



Soil uptake of carbonyl sulfide in subtropical forests with different successional stages in south China

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[1] The uptake rates of carbonyl sulfide (COS) by soils in subtropical forests with different successional stages were measured using static chambers in Dinghushan Biosphere Reserve (DBR) in south China from July 2004 to March 2005. The three typical tropical forests studied included monsoon evergreen broad-leaf forest (BF), pine and broad-leaf mixed forest (MF) and pine forest (PF), representing forests with different successional stages in the region. COS exchange rates were also compared between the plots with litter-fall remaining (plots L) and those with litter-fall removed (plots S) in each forest. Results showed that these forest soils all acted as sinks for COS with exchange rates of -1.22 to -11.82 $\text{pmol m}^{-2} \text{s}^{-1}$. The MF in the midsuccessional stage had significantly higher uptake rates, and the mean exchange rates in the BF, MF, and PF were -3.90 , -4.77 , and -3.65 $\text{pmol m}^{-2} \text{s}^{-1}$, respectively. COS uptake rates at plots L were higher than those at plots S. Mean COS fluxes were significantly higher in March (-6.06 $\text{pmol m}^{-2} \text{s}^{-1}$) than those in July (-3.60 $\text{pmol m}^{-2} \text{s}^{-1}$), August (-3.82 $\text{pmol m}^{-2} \text{s}^{-1}$), September (-3.45 $\text{pmol m}^{-2} \text{s}^{-1}$), and October (-3.54 $\text{pmol m}^{-2} \text{s}^{-1}$). Significant correlation was observed between the COS uptake rates and soil respiration rates or microbial biomass, indicating that microbial activity was an important factor controlling the soil uptake of COS. Significant correlations between COS fluxes and initial COS mixing ratios were only observed in the BF and MF. COS fluxes showed no correlation with soil temperature or water content alone in any of the three forests, but do correlate well with soil temperature and water content together in polynomial forms with an order of 2.

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1. Introduction

[2] As the most abundant sulfur-containing trace gas in the atmosphere, carbonyl sulfide (COS) has a low reactivity in the gas phase and a longer lifetime relative to its atmospheric mixing times (>1 year). Therefore it can reach the stratosphere, where it is oxidized and contributes to the stratospheric sulfate aerosol (SSA). COS was once recognized to be the main source of sulfate in the stratosphere during nonvolcanic periods [Crutzen, 1976; Engel and Schmidt, 1994]. But later studies suggested that COS may account for a smaller fraction of the sulfate present in the stratospheric Junge layer than previously thought [Chin and Davis, 1995; Kjellstrom, 1998]. On the basis of a global

three-dimensional model, Pitari *et al.* [2002] estimated that COS photochemical oxidation could account for 43% of the total background SSA, while the upward transport of tropospheric sulfate and SO_2 contributes 30 and 27%, respectively. Due to the importance of SSA in the radiative balance of the atmosphere [Turco *et al.*, 1980; Charlson *et al.*, 1987] and in the ozone-depleting chemistry [Fahey *et al.*, 1993; Roche *et al.*, 1994; Solomon *et al.*, 1996], the investigation of sources and sinks with regard to COS has been intensified in recent decades.

[3] COS has a variety of natural and anthropogenic emission sources [Andreae and Ferek, 1992; Chin and Davis, 1993; Nguyen *et al.*, 1995; Weiss *et al.*, 1995; Ulshöfer *et al.*, 1996; Ulshöfer and Andreae, 1997; Watts, 2000], and is also formed by oxidation of carbon disulfide (CS_2) and dimethyl sulfide (DMS) [Chin and Davis, 1993; Barnes *et al.*, 1994]. The major sinks of COS include vegetation [Hofmann, 1993; Kesselmeier and Merk, 1993; Kuhn *et al.*, 1999], soils [De Mello and Hines, 1994], and oxidation and photolysis in the atmosphere [Chin and Davis, 1993]. Previous estimates of global sources and sinks of COS all indicated a predominance of sources over sinks [Chin and Davis, 1993; Watts, 2000], with sources

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exceeding sinks by about a factor of 2 in earlier works [Chin and Davis, 1993], or by $\sim 30\%$ in best recent estimates [Watts, 2000]. These imbalanced budgets, especially the earlier budgets with deficits ranging between 0.7 to 1.0 Tg a⁻¹ [Toon et al., 1987; Chin and Davis, 1993], were obviously in conflict with periodic surface measurements [Bandy et al., 1992; Thornton et al., 1996], with the results of total column abundances [Mahieu et al., 1997; Griffith et al., 1998; Rinsland et al., 2002], and with firm air records in both hemispheres [Sturges et al., 2001]. All these observations showed no positive trends implied by such an imbalance, but even a slight decrease [Mahieu et al., 1997; Sturges et al., 2001; Rinsland et al., 2002]. This disagreement suggests the presence of undiscovered sinks, severely underestimated sink strengths [Sandoval-Soto et al., 2005] or overestimates of the source strengths.

[4] Much more balanced budgets with similar magnitude of sinks and sources [Watts, 2000] came with a revision of the net influence of open and coastal oceans [Andreae and Ferek, 1992; Ulshöfer et al., 1995; Weiss et al., 1995; Ulshöfer and Andreae, 1997] and especially with the new understanding of soil-atmosphere fluxes. Soil emission studies before 1990 used COS-free air as a sweep gas in the soil flux chamber. These methods generated an artificial COS gas concentration gradient between the headspace of the enclosure and the soil, and thus not only led to an overestimation of natural emission strength by enhancing the diffusion of COS from the soil into the headspace, but also masked the potential of soils as a sink. As a result, these estimates all indicated that soils are a source of COS [Aneja et al., 1979; Steudler and Peterson, 1985; Carroll et al., 1986; Goldan et al., 1987; Fall et al., 1988; Staubes et al., 1989], contributing around 21–25% of the total global source [Khalil and Rasmussen, 1984; Chin and Davis, 1993; Johnson et al., 1993]. In contrast, Castro and Galloway [1991] suggested a much enhanced role for soils in the removal of COS from the atmosphere, and De Mello and Hines [1994], using ambient air as sweep gases, consistently found that soils took up COS at rates of 3 to 30 ng S m⁻² min⁻¹ (1.6–15.6 pmol m⁻² s⁻¹). These findings were also confirmed by more recent field or laboratory works using enclosures employing ambient air as a sweep gas [Kesselmeier et al., 1999; Kuhn et al., 1999; Simmons et al., 1999; Geng and Mu, 2004; Steinbacher et al., 2004]. With these observations and new understanding, soils had changed from the third largest source in the COS budgets according to Chin and Davis [1993] to the most important sink in the global budgets of COS according to Watts [2000].

