ionized water to full saturation (soil surface covered with a water film), indicating that water cover prevents gas exchange with the atmosphere. It should be noted that the incubation of the soils under this condition lasted for less than 2 h. Therefore, the zero exchange rate observed in this study might be due to the non-equilibrium of COS between the soils and the water.

COS exchange rates were also investigated in the paddy field of Jiaxing, Zhejiang province. The measured exchange rates, soil temperatures, the actual ambient COS concentration in the field, and soil water contents for three patches are

Table 4. Field measurements for COS exchange rates from the paddy soil in Jiaxing, Zhejiang province.

Patch	Soil temperature (°C)	Soil water content (%)	Ambient COS concentration (ppt)	Exchange Rate (pmol m^{-2} s^{-1})
1	22	19.6	3008	−57.9 (sink)
			1390	19.6 (source)
2	26	25.3	1695	26.8 (source)
			1866	18.0 (source)
3	24	31.0 (under waterlogging)	1764	−2.11(sink)
			1762	0

listed in Table 4. In general, the field measurements agreed with the laboratory simulation. As shown in Table 4, COS exchange rate and its direction on the paddy soil strongly depend on ambient COS concentration. The strength of COS emission was much higher at 26 °C than at 22 °C, although the water content was greater in the patch with soil temperature of 26 °C than the patch of 22 °C. COS exchange rates under waterlogged conditions were also close to zero. The compensation point for the paddy soil from Jiaxing obtained by laboratory simulation was about 765 ppt at 25 °C (Table 3). However, obvious emission was observed by field measurements when ambient COS concentration was around 1500 ppt. The soil samples were strongly disturbed by sampling and treatments, e.g., the soils would become loose after sieving, and the redox potential of the soils would become higher due to the increasing probability of the air contacting with the soils. The influence of treatments on the investigated paddy soils may be more serious than the wheat soils, because the field paddy soils are always under anoxic condition. The increasing redox potential of the paddy soils would result in less COS production rate and lower compensation points, and the compensation points for the two paddy soils obtained by this study only represented their lower limits.

It should be mentioned that the ambient COS concentration in Jiaxing was extremely high; it was higher than the background COS concentration by a factor of 3. The memory effect of the Teflon bags was checked by using the ambient air of Beijing three times, and an increment in COS concentration of about 10% was found during three days' storage. The high COS concentration in the field may be ascribed to the strong COS emission by the soil, the direct sources from a power plant about 1 kilometer away and a pig factory nearby the field.

4 Discussion

Paddy soils, which are always in a waterlogged condition, tend toward "anoxic" conditions. The laboratory simulation and short-term field measurements in this study further confirmed that most paddy soils act as sources of atmospheric COS. COS emission from these types of soil have been recognized previously (Devai and Delaune, 1995; Kanda et al., 1992; Yang et al., 1996, 1998; Yi et al., 2008). Yang et al. (1998) found that COS mainly exhibited emission (only sometimes with uptake) from a paddy field (including rice plant) in Nanjing. Kanda et al. (1992) also observed net COS emission from a pay field in Japan after harvest when the paddy soil was dry. The preliminary field measurement in this study supported their findings, because strong COS emission potential of the paddy soils during non-waterlogged period (Table 4). The results of laboratory simulation in this study indicated that COS emission potential (the compensation points and the emission rates under various conditions) of the paddy soil from Guangzhou was much higher than the paddy soil from Jiaxing (Fig. 4). However, Yi et al. (2008) observed net sink of COS from the paddy soil of Guangzhou (the paddy soil of P2 in this study was from the same field) during non-waterlogged period, which was inconsistent with our field measurement and those investigated by Kanda et al. (1992) and Yang et al. (1998).

The emission rates from the two paddy soils investigated in this study decreased significantly as the soils' water content increased, especially when the soils were waterlogged. As for waterlogged soils, the laboratory simulation in this study may underestimate COS emission strength due to short time incubation. However, the field measurement for the waterlogged paddy soil (it was under waterlogged status for at least one month) in Jiaxing was in good agreement with the laboratory simulation. The results of this study for the waterlogged soil were inconsistent with previous studies both on field measurements (Kanda et al., 1992; Yang et al., 1998; Yi et al., 2008) and laboratory simulation (Devai and DeLaune, 1995; Yang et al., 1996). In addition to the short time incubation for laboratory simulation, the dynamic chamber setup used in this study was responsible for underestimation of COS emission from the waterlogged soil. Gas exchange between the air and water surface mainly depends on the degree of turbulence in the fluids (Liss and Slater, 1974). Compared with those of static chambers using fans for mixing the air (Kanda et al., 1992; Yi et al., 2008) and that using purge method (Devai and DeLaune, 1995), the turbulence of

