

## Air-soil exchange of dimethyl sulfide, carbon disulfide, and dimethyl disulfide in three subtropical forests in south China

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[1] The exchange of dimethyl sulfide (DMS), carbon disulfide (CS<sub>2</sub>), and dimethyl disulfide (DMDS) between soil and the atmosphere was investigated in three subtropical forests in south China, namely, a monsoon evergreen broadleaf forest (BF) in climax successional stage, a pine and broadleaf mixed forest (MF) in midsuccessional stage, and a pine forest (PF) in primary successional stage. The forest soils acted as sources for DMS with average flux in BF ( $1.27 \pm 1.40 \text{ pmol m}^{-2} \text{ s}^{-1}$ ) significantly higher than those in MF ( $0.46 \pm 0.30 \text{ pmol m}^{-2} \text{ s}^{-1}$ ) or in PF ( $0.47 \pm 0.36 \text{ pmol m}^{-2} \text{ s}^{-1}$ ). Litter-removed plots showed 55%, 21%, and 53% lower DMS emission fluxes compared to litter-remained plots in BF, MF, and PF, respectively, suggesting the litter layer made evident contribution to DMS emission. DMS fluxes were significantly higher in rain seasons than in dry seasons. Dependence of DMS fluxes on soil temperature varied in the three forests, and significant correlations between DMS fluxes and soil temperature were only observed in BF and MF. No significant correlation was found between soil water content and DMS fluxes. However, DMS fluxes were found to be significantly correlated with soil temperature and water content together in polynomial forms with an order of 2. DMS fluxes were also exponentially correlated with CO<sub>2</sub> fluxes. CS<sub>2</sub> and DMDS fluxes showed no consistent direction. CS<sub>2</sub> fluxes varied between  $-8.51$  and  $4.72 \text{ pmol m}^{-2} \text{ s}^{-1}$  and DMDS fluxes between  $-0.25$  and  $2.00 \text{ pmol m}^{-2} \text{ s}^{-1}$ , respectively. No clear patterns were found for the influence of litter layer on the CS<sub>2</sub> or DMDS fluxes.

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### 1. Introduction

[2] Dimethyl sulfide (DMS), carbon disulfide (CS<sub>2</sub>), and dimethyl disulfide (DMDS) are among the most abundant reduced volatile sulfur compounds (VSCs) in the atmosphere. These VSCs are involved in the chemical processes of atmospheric aerosol and cloud formation [Kesselmeier and Hubert, 2002]. Most of the released DMS is oxidized in the troposphere to sulfate, which acts as cloud condensation nuclei (CCN), especially for marine clouds; therefore, emissions of DMS would influence cloud albedo and consequently climate [Charlson *et al.*, 1987; Andreae and Crutzen, 1997]. CS<sub>2</sub> can contribute to stratospheric sulfate aerosol (SSA) by being oxidized to COS either by reaction with OH radicals

and oxygen atoms or by spontaneous photodissociation in the atmosphere [Jones *et al.*, 1982]. DMDS can be quickly oxidized during daylight times to sulfur dioxide (SO<sub>2</sub>) and methane sulfonic acid (MSA), which plays an important role in tropospheric chemistry [Andreae and Crutzen, 1997].

[3] Despite their importance in atmospheric chemistry, large uncertainties still remain in the chemical speciation and the magnitude of natural emission of these sulfur gases to the atmosphere [Watts, 2000]. Most studies about DMS fluxes were carried out in midlatitude and low-latitude oceans, since oceans are recognized as the predominant source of atmospheric DMS [Ferek *et al.*, 1995; Huebert *et al.*, 2004; Kettle *et al.*, 2001]. Much less attention has been paid to terrestrial ecosystems [Staubes *et al.*, 1989; Geng and Mu, 2004, 2006; Yang *et al.*, 1998; Yi *et al.*, 2008]. The existing studies indicated that terrestrial ecosystems in general acted as a source for atmospheric DMS [Aneja and Cooper, 1989; Staubes *et al.*, 1989; Geng and Mu, 2004, 2006; Yi *et al.*, 2008]. For fluxes of CS<sub>2</sub> and DMDS, few studies were carried out in terrestrial ecosystems [Steinbacher *et al.*, 2004]. CS<sub>2</sub> fluxes in a spruce forest ecosystem in Germany ranged  $-0.11$ – $0.23 \text{ pmol m}^{-2} \text{ s}^{-1}$  with no consistent direction [Steinbacher *et al.*, 2004]. Similar results were observed in a laboratory study with forest leaf litter [Kesselmeier and Hubert, 2002].