[5] Although the understanding of soils as a major sink helps to explain the “missing sinks” for COS, soil uptakes still show a wide scattering among different environments, and the data obtained by the ambient-air method are still too sparse to derive a reliable global estimate of soil sinks for COS; there may exist an uncertainty of 50–100% on the global COS uptake by soils [Andreae and Crutzen, 1997; Kettle et al., 2002; Watts, 2000]. Watts [2000] pointed out that the main uncertainties of COS global budgets are in the sinks, and that the estimate of soil uptake is the most precarious. While the ocean-atmosphere exchange of COS is described and characterized with growing confidence, obviously there is a need for field studies of COS exchange in natural terrestrial ecosystems to obtain reliable quantita-

tive data for COS budget estimations [Andreae and Crutzen, 1997], especially those in forest ecosystems and between soil and atmosphere. Improved estimates of soil sinks for COS would require extended field measurements to cover various terrestrial environments for soil-atmosphere exchange of COS and that some important parameters governing the emissions or uptakes of COS are well characterized.

[6] In China, studies on COS have been carried out by incubating paddy soils in the laboratory [Yang et al., 1996, 1998]. A few studies were also performed recently in natural terrestrial ecosystems, including agricultural ecosystems [Nie et al., 2001; Zhang et al., 2003] and a lawn ecosystem [Geng and Mu, 2004]. As for COS exchange between atmosphere and forest soils, no data have been reported yet in China. On a regional or global scale, COS flux between soil and atmosphere in tropical/subtropical forests has not been well documented, which will prevent us from understanding the role of forest soils within this region in the global COS budget.

[7] In the present study, three main types of subtropical forests, including monsoon evergreen broad-leaf forest (BF), pine and broad-leaf mixed forest (MF), and pine forest (PF), were selected for measuring soil-air COS exchange fluxes. These three forest types represent different stages in the succession series, with BF being the climax vegetation and PF being the primary one. In addition to measuring COS exchange fluxes between atmosphere and forest soils, the influence of a number of environmental factors, such as ambient COS mixing ratios, soil microorganisms, litter-falls, temperature, and soil water contents, were also investigated.

2. Experiment

2.1. Site Description

[8] Field works were conducted from July 2004 to March 2005 at Dinghushan Biosphere Reserve (DBR, 23°09'21"~23°11'30"N, and 112°30'39"~112°33'41"E) in Guangdong Province, south China. DBR lies in the low mountains of the Dayunwu Mountain Range of the Cathayian Platform, formed in the Sinian Period. The soils in this area are mainly lateritic red-earth and yellow-earth. Soil characteristics were analyzed, and are summarized in Table 1. The annual mean temperature is 21°C at DBR, with a maximum monthly mean of 28.0°C in July and a minimum monthly mean of 12.6°C in January. The mean annual rainfall there is 1927 mm. The rainy season (April to September) has a monthly mean rainfall of 200 mm, and the dry season (November to January) has a monthly mean rainfall of only 22–50 mm. Relative humidity (RH) is high and fairly constant throughout the year at DBR, with the highest RH of 86.5% in March and the lowest RH of 73.5% in December [Ding et al., 2001]. BF, MF, and PF investigated in the present study are three major forest types in the area, representing climax, midsuccessional and early successional forest communities, respectively. The forests are quite near the Pearl River Delta, one of the most densely populated and industrialized areas in China. The COS concentration in the whole Pearl River Delta region is relatively high, possibly due to vast emissions from coal-fired power stations. PF is near a village and BF is near a tourist site, while MF is far from human disturbance. In the

Table 1. Characteristics of the Experimental Sites

Forest Type ^a	Elevation Above Sea Level, m	Soil Properties ^b				
		Bulk Density	pH	Organic Carbon, g kg ⁻¹	Total Sulfur, mg kg ⁻¹	Available Sulfur, mg kg ⁻¹
BF	270–300	0.91 ± 0.12	3.7 ± 0.2	39.5 ± 14.0	410.4 ± 62.8	80.7 ± 10.1
MF	~300	1.05 ± 0.18	3.8 ± 0.5	25.1 ± 4.4	244.7 ± 9.0	52.5 ± 14.8
PF	70–80	1.50 ± 1.15	4.3 ± 0.3	15.1 ± 3.1	112.9 ± 27.1	39.5 ± 17.0

^aBF: Monsoon evergreen broad-leaf forest; MF: pine and broad-leaf mixed forest; PF: pine forest.

^bThe mean values of 0–15 cm deep soil, $n = 6$.

present study in BF, PF, and MF, plots with litter remaining (plots L) and with litter removed (plots S) were measured simultaneously in each forest to investigate soil uptake of COS as well as the impact of litter falls.

2.2. Construction and Performance of Static Chamber Systems

[9] COS fluxes in the field were determined using the static enclosure technique. Cubic chambers (50 × 50 × 50 cm) were made of stainless steel plates with their inner walls coated with Teflon films. Each chamber was placed on a Teflon-lined collar that was installed 2 weeks before the field measurement. All photoactive materials were avoided in the enclosed area. To observe the effect of litter-falls on COS uptake by soils, in each forest there were three enclosed plots with litter falls removed and three other enclosed plots where litter falls were not removed. Two fans were installed inside the chamber to ensure that the air was well mixed. Air samples were collected into 0.5-L Tedlar sampling bags (SKC Inc., USA) at 0, 5, 10, 20, and 30 min after the chamber was placed on the collar. All field observations were conducted between 10:00 and 13:00, and the diurnal variation of COS fluxes were only observed in October. Besides plots L and plots S, a control chamber with bottom soils covered by Teflon sheets was also measured in the same manner to evaluate possible enclosure loss or contamination problems of COS inside the enclosure.

[10] Air temperature inside the chamber and soil temperature at a depth of 5 cm were measured with thermocouples (TES Electrical Electronic Corp., Taipei, Taiwan), and soil water content was measured with Delta-T's ML2X soil water sensor (Delta-T Devices Ltd., Cambridge, England) simultaneously. Soil microbes were also measured by viable counting methods. The culture mediums were Nutrient Agar for bacteria, Rose Bengal-Martin for fungi and Gao's No. 1 for actinomycete. After inoculating, samples were incubated at 28°C for 1–2 d for bacteria, 4–6 d for fungi, and 7–8 d for actinomycete, and the amount of the microbes were counted. Soil microbial biomass C was measured by fumigation-incubation method (FI) [Jenkinson and Powlson, 1976] with minor modifications. Briefly, 200-g fresh soil in a small beaker was fumigated with chloroform vapor for 24 h. After removal of chloroform, each soil sample was inoculated with 1 g of original fresh soil and adjusted to an appropriate moisture content (about 56% water holding capacity), then incubated at 28°C for 10 d. The same procedures were applied to the control soil samples except for fumigation. The biomass was calculated from the difference of the amount of CO₂ evolved during incubation between fumigated and control soil. Microbial biomass C

was calculated using the conversion coefficient of 0.41 [Anderson and Domsch, 1978].