the interface between the air and water under the steady and slow air flow rate in the dynamic chambers might be negligible. In addition, the photochemical production of COS in water covered by transparent static chambers (Yi et al., 2008) made of Teflon film may also result in strong COS emission for the waterlogged soil because a large quantity of COS precursor(s), which is/are easily converted to COS under sunlight, existed in water system (Andreae and Ferek, 1992; Mu et al., 2004).

With the exception of paddy soils, all soils investigated in this study acted as sinks for atmospheric COS, the range of exchange rates was 0–(-4.90) pmol m^{-2} s^{-1}, which agrees with field experiments: 0–(-6.52) pmol m^{-2} s^{-1} (Geng and Mu, 2004) for lawn soil in Beijing, China; -1.4–(-8.4) pmol m^{-2} s^{-1} for un-vegetated forest soil (Castro and Galloway, 1991); and -1.5–(-10.3) pmol m^{-2} s^{-1} for arable soil (Kesselmeier, et al., 1999). The large difference for COS exchange rates among different soils as well as the complicated influencing factors indicated that the estimations of COS emission from "oxic" soils based on only two types of soils must be made with caution (Watts, 2000).

Van Diest and Kesselmeier (2008) investigated COS exchanges between four kinds of soils and the atmosphere and found the same optimal COS uptake at 19% WFPS for the three different boreal soils (two arable soils from China and Finland and one forest soil from Siberia). Supposing the bulk density of the investigated soils were about 1 g cm^{-3} (the bulk densities of the investigated soils were not measured), WFPS can be calculated according to the general particle density using the formula adopted by Van Diest and Kesselmeier (2008). The calculated WFPS value of optimal COS uptake for W1 soil was 21.5% which is coincident with that of Van Diest and Kesselmeier (2008). However, the values for W2 (36.9%) and F (93.6%) soils were much higher than 19%, indicating large difference of the optimal WFPS values among various soils from boreal soils.

5 Conclusions

Large differences in COS exchange were observed among the 18 types of soil samples from 12 provinces in China investigated in this study. Soil temperature, soil water content, and COS concentration are important influencing factors for the direction and the magnitude of COS exchange. The compensation points for various soils were significantly different and were strongly dependent upon soil temperature. Most agricultural soils, except for paddy soils, should be considered as COS sinks under natural conditions.

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References

Adams, D. F., Farwell, S. O., Robinson, E., Pack, M. R., and Bamesberger, W. L.: Biogenic sulfur source strengths, Environ. Sci. Technol., 15, 1493–1498, doi:10.1021/es00094a012, 1981.

Andreae, M. O. and Crutzen, P. J.: Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052–1058, doi:10.1126/science.276.5315.1052, 1997.

Andreae, M. O. and Ferek, R. J.: Photochemical production of carbonyl sulfide in seawater and its emission to the atmosphere, Global Biogeochem. Cy., 6, 175–183, doi:10.1029/91GB02809, 1992.

Aneja, V. P., Overton Jr., J. H., Cupitt, L. T., Durham, J. L., and Wilson, W. E.: Direct measurements of emission rates of some atmospheric biogenic sulfur compounds, Tellus, 31, 174–178, 1979.

Badger, M. R. and Price, G. D.: Carbon oxysulfide is an inhibitor of both CO_2 and HCO_3^- uptake in the cyanobacterium synechococcus PCC7942, Plant Physiol., 94, 35–39, doi:10.1104/pp.94.1.35, 1990.

Bartell, U., Hofmann, U., Hofmann, R., Kreuzburg, B., Andreae, M. O., and Kesselmeier, J.: COS and H_2S fluxes over a wet meadow in relation to photosynthetic activity: an analysis of measurements made on 6 September 1990, Atmos. Environ., 27A, 1851–1864, doi:10.1016/0960-1686(93)90290-F, 1993.

Bremner, J. M. and Banwart, W. L.: Sorption of sulfur gases by soils, Soil Biol. Biochem., 8, 79–83, doi:10.1016/0038-0717(76)90068-7, 1976.