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**Table 1.** Surface Soil (0–15 cm Depth) Properties in the Three Forests

Forest Type	Bulk Density (g cm <sup>-3</sup> )	pH	Organic Carbon (g kg <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> -N (mg kg <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> -N (mg kg <sup>-1</sup> )	Total Sulfur (mg kg <sup>-1</sup> )	Available Sulfur (mg kg <sup>-1</sup> )
BF	0.91	3.7	39.5	4.97	7.03	410.4	80.7
MF	1.05	3.8	25.1	5.80	6.97	244.7	52.5
PF	1.50	4.3	15.1	5.96	6.13	112.9	39.5

For systematic understanding of global emission inventories of these VSCs, more field measurements of terrestrial ecosystem fluxes are needed.

[4] In 2002, a project supported by Ministry of Science and Technology of China was initiated for the study of trace gas exchange in subtropical ecosystems in the Pearl River Delta region, south China. Results describing carbonyl sulfide (COS) uptake in forests, NO emission, and VSCs from paddy fields have also been presented [Li and Wang, 2007; Li et al., 2007; Yi et al., 2007; Li and Wang, 2008; Li et al., 2008; Yi et al., 2008]. The present study reports DMS, CS<sub>2</sub>, and DMDS fluxes between soil and the atmosphere in three typical subtropical forests, namely, monsoon evergreen broadleaf forest (BF), pine and broadleaf mixed forest (MF), and pine forest (PF). These three forests represent different stages in the successional series, with BF being the climax vegetation and PF being the primary one. Objectives of this study were to investigate (1) VSC fluxes in the three forests and their temporal patterns and (2) controlling factors of VSC fluxes based on field observation.

## 2. Materials and Methods

### 2.1. Site Description

[5] The study was performed in a broadleaf forest (BF), a pine and broadleaf mixed forest (MF), and a pine forest (PF) at Dinghushan Biosphere Reserve (DBR, 23°09′–23°11′N and 112°30′E–112°33′E). The reserve is located in the subtropical humid forest life zone with a monsoon climate. Annual mean relative humidity is about 80%. The averaged annual rainfall is about 1927 mm with a distinct seasonal pattern. Typically the period from April to September is wet season, and that from October to March is dry season. Annual mean air temperature is about 21°C, with monthly means the lowest in January (13°C) and the highest in July (28°C). Soil in these forests is lateritic red earth. Some soil properties were presented in Table 1. More details about the three forests were described in our previous study [Yi et al., 2007].

### 2.2. Flux Measurements

[6] In each forest, six neighboring plots were selected, with litter remained in three plots (plot L) and removed in the other three plots (plot S). Flux measurements were performed in July, August, September, October 2004 and March 2005. In each sampling day, measurements were typically carried out from 1000 to 1300 h except for the diurnal variation measurements in October, when measurements were conducted every 3 h for 24 h in each forest.

[7] Static chamber method was employed to measure VSC fluxes. This method was described in detail elsewhere [Yi et al., 2007]. Briefly, the chamber had a cubical shape with edges of 50 cm in length. The wall of the chambers were constructed of stainless steel with Teflon film covering the

inside walls. Inside each chamber, two fans were fixed to ensure sufficient mixing of air inside the chamber. To avoid disturbing the soil, Teflon-lined collars were installed 2 weeks before field measurement began. Five air samples inside the chamber were collected into 0.5 L Tedlar sampling bags (SKC Inc., USA) at 0, 5, 10, 20, and 30 min after the chamber was put onto the collars. Before field campaign, to check if there were interferences during storage of samples, we prepared 100 pptv target VSCs in the same type 3 L sampling bags and analyzed 5 times (every 6 h) the same way as field samples. The relative standard deviations were <8%.

[8] Within 48 h after sample collection, VSC species were analyzed by a GC-MSD system (6890/5973N, Agilent Technologies, USA) coupled with an Entech Preconcentrator (Entech Instruments Inc., CA, USA). CO<sub>2</sub> was analyzed with HP 4890D gas chromatography. Details about sample analysis, standard preparation and calibration, and flux calculation were similar to those presented previously [Yi et al., 2007, 2008].

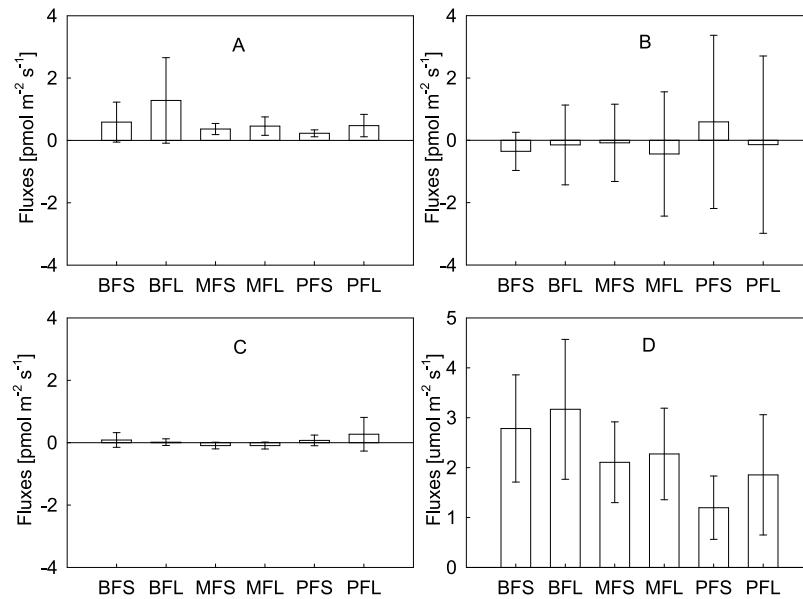
### 2.3. Data Analysis

[9] ANOVA analyses with post hoc LSD test were performed to compare the difference between the campaigns or the forests. Difference between the plots L and S was tested by independent samples *t* test. In this paper, analyses with *p* values of <0.05 were considered significant.