2.3. Laboratory Analytical Methods

[11] COS was analyzed by an Entech model 7100 Pre-concentrator (Entech Instruments Inc., CA, USA) coupled to an Agilent 5973N gas chromatography-mass selective detector (GC-MSD, Agilent Technologies, USA). For the preconcentration of COS in air samples there are three stages of trapping in the Entech Preconcentrator. In the first stage, 250 mL (1 atm, 0°C) air samples were drawn through a liquid nitrogen trap at –160°C to trap the COS. After this, the first-stage trap was heated to 10°C and the trapped gases were transferred by 40 mL helium at a flow of 10 mL/min to a second-stage trap with Tenax sorbents at –40°C. Most of the CO₂ was removed during this stage. Then the second-stage trap was heated to 150°C and the thermally desorbed gases were transferred to a third-stage cryo-focusing trap at –170°C by 30 mL helium at a rate of 10 mL/min. This cryogenic focusing is necessary to improve the separation in the GC column and to improve the shapes of the GC peaks. A HP-1 capillary column (60 m in length × 320 μm I.D. × 1.0 μm film thickness, Agilent Technologies, USA) was used, and the GC oven temperature was programmed initially at –50°C, holding for 2 min, increasing to 100°C at 5°C min⁻¹, then to 250°C at 10°C min⁻¹, and then holding for 10 min. The MSD was used in selected ion monitoring (SIM) mode and the ionization method was electron impacting (EI). For measuring COS, m/z 60 was set as the target ion.

[12] A 100-μL COS (purity > 99%, Sigma-Aldrich, Inc., St. Louis, USA) was drawn with a gas-tight syringe and injected into 100-L pure nitrogen in a Teflon bag (Cat. No. 231-50, SKC Inc., USA) to get the 1.0-ppmv primary COS standard. This primary standard was further dynamically diluted with pure nitrogen to calibration standards by using mass flow controllers and a mixing chamber. Calibration curves were obtained by running 250-mL standard gas with COS levels of 0, 250, 500, 1000, 1500, and 2000 pptv in nitrogen, respectively. The method detection limit for COS was less than 20 pptv with a sample volume of 250 mL; the relative standard deviations were all less than 6% based on 10 duplicates running for 10 consecutive days with COS standards of 100 and 1000 pptv.

[13] CO₂ mixing ratios were measured with a HP 4890D gas chromatography. A 20-mL air samples were injected directly into the GC. After being transformed to methane in a catalytic hydrogenation reactor, CO₂ was detected by a flame ionization detector (FID). The concentration of CO₂ was calibrated with samples from a standard gas mixture of

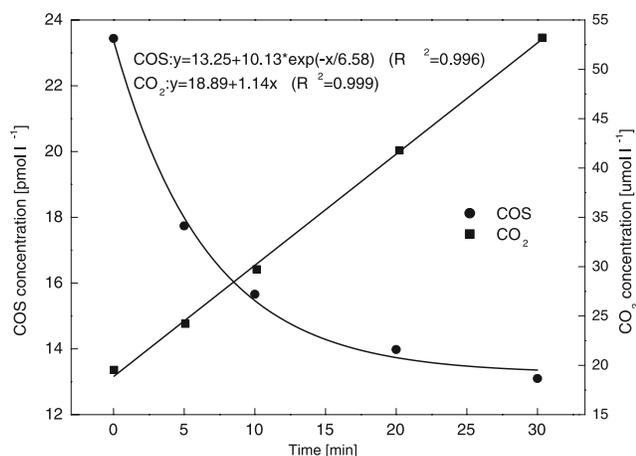


Figure 1. Typical COS and CO₂ evolution in the chamber for the flux measurements.

390 ppm (Foshan Kedi Gas Chemical Industry Co., Ltd, China).

2.4. COS Flux Calculation

[14] The gas exchange rate F in the chamber was calculated using the following equation

$$F = H \times \left(\frac{dC}{dt} \right)_{t=0} \quad (1)$$

where H is the enclosure geometry factor, i.e., the ratio of the chamber volume to the enclosed soil area, and $[dC / dt]_{t=0}$ is the slope of the curve of the gas mixing ratio change within the enclosure headspace at time 0, assuming uniform mixing within the enclosure [Matthias *et al.*, 1978]. To calculate $[dC / dt]_{t=0}$, the mixing ratio versus time data were fitted to an exponential equation of the form

$$C(t) = a - b \times \exp(-kt) \quad (2)$$

where $a = C_{\max}$, which is the COS mixing ratio reached within the enclosure headspace equals the COS mixing ratio in the soil atmosphere; $b = C_{\max}$ minus the COS mixing ratio at $t = 0$ (C_{air}), and k is the rate constant. C_{\max} and k were iteratively derived by computer and then used to calculate $[dC / dt]_{t=0}$ from the equation

$$\left(\frac{dC}{dt} \right)_{t=0} = k \times b = k(C_{\max} - C_{\text{air}}) \quad (3)$$

which was then incorporated in equation (1) to calculate the flux in mass per unit area per time [De Mello and Hines, 1994]. For CO₂, the mixing ratio versus time data were fitted to linear equation, and the soil respiration rate (Re) was calculated using the following equation

$$\text{Re} = H \times K \quad (4)$$

where K is the slope of CO₂ mixing ratio versus time, H is the same as equation (1). A typical COS and CO₂ evolution in the chamber is shown in Figure 1.

2.5. Data Analysis

[15] A one-way ANOVA was performed to test the significant variance between the samples. A post hoc examination was conducted to test the significance using the LSD test. The difference between plots L and plots S was tested by independent samples t test. The significance level was set as $p < 0.05$. Statistical analysis was performed using SPSS 10.0 for Windows. The correlation test was performed using SigmaPlot 9.0.

3. Results and Discussion

3.1. Measured Fluxes and Their Diurnal/Seasonal Variations

[16] As Conrad [1994] pointed out, gas exchange between soil and atmosphere could be regarded as a result of simultaneously operating production and consumption processes. This implies that there exists a dynamic balance of COS flux and a so-called compensation point, which is an ambient concentration where the consumption rates are equal to the production rates and the net flux is zero. Ambient concentrations below the compensation point concentration results in net emission, and a concentration above it results in net deposition. The applicability of this concept has been empirically confirmed for exchange of various biogenic trace gases with soils [Remde *et al.*, 1993; Conrad, 1994]. The lowest ambient COS mixing ratio in the present study was 232 pptv, much higher than the compensation point for soil (53 pptv) reported by Kesselmeier *et al.* [1999] and for plants (90–150 pptv) reported by Kesselmeier and Merk [1993].