Castro, M. S. and Galloway, J. N.: A comparison of sulfur–free and ambient air enclosure techniques for measuring the exchange of reduced sulfur gases between soils and the atmosphere, J. Geophys. Res., 96, 15427–15437, doi:10.1029/91JD01399, 1991.

Chengelis, C. P. and Neal, R. A.: Hepatic carbonyl sulfide metabolism, Biochem. Biophys. Res. Commun., 90, 993–999, doi:10.1016/0006-291X(79)91925-9, 1979.

Chengelis, C. P. and Neal, R. A.: Studies of carbonyl sulfide toxicity: Metabolism by carbonic anhydrase, Toxicol. Appl. Pharmacol., 55, 198–202, doi:10.1016/0041-008X(80)90236-7, 1980.

Chin, M. and Davis, D. D.: Global sources and sinks of OCS and CS_2 and their distributions, Global Biogeochem. Cy., 7, 321–337, doi:10.1029/93GB00568, 1993.

Conrad, R. and Meuser, K.: Soils contain more than one activity consuming carbonyl sulfide, Atmos. Environ., 34, 3635–3639, doi:10.1016/S1352-2310(00)00136-9, 2000.

Conrad, R.: Compensation concentration as a critical variable for regulating the flux of trace gases between soil and atmosphere, Biogeochemistry, 27, 155–170, doi:10.1007/BF00000582, 1994.

Conrad, R.: Soil microbial processes and the cycling of atmospheric trace gases, Phil. Trans. Roy. Soc. Lond. A, 351, 219–230, doi:10.1098/rsta.1995.0030, 1995.

Crutzen, P. J.: The possible importance of CSO for the sulfate layer of the stratosphere, Geophys. Res. Lett., 3, 73–76, doi:10.1029/GL003i002p00073, 1976.

de Mello, W. Z. and Hines, M. E.: Application of static and dynamic enclosures for determining dimethyl sulfide and carbonyl sulfide exchange in Sphagnum peatlands: implications for the magnitude and direction of flux, J. Geophys. Res., 99, 14601–14607, 1994.

de Mello, W. Z.: Factors controlling fluxes of volatile sulfur compounds in Sphagnum peatlands, Ph. D. thesis, Univ. of New Hampshire, Durham, 1992.

Devai, I. and Delaune, R. D.: Formation of volatile sulfur compounds in salt marsh sediment as influenced by soil redox condition, Org. Geochem., 23, 283–287, doi:10.1016/0146-6380(95)00024-9, 1995.

Doerffel, K.: Statistik in der analytischen Chemie, 3rd Edition, Verlag Chemie, Weinheim, Germany, 1984.

Engel, A. and Schmidt, U.: Vertical profile measurements of carbonyl sulfide in the stratosphere, Geophys. Res. Lett., 21, 2219–2222, doi:10.1029/94GL01461, 1994.

Fried, A., Klinger, L. F., and Erickson III, D. J.: Atmospheric carbonyl sulfide exchange in bog microcosms, Geophys. Res. Lett., 20, 129–132, doi:10.1029/93GL00062, 1993.

Geng, C. M. and Mu, Y. J.: Carbonyl sulfide and dimethyl sulfide exchange between lawn and the atmosphere, J. Geophys. Res., 109, D12302, doi:10.1029/2003JD004492, 2004.

Goldan, P. D., Kuster, W. C., Albritton, D. L., and Fehsenfeld, F. C.: The measurement of natural sulfur emissions from soils and vegetation: three sites in the eastern United States revisited, J. Atmos. Chem., 5, 439–467, doi:10.1007/BF00113905, 1987.

Gries, C., Nash III, T. H., and Kesselmeier, J.: Exchange of reduced sulfur gases between lichens and the atmosphere, Biogeochemistry, 26, 25–39, doi:10.1007/BF02180402, 1994.

Hill, F. B., Aneja, V. P., and Felder, R. M.: A technique for measurement of biogenic sulfur emission fluxes, J. Environ. Sci. Heal. A, 13, 199–225, doi:10.1080/10934527809374804, 1978.

Hofmann, D. J.: Increase in the stratospheric background sulfuric acid aerosol mass in the past 10 years, Science, 248, 996–1000, doi:10.1126/science.248.4958.996, 1990.

Hofmann, U., Hofmann, R., and Kesselmeier, J.: Cryogenic trapping of reduced sulfur compounds using a nafion drier and cotton wadding as an oxidant scavenger, Atmos. Environ., 26A, 2445–2449, doi:10.1016/0960-1686(92)90374-T, 1992.