## 3. Results and Discussion

### 3.1. VSCs Fluxes in the Litter-Remained Plots and Their Temporal Patterns

[10] In litter-remained plots, litter was maintained undisturbed in its natural state, so VSC fluxes measured in these plots largely reflected those under natural conditions. DMS fluxes ranged from -0.07 to 5.63 pmol m<sup>-2</sup> s<sup>-1</sup> (negative denotes fluxes from the atmosphere to the soil and vice versa) in the three forests with an average of 0.64 ± 0.80 pmol m<sup>-2</sup> s<sup>-1</sup>. But substantial differences existed among forests. The forest floors acted as emission sources of DMS with averaged fluxes of 1.27 ± 1.40 pmol m<sup>-2</sup> s<sup>-1</sup> in BF, 0.46 ± 0.30 pmol m<sup>-2</sup> s<sup>-1</sup> in MF, and 0.47 ± 0.36 pmol m<sup>-2</sup> s<sup>-1</sup> in PF. Emission rates in BF were significantly higher than in MF or in PF (Figure 1a). It is worth noting that the selected forests were less than 2 km apart from each other in their horizontal distances. The variations among the forests in successional series revealed the difficulty and uncertainty in the estimation of soil-atmosphere fluxes of trace gases in forest ecosystems. According to the previous studies, the decomposing or synthesizing of such sulfur-containing compounds in soils, such as cystine, cysteine, and methionine, might contribute to the fluxes of VSCs, like DMS [Caron and Kramer, 1994; Zhang et al., 2004].



**Figure 1.** Fluxes of (a) DMS, (b) CS<sub>2</sub>, (c) DMDS, and (d) CO<sub>2</sub> from plots with litter (L) and without litter (S) in the monsoon evergreen broadleaf forest (BF), broadleaf mixed forest (MF), and pine forest (PF).

[11] CS<sub>2</sub> and DMDS fluxes, however, did not show constant flux direction. CS<sub>2</sub> fluxes varied between  $-8.51$  and  $4.72$  pmol m<sup>-2</sup> s<sup>-1</sup> at plots L with the mean values of  $-0.15 \pm 1.28$ ,  $-0.44 \pm 1.99$ , and  $-0.14 \pm 2.84$  pmol m<sup>-2</sup> s<sup>-1</sup> in BF, MF, and PF, respectively (Figure 1b). DMDS fluxes ranged from  $-0.25$  to  $2.00$  pmol m<sup>-2</sup> s<sup>-1</sup>, with the mean values of  $0.02 \pm 0.11$ ,  $0.09 \pm 0.11$ , and  $0.27 \pm 0.54$  pmol m<sup>-2</sup> s<sup>-1</sup> in

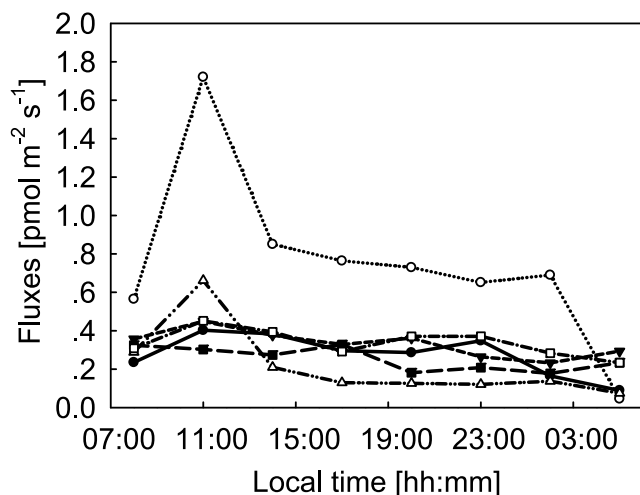
BF, MF and PF, respectively (Figure 1c). DMDS fluxes in PF were significantly higher than those in BF. As reported previously [e.g., Yang *et al.*, 1998], large relative errors of CS<sub>2</sub> and DMDS fluxes (Table 2) implied that fluxes of CS<sub>2</sub> and DMDS exhibited high spatial and temporal variability. This high variability suggested that a large pool of measured data is needed for acceptable CS<sub>2</sub> and DMDS fluxes.