[17] The results of the present study clearly demonstrate that forest soils in DBR, either with or without litter fall, were serving as significant sinks for atmospheric COS, with uptake rates between -1.22 and -11.82 pmol m⁻² s⁻¹. These uptake rates are within the range of the values reported by other researchers (Table 2). The average COS fluxes were -3.90 ± 0.81 pmol m⁻² s⁻¹, -4.77 ± 2.85 pmol m⁻² s⁻¹ and -3.65 ± 2.05 pmol m⁻² s⁻¹ in BF, MF, and PF, respectively. The average COS uptake rate was significantly higher in MF than in PF.

[18] Diurnal and seasonal variations of COS fluxes were also investigated in this study. On the basis of the field measurements every three hours during one day in October 2004, no obvious diurnal COS flux cycles were observed for soils in all three forests, though COS fluxes in the daytime (9:00–18:00) tended to be higher than at night (21:00–6:00). This was in agreement with results reported by Geng and Mu [2004], who did not observe a diurnal cycle of COS uptake for lawn soils. Kuhn *et al.* [1999] also found that uptake was greater during the daytime, with declining but persistent values at night. The uptake rates in different months, however, were significantly different, with values of -3.63 to -11.82 pmol m⁻² s⁻¹ in March, which were significantly higher than those in other months (-1.22 to -6.87 pmol m⁻² s⁻¹) (Table 3). This seasonal variation might be attributed to the change of ambient COS concentrations, temperatures and soil water content, according to previous studies [Kesselmeier *et al.*, 1999; Kuhn *et al.*, 1999; Kuhn and Kesselmeier, 2000; Geng and Mu, 2004]. Our seasonal patterns of COS fluxes were in good agreement with those found in other studies [Kuhn *et al.*, 1999;

Table 2. COS Exchange Rates at DBR in Comparison With Other Reported Values

Soils	COS Exchange Rate, $\text{pmol m}^{-2} \text{s}^{-1}$	Reference
BF Soil	-3.90 ± 0.81^a ($n = 39$)	This paper
MF Soil	-4.77 ± 2.85 ($n = 42$)	This paper
PF Soil	-3.65 ± 2.05 ($n = 24$)	This paper
City Lawn Soil	0 to -6.52	<i>Geng and Mu</i> [2004]
Unvegetated Forest Soil	-1.4 to -8.4	<i>Castro and Galloway</i> [1991]
Intact Peat Soil	-1.25 to -4.2	<i>Fried et al.</i> [1993]
Intact Peat Soil	-1.0 to -15.3	<i>De Mello and Hines</i> [1994]
Vegetated Coniferous Boreal Forest Soil	-3.58 ± 2.67	<i>Simmons et al.</i> [1999]
Unvegetated Coniferous Boreal Forest Soil	-2.5 ± 1.3	<i>Simmons et al.</i> [1999]
Open Oak Woodland Soil	-8.8 to -13.3	<i>Kuhn et al.</i> [1999]
Spruce Forest Soil	-0.23 to -1.38	<i>Steinbacher et al.</i> [2004]
Barley Soil	-1.5 to -10.3	<i>Kesselmeier et al.</i> [1999]

^aMean \pm standard deviation.

Geng and Mu, 2004], but seasonal variation of COS uptake in spruce forest was not found in the study conducted by *Xu et al.* [2002].

3.2. Soil Uptake Rates in Different Successional Forests

[19] In the present study, though the selected BF, MF, and PF are less than 2 km from each other in their horizontal distances, there exist significant differences in their soil COS uptake rates. The MF in the midsuccessional stage had significantly higher soil uptake rates than BF in the climax successional stage or PF in the primary successional stage. This variation with successional stages reveals the difficulty and uncertainty in the estimation of soil-atmosphere fluxes of trace gases in forest ecosystems. Ecological succession occurs with the change in species composition of a natural community. Early successional stages are characterized by pioneer species, low biomass and often low nutrient levels. Community complexity increases as succession progresses,

often peaking in the midsuccessional stage. In forest ecosystems, the change of plant species assemblages in different successional stages will probably influence the COS uptakes by forest plant leaves. On the other hand, as shown in Table 1, soil contents of macroelements, like C, N, and S, will also change as succession progresses from PF to BF. This change in physical, chemical, and biological properties of forest soils with succession stages would certainly lead to changes of COS uptake rates. Due to the different successional stages for forests in an area, care should be taken when compiling the soil uptake of trace gases from limited field measurements, and a better estimation should consider the difference in forest types.

[20] Previous studies showed that soil redox condition, soil organic matter (SOM), soil nitrogen and sulfur content, soil microorganisms, and other factors would all influence soil COS flux [*Devai and DeLaune*, 1995; *Kesselmeier et al.*, 1999; *Kettle et al.*, 2002]. As shown in Table 1, the

Table 3. COS Exchange Rates ($\text{pmol m}^{-2} \text{s}^{-1}$) Between the Forest Soils and the Atmosphere Between July 2004 and March 2005 at DBR

Date	Forest type	Ambient COS, pptv	Plot ^a	n	COS Exchange, $\text{pmol m}^{-2} \text{s}^{-1}$
Jul. 2004	BF	630 ± 144	S	6	-2.32 ± 0.99
			L	9	-4.35 ± 0.91
	MF	730 ± 299	S	9	-3.37 ± 2.55
			L	9	-6.87 ± 3.27
	PF	400 ± 82	S	3	-1.78 ± 0.34
			L	3	-2.91 ± 0.32
Aug. 2004	BF	495 ± 46	S	3	-3.02 ± 0.61
			L	3	-3.25 ± 0.79
	MF	517 ± 39	S	3	-2.26 ± 0.98
			L	3	-4.54 ± 1.47
	PF	465 ± 28	S	3	-4.60 ± 1.48
			L	3	-5.23 ± 1.01
Sep. 2004	BF	685 ± 173	S	3	-3.73 ± 1.02
			L	3	-4.35 ± 3.68
	MF	649 ± 226	S	3	-2.22 ± 0.57
			L	3	-3.48 ± 1.98
Oct. 2004	BF	851 ± 41	S	3	-4.11 ± 0.34
			L	3	-4.81 ± 1.92
	MF	870 ± 101	S	3	-4.04 ± 1.30
			L	3	-5.44 ± 1.18
	PF	980 ± 240	S	3	-1.22 ± 0.16
			L	3	-1.62 ± 0.47
Mar. 2005	BF	810 ± 142	S	3	-4.74 ± 3.58
			L	3	-4.30 ± 0.88
	MF	1086 ± 116	S	3	-3.63 ± 2.66
			L	3	-11.82 ± 0.27
	PF	1312 ± 68	S	3	-5.05 ± 1.77
			L	3	-6.79 ± 2.51

^aL: Plot with litter; S: plot with litter removed.