Kanda, K., Tsuruta, H., and Minami, K.: Emission of dimethyl sulfide, carbonyl sulfide, and carbon disulfide from paddy fields, Soil Sci. Plant Nutr., 38, 709–716, 1992.

Kesselmeier, J. and Merk, L.: Exchange of carbonyl sulfide (COS) between agricultural plants and the atmosphere: studies on the deposition of COS to peas, corn and rapeseed, Biogeochemistry, 23, 47–59, doi:10.1007/BF00002922, 1993.

Kesselmeier, J., Meixner, F. X., Hofmann, U., Ajavon, A., Leimbach, S., and Andreae, M. O.: Reduced sulfur compound exchange between the atmosphere and tropical tree species in southern Cameroon, Biogeochemisty, 23, 23–45, doi:10.1007/BF00002921, 1993.

Kesselmeier, J., Teusch, N., and Kuhn, U. Controlling variables for the uptake of atmospheric carbonyl sulfide by soil, J. Geophys. Res., 104, 11577–11584, doi:10.1029/1999JD900090, 1999.

Kettle, A. J., Kuhn, U., von Hobe, M., Kesselmeier, J., and Andreae, M. O.: Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks, J. Geophys. Res., 107, 4658, doi:10.1029/2002JD002187, 2002.

Khalil, M. A. K. and Rasmussen, R. A.: Global sources, lifetimes and mass balances of carbonyl sulfide (OCS) and carbon disulfide (CS_2) in the Earth's atmosphere, Atmos. Environ., 18, 1805–1813, doi:10.1016/0004-6981(84)90356-1, 1984.

Kluczewski, S. M., Brown, K. A., and Bell, J. N. B.: Deposition of [^{35}S]-carbonyl sulphide to vegetable crops, Radiat. Prot. Dosim., 11, 173–177, 1985.

Kuhn, U., Ammann, C., Wolf, A., Meixner, F. X., Andreae, M. O., and Kesselmeier, J.: Carbonyl sulfide exchange on an ecosystem scale: soil represents a dominant sink for atmospheric COS, Atmos. Environ., 33, 995–1008, doi:10.1016/S1352-2310(98)00211-8, 1999.

Kuhn, U., Wolf, A., Gries, C., Nash III, T. H., and Kesselmeier, J.: Field measurements on the exchange of carbonyl sulfide between lichens and the atmosphere, Atmos. Environ., 34, 4867–4878, doi:10.1016/S1352-2310(00)00235-1, 2000.

Lamb, B., Westberg, H., Allwine, G., Bamesberger, L., and Guenther, A.: Measurement of biogenic sulfur emissions from soils and vegetation: application of dynamic enclosure methods with Natusch Filter and GC/FPD analysis, J. Atmos. Chem., 5, 469–491, doi:10.1007/BF00113906, 1987.

Lehmann, S. and Conrad, R.: Characteristics of turnover of carbonyl sulfide in four different soils, J. Atmos. Chem., 23, 193–207, doi:10.1007/BF00048260, 1996.

Liss, P. S. and Slater, P. G.: Flux of gases across the air-sea interface, Nature, 247, 181–184, doi:10.1038/247181a0, 1974.

Liu, G. S.: Soil physical and chemical analysis & description of soil profiles, Standards Press of China, Beijing, China, 1996.

MacTaggart, D. L., Adams, D. F., and Farwell, S. O.: Measurement of biogenic sulfur emissions from soils and vegetation using dynamic enclosure methods: total sulfur gas emissions via MFC/FD/FPD determinations, J. Atmos. Chem., 5, 417–437, doi:10.1007/BF00113904, 1987.

Meixner, F. X., Fickinger, Th., Marufu, L., Serça, D., Nathaus, F. J., Makina, E., Mukurumbira, L., and Andreae, M. O.: Preliminary results on nitric oxide emission from a southern African savanna ecosystem, Nutr. Cycl. Agroecosys., 48, 123–138, doi:10.1023/A:1009765510538, 1997.

Miller, A. G., Espie, G. S., and Canvin, D. T.: Use of carbon oxysulfide, a structural analog of CO_2, to study active CO_2 transport in the cyanobacterium Synechococcus UTEX 625, Plant Physiol., 90, 1221–1231, doi:10.1104/pp.90.3.1221, 1989.

Mu, Y. J., Geng, C. M., Wang, M. Z., Wu, H., Zhang, X. S., and Jiang, G. B.: Photochemical production of carbonyl sulfide in precipitation, J. Geophys. Res., 109, D13301, doi:10.1029/2003JD004206, 2004.