**Table 2.** Fluxes of DMS, CS<sub>2</sub>, DMDS, and CO<sub>2</sub> in Different Months in BF, MF, and PF<sup>a</sup>

Date	Forest	Plot <sup>b</sup>	DMS	CS <sub>2</sub>	DMDS	CO <sub>2</sub>
Jul 2004	BF	S	$0.71 \pm 0.80$	$-0.13 \pm 0.53$	$0.14 \pm 0.18$	$3.73 \pm 1.26$
		L	$1.43 \pm 1.98$	$-0.35 \pm 0.61$	$0.05 \pm 0.06$	$4.31 \pm 1.37$
	MF	S	$0.30 \pm 0.16$	$0.75 \pm 1.39$	$0.16 \pm 0.11$	$2.53 \pm 0.63$
		L	$0.50 \pm 0.34$	$0.19 \pm 0.47$	$0.16 \pm 0.09$	$2.99 \pm 0.98$
	PF	S	$0.11 \pm 0.05$	$4.35 \pm 3.94$	$0.05 \pm 0.04$	$1.70 \pm 0.30$
		L	$1.05 \pm 0.26$	$2.91 \pm 0.87$	$0.07 \pm 0.04$	$3.12 \pm 0.83$
Aug 2004	BF	S	$0.85 \pm 0.68$	$-1.07 \pm 0.15$	$-0.11 \pm 0.03$	$3.15 \pm 0.19$
		L	$2.08 \pm 1.48$	$-1.00 \pm 0.05$	$-0.12 \pm 0.05$	$3.46 \pm 0.70$
	MF	S	$0.43 \pm 0.18$	$-0.01 \pm 0.02$	$0.10 \pm 0.10$	$2.56 \pm 0.18$
		L	$0.54 \pm 0.20$	$0.36 \pm 0.40$	$0.09 \pm 0.04$	$2.07 \pm 0.86$
	PF	S	$0.37 \pm 0.07$	$-0.41 \pm 0.07$	$0.07 \pm 0.07$	$1.91 \pm 0.62$
		L	$0.32 \pm 0.34$	$-0.05 \pm 0.61$	$0.12 \pm 0.06$	$2.81 \pm 0.95$
Sep 2004	BF	S	$1.02 \pm 0.93$	$-0.37 \pm 0.63$	$-0.02 \pm 0.34$	$2.58 \pm 0.27$
		L	$1.45 \pm 0.30$	$-0.19 \pm 0.52$	$0.01 \pm 0.03$	$2.12 \pm 0.63$
	MF	S	$0.66 \pm 0.12$	$-0.59 \pm 0.15$	$0.00 \pm 0.06$	$2.68 \pm 0.62$
		L	$0.79 \pm 0.07$	$0.16 \pm 0.32$	$0.03 \pm 0.09$	$2.15 \pm 0.24$
	PF	S	$0.24 \pm 0.10$	$-0.29 \pm 0.75$	$0.19 \pm 0.28$	$2.26 \pm 0.55$
		L	$0.88 \pm 0.42$	$0.74 \pm 1.96$	$0.05 \pm 0.16$	$2.29 \pm 0.71$
Oct 2004	BF	S	$0.34 \pm 0.07$	$-1.13 \pm 0.96$	$0.06 \pm 0.08$	$1.50 \pm 0.43$
		L	$0.25 \pm 0.21$	$-2.15 \pm 3.49$	$0.02 \pm 0.13$	$1.67 \pm 0.30$
	MF	S	$0.25 \pm 0.07$	$-0.48 \pm 1.75$	$0.09 \pm 0.27$	$0.70 \pm 0.21$
		L	$0.33 \pm 0.08$	$-0.95 \pm 3.04$	$0.44 \pm 0.81$	$0.99 \pm 0.72$
	PF	S	$0.19 \pm 0.01$	$-0.14 \pm 0.09$	$0.03 \pm 0.11$	$1.28 \pm 0.57$
		L	$0.41 \pm 0.04$	$-0.56 \pm 0.76$	$-0.05 \pm 0.05$	$1.77 \pm 0.10$
Mar 2005	BF	S	$0.17 \pm 0.02$	$-0.06 \pm 0.04$	$0.02 \pm 0.01$	$0.93 \pm 0.68$
		L	$0.31 \pm 0.05$	$-0.22 \pm 0.10$	$0.11 \pm 0.08$	$1.38 \pm 0.40$
	MF	S	$0.13 \pm 0.03$	$-0.36 \pm 0.05$	$0.05 \pm 0.06$	$0.85 \pm 0.16$
		L	$0.29 \pm 0.02$	$-2.58 \pm 3.58$	$0.29 \pm 0.39$	$1.12 \pm 0.07$

<sup>a</sup>Mean  $\pm$  standard deviation; values are presented in pmol m<sup>-2</sup> s<sup>-1</sup> for DMS, CS<sub>2</sub>, and DMDS and  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> for CO<sub>2</sub>.