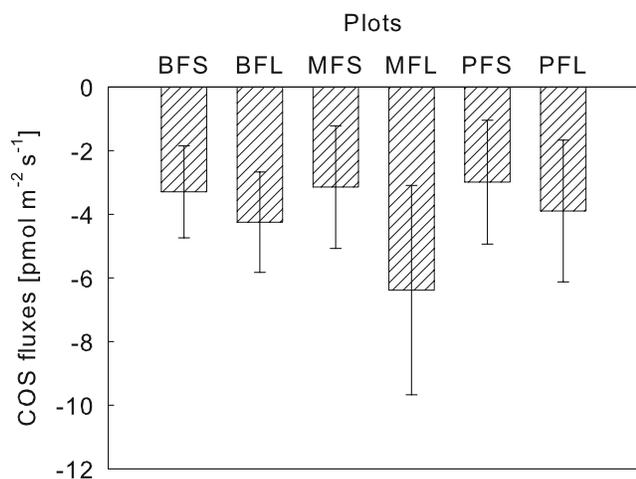


Figure 2. Mean COS fluxes from July 2004 to March 2005. BFS ($n = 18$) and BFL ($n = 21$) represent plots without and with litter, respectively, in the broadleaf forest. MFS ($n = 21$) and MFL ($n = 21$) represent plots without and with litter, respectively, in the mixed forest. PFS ($n = 12$) and PFL ($n = 12$) represent plots with and without litter, respectively, in pine forest. Error bars represent the standard deviation.

variations of soil organic carbon (OC), total sulfur (TS), and available sulfur (AS) were significant among the three forests, with the highest in the BF and the lowest in the PF. The lowest OC, TS, and AS in the PF might be part of the reason for the significantly low COS fluxes in the PF. But only the content of OC, TS and AS could not explain the highest COS fluxes in the MF. Simmons *et al.* [1999] indicated that the available N, rather than S, might be more important influencing COS uptake by soils. They also found that the addition of sulfur might otherwise decrease the COS uptake by soils, and net COS consumption was low in a S-amended site due to a surplus of available S. Though further research on the effect of nitrogen and sulfur on soil COS fluxes is needed, one would not expect a simple relationship between macroelements and COS fluxes considering the complex nature of soils. As discussed below, soil microbial activity shows a much closer relationship with the soil uptake rate of COS.

3.3. Effect of Litter Falls on COS Consumption

[21] COS fluxes in plots L and plots S are shown in Figure 2. In each forest, litter fall removed and litter fall remained plots were 2–3 meters from each other. Average COS exchange rates at plots L were -4.25 , -6.38 , and -3.90 $\text{pmol m}^{-2} \text{s}^{-1}$ in BF, MF, and PF, respectively. They were larger than those at plots S, which averaged -3.30 , -3.15 , and -2.99 $\text{pmol m}^{-2} \text{s}^{-1}$ in BF, MF, and PF, respectively. The differences between plots S and plots L were significant in MF, but not significant in BF and PF. COS exchange rates between litter and atmosphere were obtained by subtracting COS fluxes in plots L from those in plots S, and the results are shown in Figure 3. Litter acted as COS sinks in all three forests except in BF in March. The exchange rates were 0.44 to -8.19 $\text{pmol m}^{-2} \text{s}^{-1}$, with a sharp increase in MF and PF in March.

[22] In previous studies, most results of soil COS uptakes in forest ecosystems were obtained with litter removed from soils. Litter itself might be of relevance as a sink for COS [Kesselmeier and Hubert, 2002], and the influence of litter on soil temperature and microorganisms might be also reasons for the higher COS fluxes for plots with litter. First, litter provides shelter for soils, thus causing the soil surface temperature to be 1–2°C lower under the litter than where there is no litter. As observed, soil temperatures in subtropical forest soil were higher than the optimum temperature (16–20°C) for COS uptake [Kesselmeier *et al.*, 1999], and a small drop in soil temperature would increase the COS uptake by soils. For the influence of litter on soil microorganisms, as Ding *et al.* [1992] reported, soil microbial biomass and microbial activity in barren land were significantly lower than those in secondary monsoon forest soils. A decrease of microorganisms would decrease the activity of the CA enzyme (carbonic anhydrase), a key enzyme influencing COS uptake by soils or COS metabolism as tested with rat hepatocytes [Chengelis and Neal, 1980; Protoschill-Krebs *et al.*, 1996; Kesselmeier *et al.*, 1999]. It is worth noting that leaf litter will decrease the soil-air exchange by acting as a diffusion barrier. The net effect of litter might be even higher than indicated by those in Figure 3.

[23] As shown in Figure 2, COS uptake rates for soils at plots L in the MF were higher than those in the BF and PF. This might be related to the amounts and decomposition rates of litter fall in each forest. The litter fall was highest in the MF with amounts of litter of 11.0, 16.3, and 6.1 t ha^{-1} in the BF, MF, and PF, respectively. Zhang *et al.* [2000] reported that the mean annual decomposition rates (%) of litter were 49.15, 40.84, and 36.94 in the BF, MF, and PF, respectively. If the decomposition rates in 2004 were the same as those reported by Zhang *et al.* [2000], about 5.41, 6.66, and 2.25 t ha^{-1} litter fall was decomposed in 2004 in the BF, MF, and PF, respectively. The higher amount of litter fall decomposed in the MF might be related to the higher microbial content and microbial biomass as discussed below, and might also be the main reason why

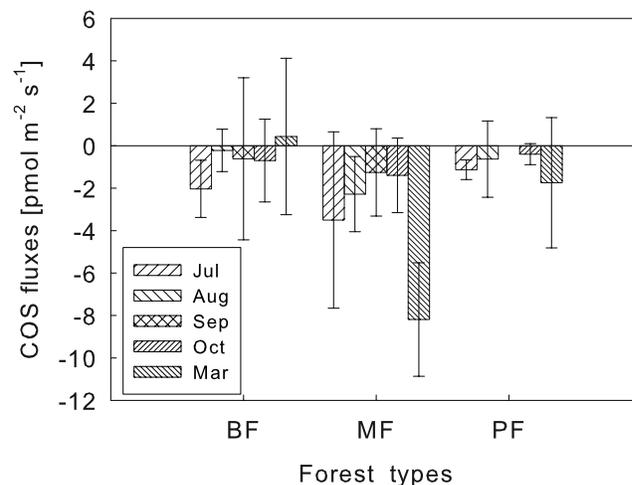


Figure 3. COS fluxes between litter and atmosphere from July 2004 to March 2005 in DBR. BF, MF, and PF represent broadleaf forest, mixed forest and pine forest, respectively. Error bars are the standard deviations.

Table 4. The Amount of Soil Microbes ($10^6 \text{ g}^{-1} \text{ DW}$) and Soil Microbial Biomass ($\mu\text{g C g}^{-1} \text{ soil}$) in October 2004 in Dinghushan Biosphere Reserve

Forest type ^a	Microbial Amount	Bacteria	Fungi	Actinomycetes	Microbial Biomass
BF	2.085	1.953	0.066	0.066	763 ± 73
MF	2.806	2.583	0.195	0.0273	968 ± 108
PF	1.168	1.034	0.0973	0.0369	551 ± 127

^aBF: Monsoon evergreen broad-leaf forest; MF: pine and broad-leaf mixed forest; and PF: pine forest.