Mu, Y. J., Wu, H., Zhang, X. S., and Jiang, G. B.: Impact of anthropogenic sources on carbonyl sulfide in Beijing city, J. Geophys. Res., 107, 4769, doi:10.1029/2002JD002245, 2002.

Protoschill-Krebs, G. and Kesselmeier, J.: Enzymatic pathways for the consumption of carbonyl sulfide (COS) by higher plants, Bot. Acta, 105, 206–212, 1992.

Protoschill-Krebs, G., Wilhelm, C., and Kesselmeier, J.: Consumption of carbonyl sulfide by Chlamydomonas reinrardtii with different activities of carbonic anhydrase (CA) induced by different CO_2 growing rates, Bot. Acta, 108, 445–448, 1995.

Protoschill-Krebs, G., Wilhelm, C., and Kesselmeier, J.: Consumption of carbonyl sulphide (COS) by higher plant carbonic anyhydrase (CA), Atmos. Environ., 30, 3151–3156, doi:10.1016/1352-

2310(96)00026-X, 1996.

Roche, A. E., Kumer, J. B., Mergenthaler, J. L., Nightingale, R. W., Uplinger, W. G., Ely, G. A., and Potter, J. F.: Observations of lower-stratospheric $ClNO_2$, HNO_3, and aerosol by the UARS CLAES experiment between January 1992 and April 1993, J. Atmos. Sci., 51, 2877–2902, doi:10.1175/1520-0469(1994)051<2877:OOLSCH>2.0.CO;2, 1994.

Sandoval-Soto, L., Stanimirov, M., von Hobe, M., Schmitt, V., Valdes, J., Wild, A., and Kesselmeier, J.: Global uptake of carbonyl sulfide (COS) by terrestrial vegetation: Estimates corrected by deposition velocities normalized to the uptake of carbon dioxide (CO_2), Biogeosciences, 2, 125–132, 2005, http://www.biogeosciences.net/2/125/2005/.

Solomon, S., Sanders, R. W., Garcia, R. R., and Keys, J. G.: Increased chlorine dioxide over Antarctica caused by volcanic aerosols from Mount Pinatubo, Nature, 363, 245–248, doi:10.1038/363245a0, 1993.

Turco, R. P., Whitten, R. C., Toon, O. B., Pollack, J. B., and Hamill, P.: OCS, stratospheric aerosols and climate, Nature, 283, 283–286, doi:10.1038/283283a0, 1980.

Van Diest, H. and Kesselmeier, J.: Soil atmosphere exchange of carbonyl sulfide (COS) regulated by diffusivity depending on water-filled pore space, Biogeosciences, 5, 475–483, 2008, http://www.biogeosciences.net/5/475/2008/.

Watts, S. F.: The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide, Atmos. Environ., 34, 761–779, doi:10.1016/S1352-2310(99)00342-8, 2000.

Xu, X., Bingemer, H. G., and Schmidt, U.: The flux of carbonyl sulfide and carbon disulfide between the atmosphere and a spruce forest, Atmos. Chem. Phys., 2, 171–181, 2002, http://www.atmos-chem-phys.net/2/171/2002/.

Yang, Z., Kanda, K., Tsuruta, H., and Minami, K.: Measurement of biogenic sulfur gases emission from some Chinese and Japanese soils, Atmos. Environ., 30, 2399–2405, doi:10.1016/1352-2310(95)00247-2, 1996.

Yang, Z., Kong L., Zhang, J., Wang, L. and Xi, S.: Emission of biogenic sulfur gases from Chinese rice paddies, Sci. Total. Environ., 224, 1–8, doi:10.1016/S0048-9697(98)00207-1, 1998.

Yi, Z. G., Wang X. M., Sheng, G. Y., and Fu, J. M.: Exchange of carbonyl sulfide (OCS) and dimethyl sulfide (DMS) between rice paddy fields and the atmosphere in subtropical China, Agr. Ecosyst. Environ., 123, 116–124, doi:10.1016/j.agee.2007.05.011, 2008.

Yi, Z. G., Wang X. M., Sheng, G. Y., Zhang, D. Q., Zhou, G. Y., and Fu, J. M.: Soil uptake of carbonyl sulfide in subtropical forests with different successional stages in south China, J. Geophys. Res., 112, D08302, doi:10.1029/2006JD008048, 2007.