<sup>b</sup>L and S denote plots with and without litter, respectively.



**Figure 2.** Diurnal variations of DMS fluxes for the plots L (solid circles and solid line) and plots S (blank circles and dotted line) in BF, plots L (solid triangles and long dashed line) and plot S (blank triangles and dash-dotted line) in MF, plots L (solid square and short dashed line) and plots S (blank square and dash-dot-dotted line) in PF.

[12] As showed in Table 2, DMS fluxes in the rain season (July to September) were significantly higher than those in the dry season (October and March), with the former being 2.2–2.6 times of the latter. Mean DMS flux in the rain season ( $1.02 \text{ pmol m}^{-2} \text{ s}^{-1}$ ) was 2.5 times that in the dry season ( $0.41 \text{ pmol m}^{-2} \text{ s}^{-1}$ ). For CS<sub>2</sub> and DMDS fluxes, no clear variation pattern was found.

[13] Similar to seasonal variation, no clear diurnal variation pattern was found for fluxes of CS<sub>2</sub> and DMDS. For DMS, fluxes in daytime ( $0.45 \pm 0.32 \text{ pmol m}^{-2} \text{ s}^{-1}$ ) were significantly higher than those in nighttime ( $0.28 \pm 0.18 \text{ pmol m}^{-2} \text{ s}^{-1}$ ) (Figure 2). This diurnal pattern was similar to those reported previously [Geng and Mu, 2004; Kanda et al., 1995; Yang et al., 1998].

[14] Few studies reported DMS fluxes in forests, but studies on DMS fluxes in other ecosystems are available. For example, DMS emission rates of  $3.8 \pm 0.74 \text{ pmol m}^{-2} \text{ s}^{-1}$  for nonplanted waterlogged paddy fields and  $51.2 \pm 37.5 \text{ pmol m}^{-2} \text{ s}^{-1}$  for planted waterlogged paddy fields in Pearl River Delta, south China [Yi et al., 2008],  $0\text{--}3.14 \text{ pmol m}^{-2} \text{ s}^{-1}$  for city Lawn soil [Geng and Mu, 2004], and  $2.53 \pm 0.26 \text{ pmol m}^{-2} \text{ s}^{-1}$  for maize and wheat soil were reported [Kanda et al., 1995]. Our measured DMS fluxes in forest ecosystems were a little lower than those in agricultural ecosystems, especially lower than the ecosystems with plants. With regard to CS<sub>2</sub>, larger variation of fluxes (from  $-8.51$  to  $4.72 \text{ pmol m}^{-2} \text{ s}^{-1}$ ) at plots L in the present study were observed compared to those reported by Steinbacher et al. [2004] in a spruce forest in central Germany, with measured CS<sub>2</sub> fluxes between an uptake of  $0.11 \text{ pmol m}^{-2} \text{ s}^{-1}$  and an emission of  $0.23 \text{ pmol m}^{-2} \text{ s}^{-1}$ .

### 3.2. Effect of Litter on VSCs Fluxes

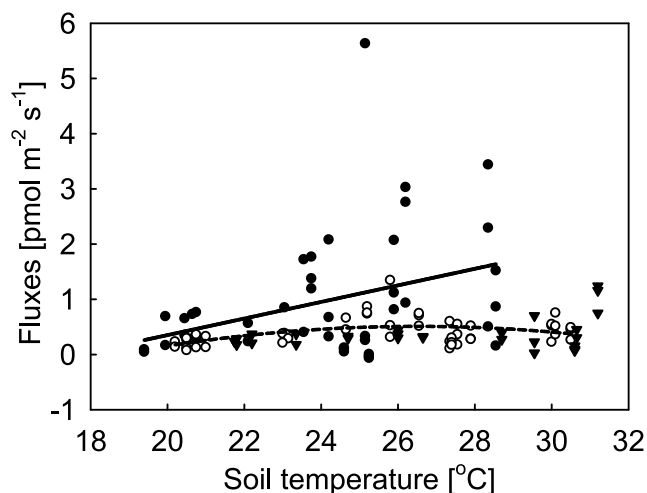
[15] Since fluxes of VSCs were measured simultaneously at the litter-remained and litter-removed plots, the role of litter in the fluxes of VSCs might be evaluated. When all the data in the three forests were pooled together, DMS

fluxes at plots L ( $0.78 \pm 0.96 \text{ pmol m}^{-2} \text{ s}^{-1}$ ) were significantly higher than those at plots S ( $0.41 \pm 0.42 \text{ pmol m}^{-2} \text{ s}^{-1}$ ). Significant difference of DMS fluxes between plots L and plots S were mainly found in BF and PF. The averaged DMS fluxes were  $1.28 \pm 1.37$  for plots L and  $0.58 \pm 0.64 \text{ pmol m}^{-2} \text{ s}^{-1}$  for plots S in BF and  $0.47 \pm 0.36$  for plots L and  $0.23 \pm 0.11 \text{ pmol m}^{-2} \text{ s}^{-1}$  for plots S in PF. In MF, although the difference was not significant, DMS fluxes tended to be greater in the plots L ( $0.46 \pm 0.30 \text{ pmol m}^{-2} \text{ s}^{-1}$ ) than in plots S ( $0.36 \pm 0.18 \text{ pmol m}^{-2} \text{ s}^{-1}$ ) (Figure 1a). For CS<sub>2</sub> and DMDS fluxes, no clear patterns were found between plots L and plots S in all three forests (Figures 1b and 1c).