COS fluxes at plots L in the MF were higher than those in the BF and PF.

3.4. Microbial Activity and Soil Respiration

[24] An important factor influencing the COS uptake rates might be the soil microorganisms. Previous studies showed that microorganisms played a big role in COS uptake by soils [Bremner and Banwart, 1976; Kluczewski *et al.*, 1985; Lehmann and Conrad, 1996; Kesselmeier *et al.*, 1999]. Bremner and Banwart [1976] reported that COS uptake rates by intact soil were 50-fold faster than those by sterilized soil. Kelly *et al.* [1994] found *Thiobacillus* species could grow autotrophically on COS. Although the exact mechanism for the microbial uptake of COS was not determined, it had been widely accepted that the carbonic anhydrase (CA) enzyme in microorganisms is responsible for the consumption of COS [Chengelis and Neal, 1980; Protoschill-Krebs *et al.*, 1996]. Kesselmeier *et al.* [1999] explicitly demonstrate that the addition of 6-ethoxy-2-benzothiazole-2-sulfonamide (EZ), an inhibitor of the CA enzyme, into the soil could decrease the COS consumption by soil, indicating that CA enzyme is the main factor influencing the consumption of COS by soil. It is known that the CA enzyme can react with COS instead of CO_2 and release H_2S into the atmosphere [Kesselmeier and Merk, 1993; Protoschill-Krebs *et al.*, 1996].

[25] Experimental results of soil microorganisms' availability/activity are shown in Table 4. The total amount of microorganisms and soil bacteria were significantly different among the three forests. It was higher in the MF than in the BF and PF, with soil microbial biomass of 763 ± 73 , 968 ± 108 , and $551 \pm 127 \mu\text{g C g}^{-1} \text{ soil dry weight}$ in the BF, MF, and PF, respectively. It was obviously that forests with higher amount of soil microorganisms or microbial biomass had the higher average soil uptake rates of COS. Although the relationship between COS consumption and microorganisms was reported, there is still only rare information about these COS-consuming soil microorganisms. It would be of great interest to expand the studies to more detailed analysis of soil microorganisms, including bacteria, fungi, and Actinomycetes.

[26] Soil respiration is an important process of microorganisms. It includes microbial respiration and root respiration, and microbial activity can be detected by measurements of respiration rates [Kesselmeier and Hubert, 2002]. Higher soil respiration rates implied higher microbial activity, and therefore higher enzyme activity. Thus the relation between COS flux and soil respiration rate would reflect the influence of microbial activity on soil COS uptake. In the present study COS uptake rates against soil respiration rates were plotted in Figure 4 and, significantly, linear correlations were found for all three forests. Moreover, the

slope for BF was significantly different from the slope for MF or PF ($p < 0.05$), but slopes for MF and PF were not significantly different. Kesselmeier and Hubert [2002] also found that COS uptake by litter increased with respiration rate under lower respiration rate conditions, but COS uptake appeared to decrease at a soil respiration rate of $65 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$ ($19.9 \mu\text{mol m}^{-2} \text{ s}^{-1}$), and no COS uptake was found at higher respiration rates [Kesselmeier and Hubert, 2002]. They interpreted this to be because higher CO_2 concentrations under high respiration rates led to a competitive inhibition of the COS consumption. CA is a key enzyme speeding up the equilibrium between CO_2 and HCO_3^- [Conrad, 1996; Kesselmeier *et al.*, 1999], and COS competes with CO_2 on the enzymatic level. In the present study the soil respiration rates ($0.26\text{--}6.37 \mu\text{mol m}^{-2} \text{ s}^{-1}$) were much lower and the decrease of COS uptake with the increase of respiration rate was not observed.

3.5. Initial COS Mixing Ratios

[27] Diurnal variations for ambient COS mixing ratios and COS fluxes were investigated in the BF, MF, and PF during 1 day in October 2004. Large variations of the COS mixing ratios were observed. It varied from 556 to 914 pptv in BF, from 672 to 1344 pptv in MF, and from 232 to

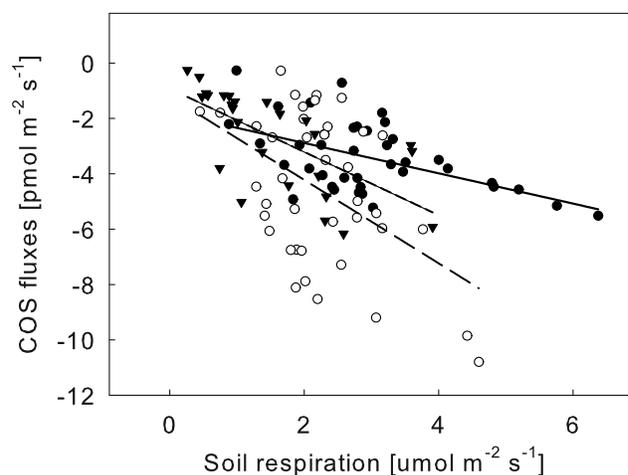


Figure 4. COS fluxes in relationship to soil respiration in plots S + L in BF (solid circles), MF (open circles), and PF (triangles). The regression equation for BF (solid) is $y = -(1.79 \pm 0.47) - (0.55 \pm 0.15) \times (n = 39, R = 0.52, p < 0.01)$, that for MF (long dash) is $y = -(1.21 \pm 1.08) - (1.51 \pm 0.45) \times (n = 40, R = 0.48, p < 0.01)$, and that for PF (short dash) is $y = -(0.92 \pm 0.48) - (1.14 \pm 0.26) \times (n = 26, R = 0.69, p < 0.01)$. Numbers after \pm in the above brackets are the standard errors.

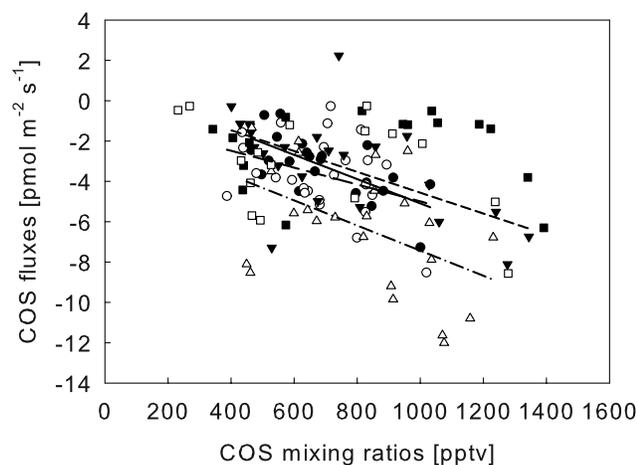


Figure 5. COS fluxes in relationship to the initial ambient mixing ratios inside the chamber in BFS (solid circles), BFL (open circles), MFS (solid triangles), MFL (open triangles), PFS (solid squares), and PFL (open squares). The regression equation for BFS (solid) is $y = 0.93 - 0.006x$ ($n = 22$, $R = 0.68$, $p < 0.01$), BFL (long dash) is $y = -0.81 - 0.004x$ ($n = 25$, $R = 0.35$, $p < 0.05$), MFS (short dash) is $y = 0.6 - 0.005x$ ($n = 24$, $R = 0.60$, $p < 0.01$) and MFL (dash-dot) is $y = -1.21 - 0.006x$ ($n = 24$, $R = 0.47$, $p < 0.05$). PFS and PFL regressions are omitted since they are not statistically significant.

1223 pptv in PF. Average COS mixing ratios in the daytime (09:00–18:00) were higher than at night (21:00–06:00). No clear diurnal cycles of COS mixing ratio were observed, which was not in agreement to those reported by *Kuhn et al.* [1999], who found that the highest mixing ratio appeared at 16:00, dropping to the lowest at 07:00 the next morning, which then rose steadily to the highest concentration again.

[28] Ambient COS mixing ratios exhibit strong seasonal variations in the present study (Table 3). The mean COS mixing ratios were between 400 and 1312 pptv, which were in the range of those reported in China [*Geng and Mu*, 2004], but higher than those reported in a southwestern Sweden forest ecosystem [*Simmons et al.*, 1999], and also higher than the average global mixing ratio (500 ± 50 pptv) [*Bandy et al.*, 1992; *Johnson et al.*, 1993]. As shown in Table 3, the mean COS concentrations between 10 am and 1 pm were lower during July to October than those in March. This could be explained by the influence of monsoon. As *Kettle et al.* [2002] reported, the flux of COS directly from the sea surface is always low at low latitudes. So in summer, moist and warm winds come from ocean and bring usually low ambient COS mixing ratios at DBR. In March, dry and cool air which is pushed down from land in the north with higher anthropogenic trace gases, might lead to elevated COS mixing ratios in the area [*Ding et al.*, 2001; *Kettle et al.*, 2002].

[29] Previous studies revealed correlation between atmospheric COS mixing ratio and COS flux [*Kesselmeier et al.*, 1999; *Kuhn and Kesselmeier*, 2000; *Geng and Mu*, 2004]. Figure 5 shows the COS fluxes versus the initial COS-mixing ratios inside the chamber in the present study. The initial COS mixing ratio had a significantly positive effect

on COS uptake in the BF and the MF. High COS fluxes in March in this present study might be partly due to high COS mixing ratios in this period. COS mixing ratio in PF showed a larger variation, possibly because of much heavier influence of human activity nearby, and significant correlation was not observed between initial COS mixing ratio and COS flux in the PF.

3.6. COS Fluxes Versus Soil Temperature and Water Contents

[30] *Goldan et al.* [1987] pointed out that temperature variations alone greatly affect sulfur gas fluxes. Temperature influences the activity of carbonic anhydrase (CA), an enzyme which increases the turnover with increasing temperature, but which is superimposed by a decrease in activity if the temperature range exceeds a certain value, owing to reorganization and/or denaturation of the enzyme structures. The optimum temperature for CA was between 16 and 20°C, and a sharp decrease in CA activity would occur at high temperatures [*Kesselmeier et al.*, 1999]. Figure 6 shows the relationship between COS uptake and temperature alone in the present study. No correlations were observed in any of the three forests. The results of the correlation between COS fluxes and soil temperatures seem not to be in agreement with other studies [*Kesselmeier et al.*, 1999; *Kuhn and Kesselmeier*, 2000; *Steinbacher et al.*, 2004]. However, observing no temperature optimums in the present study do not mean that there are none since the relationship between COS flux and temperature alone was biased by the combined influence of many parameters under natural conditions.

[31] Soil water content was also considered to be an important factor influencing COS uptake for soils in previous studies. *Kuhn et al.* [1999] concluded that water-saturated soils consumed 84% more rapidly than unsaturated soils. *Steinbacher et al.* [2004] found that the regression between COS consumption and soil water content showed polynomial fits of second order. Seasonal variations in water content were also measured in the present study, but no

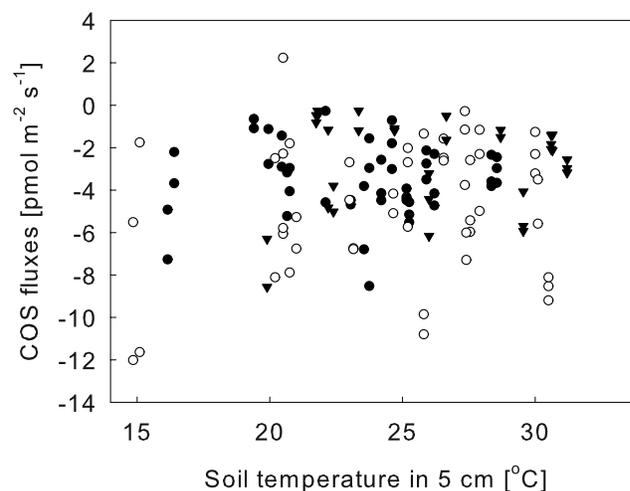


Figure 6. COS exchange rates correlated to the soil temperature in 5-cm depth in plots S + L in BF (solid circles), MF (open circles), and PF (triangles).

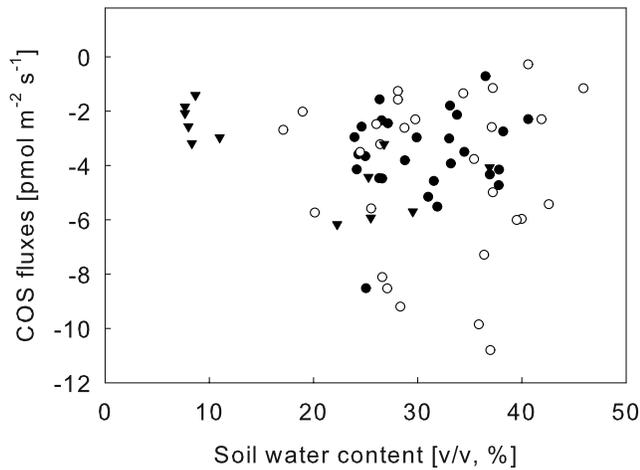


Figure 7. COS fluxes in relationship to the soil water content in polts S + L in BF (solid circles), MF (open circles), and PF (triangles).

clear correlations were found between COS fluxes and soil water content alone in all three forests (Figure 7).