[16] The fact that DMS fluxes were higher in the plots L than in the plots S indicated that the litter layer acted as a DMS source in all three forests. In fact, a laboratory study conducted by Kesselmeier and Hubert [2002] demonstrated that leaf litter collected from the uppermost litter horizon and the fermentation horizon from a 60 year old beech forest did release DMS, but the measured exchange rates were not significant. The enhancement of DMS fluxes due to the litter layers were  $0.70 \pm 0.32$ ,  $0.10 \pm 0.07$ , and  $0.25 \pm 0.10 \text{ pmol m}^{-2} \text{ s}^{-1}$  in BF, MF, and PF, respectively (Figure 1a), accounting for 55%, 21%, and 53% of the total DMS fluxes from forest floor as surrogated by plots L. Although litter was suggested to be a main contributor, the variation of DMS fluxes from the litter between forests was inconsistent with that of the amount of annual litter fall masses or the litter decomposition rates in these forests. According to Zhang et al. [2000], the amount of litter fall were 11.0, 16.3, and  $6.1 \text{ t ha}^{-1} \text{ yr}^{-1}$ , and the mean annual decomposition rates of litter were 49.15%, 40.84% and 36.94% in the BF, MF and PF, respectively. Given that the decomposition rates in 2004 were the same as those reported by Zhang et al. [2000], the decomposed litter fall were  $5.41 \text{ t ha}^{-1}$  for BF,  $6.66 \text{ t ha}^{-1}$  for MF, and  $2.25 \text{ t ha}^{-1}$  for PF in 2004. The calculated DMS emission due to litter was the lowest in MF although the decomposed litter fall was the highest. A sound explanation would require studies to investigate the role of tree species, chemical composition of litter and the microbial properties in the DMS fluxes. It should be mentioned that the emission from litter calculated by subtracting fluxes in plots S from those in plots L was oversimplified. The interaction between soil and litter would probably influence fluxes both from soil and litter. Removing litter would also change the soil property and thus the emission of DMS.

### 3.3. The Correlation of VSCs Fluxes With Temperature and Soil Water Content

[17] Soil temperature and soil water content were considered to be two important factors influencing VSCs fluxes, as they affected soil microbial activity and had been used to parameterize VSCs fluxes [Fall et al., 1988; Kanda et al., 1992; Steinbacher et al., 2004; Yang et al., 1998; Yi et al., 2007]. For example, Fall et al. [1988] reported that VSCs fluxes increased exponentially with soil temperature, and Kanda et al. [1992] found that DMS fluxes increased logarithmically with air temperature in Japanese paddy fields. The increase of VSCs fluxes with air temperature was also found in other studies [Goldan et al., 1987; Lamb et al., 1987]. Correlations between DMS and soil temperature at 5 cm depth for the present study were shown in Figure 3. During



**Figure 3.** The correlations between DMS fluxes and soil temperature at 5 cm depth in BF (solid circles and solid line,  $y = 0.15x - 2.65$ ,  $R = 0.36$ ,  $p < 0.05$ ), MF (blank circles and dashed line,  $y = -0.008x^2 + 0.45x - 5.41$ ,  $R = 0.46$ ,  $p < 0.01$ ), and PF (solid triangles).

the experimental period, soil temperature at 5 cm depth ranged from 18°C to 31°C. Within this temperature range, DMS fluxes and soil temperature were fitted in different ways in the three forests. In the BF, DMS fluxes increased linearly with temperature, while in the MF, DMS fluxes correlated with soil temperature in a quadratic way. A quadratic relation was also found between CS<sub>2</sub> fluxes and soil temperature in BF, but no significant correlation was found between DMDS fluxes and soil temperature in all the three forests. For the diurnal data only, DMS fluxes increased linearly with soil temperature in both BF and MF (Figure 4). Several studies, however, reported that diurnal DMS fluxes increased exponentially with temperature [Geng and Mu, 2004; Kanda et al., 1995; Yang et al., 1998].

[18] VSCs fluxes had been previously found to be quadratically related with soil water content [Kesselmeier and Hubert, 2002]. In the present study, no robust correlation was found between soil water content and DMS or CS<sub>2</sub> fluxes in all the three forests, but DMDS fluxes were found to increase linearly with soil water content in BF and MF (Figure 5).

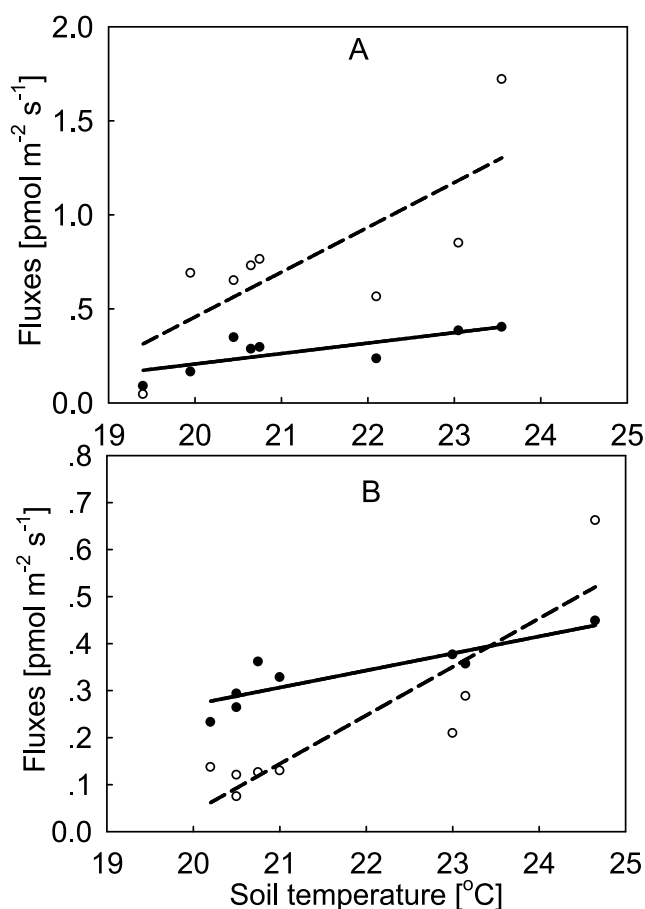
[19] Given that soil-atmosphere exchange of VSCs is a microbially controlled process, the influence of this process by soil temperature and water content would be expected just as the cases of other biogenically modified trace gases like CO<sub>2</sub>, CH<sub>4</sub>, NO, and COS as well. The lack of a clear correlation between VSCs fluxes and these two factors was probably due to the narrow range of variation of these environmental factors in the field or due to the complexity of field conditions which might have masked the effect of individual factor.

[20] When soil temperature and water content were combined, more strong correlations were found between fluxes of VSC species and soil temperature and water content in a quadratic way (Table 3). The similar correlations were also reported by Steinbacher et al. [2004].

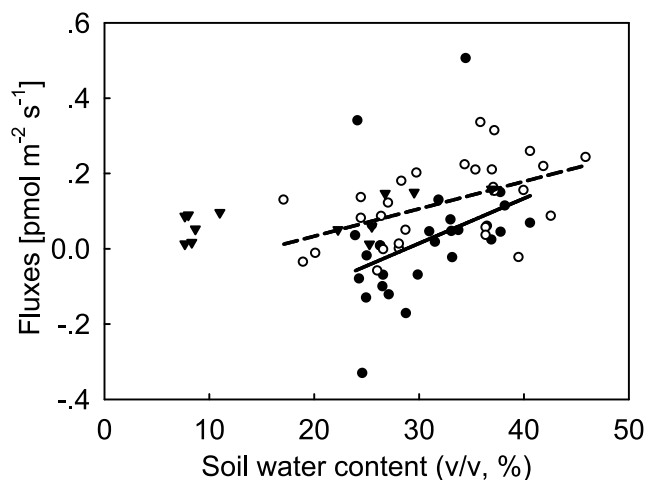
### 3.4. The Correlation Between DMS Fluxes and CO<sub>2</sub> Fluxes

[21] Flux of CO<sub>2</sub> is an important indicator of soil respiration. During the experimental period, averaged CO<sub>2</sub> fluxes were  $2.99 \pm 1.26$ ,  $2.19 \pm 0.86$  and  $1.53 \pm 1.00 \mu\text{mol m}^{-2} \text{s}^{-1}$  in BF, MF, and PF, respectively (Figure 1d). In all the three forests, CO<sub>2</sub> fluxes in plots L were higher than those in plots S (Figure 1d). A clear seasonal variation pattern of CO<sub>2</sub> fluxes were also found with those in wet seasons higher than in dry seasons (Table 2).

[22] Correlation analysis revealed that DMS fluxes were exponentially related to CO<sub>2</sub> fluxes (Figure 6), which were in agreement with those reported by Kesselmeier and Hubert [2002]. This indicated that DMS production was a process involving soil microbial activities. Nevertheless, as reported in our previous study [Yi et al., 2007], the highest microbial amount and microbial biomass were recorded in MF and the lowest in PF, which was not consistent with the variation of DMS fluxes. Further studies are undoubtedly necessary in



**Figure 4.** The correlation between diurnal DMS fluxes and soil temperature at 5 cm depth in (a) BF (solid circles and solid line for the plots S,  $y = 0.06x - 0.09$ ,  $R = 0.77$ ,  $p < 0.05$ ; blank circles and dashed line for the plots L,  $y = 0.24x - 4.31$ ,  $R = 0.77$ ,  $p < 0.05$ ) and (b) MF (solid circles and solid line for the plots S,  $y = 0.04x - 0.45$ ,  $R = 0.87$ ,  $p < 0.01$ ; blank circles and dashed line for the plots L,  $y = 0.1x - 2.02$ ,  $R = 0.89$ ,  $p < 0.01$ ).