3.7. Polynomials Least Squares Fittings

[32] In our study fluxes were measured in natural conditions instead of controlled experiments, and many factors would affect the soil uptake of COS. Therefore the effect of soil temperature or water content alone on COS flux might be masked due to coupled effects of many influential parameters. By considering both soil water content (W , %) and soil temperature (T , °C) in 5 cm as variables affecting COS fluxes (F_{COS}), multiple regressions resulted in significant correlations in polynomial fits of second order. The regression equations are

$$F_{\text{COS}} = -809 + 59.6 \times T - 1.1 \times T^2 - 1.3 \times W + 0.016 \times W^2 \quad (5)$$

in the MF ($R = 0.6$, $p < 0.05$), and

$$F_{\text{COS}} = 14.5 - 0.45 \times T + 0.002 \times T^2 - 0.71 \times W + 0.014 \times W^2 \quad (6)$$

in the PF ($R = 0.58$, $p < 0.05$). No polynomial fit is given for BF since the regression was not significant.

[33] The improved correlation considering both soil temperature and water content reflects the combined influence of soil temperature and water content on COS fluxes. Our results were similar to those of *Steinbacher et al.* [2004].

[34] It would be helpful to formulate an estimation of flux with the most available parameters, though the fitting might

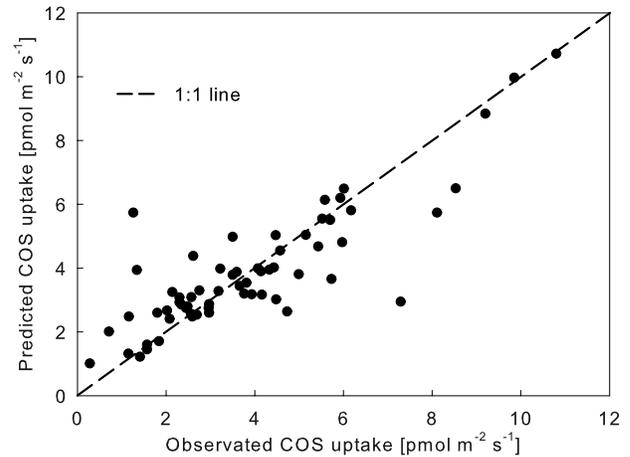


Figure 8. Estimated COS uptake rates based on equation (7) with parameters listed in Table 5 versus observed COS uptake rates.

be changeable under different natural situations. Lots of data are available for the CO_2 fluxes, temperature, and water contents of soils worldwide due to global carbon cycle studies. Furthermore, COS ambient mixing ratios can be measured or estimated with sound accuracy; hence, a multiple regression of COS uptake rate with soil temperature, soil water content, soil respiration rate (R_e , $\mu\text{mol m}^{-2} \text{s}^{-1}$), and COS ambient mixing ratio (C , pptv) was conducted as the equation below:

$$F_{\text{COS}} = a + b \times T + c \times T^2 + d \times W + e \times W^2 + f \times C + g \times R_e \quad (7)$$

[35] The regression parameters are listed in Table 5, all the formulation for BF, MF, and CF was significantly correlated. The observed COS uptake rates versus the predicted COS uptake rates by equation (7) are shown in Figure 8 and the match is fairly good.

4. Conclusions

[36] The present study provided COS exchange fluxes between soil and atmosphere in subtropical forests in south China. Whether litter fall was removed or not, forest soils all acted as consistent sinks for atmospheric COS, and also the litter itself was a significant sink. On average, COS exchange rates ranged between $-1.22 \text{ pmol m}^{-2} \text{ s}^{-1}$ and $-11.82 \text{ pmol m}^{-2} \text{ s}^{-1}$. Though the selected forests are quite near each other in their horizontal distances, soil uptake rates of COS peaked in MF and were significantly higher than those in PF and BF. Since the three forests represent

Table 5. Parameters, Correlations, and Significant Levels for the Polynomials Least Squares Fittings as Equation (7)^a

Forest Type	a	b	c	d	e	f	g	r^2	p
BF	122.70	-10.24	0.19	0.64	-0.0086	-0.0013	-0.66	0.60	<0.05
MF	-514.56	38.35	-0.69	-0.50	0.0055	-0.0010	-2.39	0.74	<0.05
PF	131.74	-8.59	0.15	-0.53	0.0109	-0.0132	-0.03	0.96	<0.05

^aBF: Monsoon evergreen broad-leaf forest; MF: pine and broad-leaf mixed forest; and PF: pine forest.

primary (PF), medium (MF), and climax (BF) successional stages in the area, their difference in soil COS uptake rates may indicate that choosing representative forests for field flux measurement would be very important for a sound estimation of net COS sinks in forest ecosystems, and source and sink calculations extrapolating from limited field measurements without considering the distribution of forest types would probably lead to uncertainties or inaccuracy of COS budgets. Moreover, as indicated in Table 3, even similar plots within 3 meters in a forest showed relatively large deviation of the COS flux. This small-range variation of COS fluxes were also reported by *Steinbacher et al.* [2004]. All these uncertainties would complicate the compiling of soil-air exchange budgets. More extensive field measurements, as well as an in-depth understanding of the kinetics and mechanism for COS uptake or emission, would benefit a better estimation.

[37] COS fluxes at the plots with litter fall were larger than those at plots with litter removed. The mean rates were -3.90 to -6.38 $\text{pmol m}^{-2} \text{s}^{-1}$ at plots with litter fall and -2.99 to -3.29 $\text{pmol m}^{-2} \text{s}^{-1}$ at the plots without litter fall. In forest ecosystems the results from plots with litter fall may reflect the real situation of COS uptake, and thus are more suitable for compiling COS budgets. The amount of litter fall and its decomposition rate are important parameters for cycling of carbon in the forests. The present study shows that litter fall and its degradation will also influence the flux of trace gases like COS. Most previous results of soil COS uptake were obtained with litter fall removed. Greater understanding of the role of litter fall in COS uptake would benefit the study of soil-atmosphere flux of COS in forests.

[38] Ambient COS mixing ratios and soil respiration rates showed close relations to COS fluxes. Higher ambient COS mixing ratio means a higher gradient between the headspace and soil, thus enhancing the diffusion from headspace to the soil. Soil respiration rate in fact is a parameter influenced in combination by chemical, physical, and biological conditions of the soil, so it might be a good indicator reflecting the impact of "the soil side" on the exchange rates, while ambient COS mixing ratio reflects the impact of "the atmosphere side" on the exchange rates.

[39] Though many other studies have investigated the impact of soil temperature and water content on COS exchange rates, the relationship between COS uptake rates and soil temperature or water content alone demonstrated by previous studies under controlled conditions was not found in the present study under natural conditions. This does not mean that soil temperature or water content has no effect on the COS uptake rate. Soils are complex multicomponent systems and because measurements in this study were conducted under natural conditions, many variables were changing simultaneously. This means that the relationship between OCS exchange rates and any given parameter found in this study may differ from those found in other more controlled laboratory based experiments.

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