**Figure 5.** The correlations between DMDS fluxes and soil water content in BF (solid circles and solid line,  $y = 0.01x - 0.34$ ,  $R = 0.39$ ,  $p < 0.05$ ), MF (blank circles and dashed line,  $y = 0.007x - 0.11$ ,  $R = 0.51$ ,  $p < 0.01$ ) and PF (solid triangles).

order to reveal the underlying mechanism of VSCs fluxes in these forests.

#### 4. Conclusions

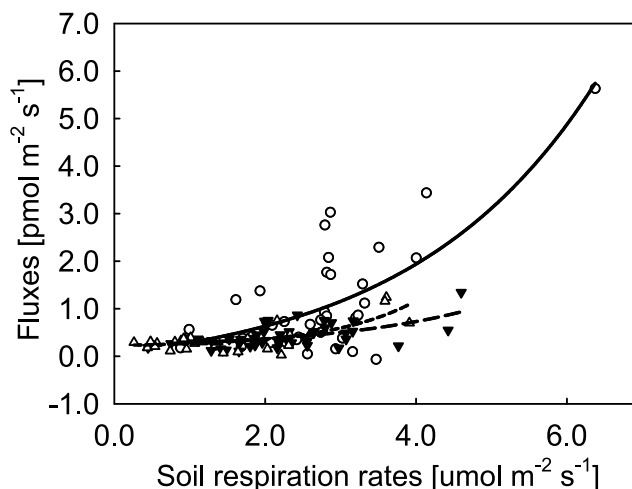
[23] The present study provided DMS, CS<sub>2</sub>, and DMDS fluxes between soil and the atmosphere in three subtropical forests in south China. The forest floors acted as sources for DMS, but fluxes of CS<sub>2</sub> and DMDS were much lower and varied inconsistently. These facts confirmed that the forest floors might play a minor role in fluxes of CS<sub>2</sub> and DMDS.

[24] The litter layer was found to be a major contributor to DMS fluxes from forest floors, with DMS emission from plots with litter removed 55%, 21%, and 53% lower than those in plots with litter remained in BF, MF, and PF, respectively. The correlation of DMS fluxes with CO<sub>2</sub> fluxes indicated that it was the microbial processes that controlled the DMS fluxes.

[25] Though the selected forests are less than 2 km apart in their horizontal distances, DMS fluxes were significantly higher in BF than those in MF and PF. This variation by its nature is a result of soil properties. The difference of DMS fluxes between forests indicated that choosing representative forests for field flux measurement would be very important

**Table 3.** Multiple Regressions Between Fluxes of VSCs ( $F$ , pmol m<sup>-2</sup> s<sup>-1</sup>) and Combination of Soil Temperature ( $T$ , °C) and Soil Water Content ( $W$ , v/v, %)

VSCs	Forest	Regression Equation	$R$	$p$
DMS	BF	$F = -259.1 + 22.27T - 1.98W - 0.42T^2 + 0.03W^2$	0.61	0.03
	MF	$F = -29.7 + 2.04T + 0.008W - 0.035T^2 - 0.0002W^2$	0.61	0.02
	PF	$F = -168.4 - 12.27T + 0.14W + 0.22T^2 - 0.002W^2$	0.89	0.02
CS <sub>2</sub>	BF	$F = 1.2 - 0.13T + 0.05W$	0.47	0.05
	PF	$F = -7.2 + 0.38T - 0.124W$	0.71	0.04
DMDS	BF	$F = 0.34 - 0.026T + 0.012W$	0.48	0.04
	MF	$F = -0.12 + 0.0002T + 0.007W$	0.51	0.02



**Figure 6.** DMS fluxes in relationship to soil respiration rates in BF (solid circles and solid line,  $y = 0.46\exp(0.41x) - 0.41$ ,  $R = 0.75$ ,  $p < 0.01$ ), MF (blank circles and long dashed line,  $y = -0.07\exp(0.51x) + 0.17$ ,  $R = 0.54$ ,  $p < 0.01$ ), and PF (solid triangles and short dashed line,  $y = 0.03\exp(0.9x) + 0.2$ ,  $R = 0.76$ ,  $p < 0.01$ ).

for a sound estimation of regional DMS fluxes. Source and sink calculations extrapolating from limited field measurements without considering the forest types would probably lead to uncertainties or inaccuracy of VSCs budgets.

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