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Carbonyl sulfide and dimethyl sulfide fluxes in an urban lawn and adjacent bare soil in Guangzhou, China

Zhigang Yi[1,2], Xinming Wang[2,*]

1. College of Resources and Environment, Fujian Agriculture and Forestry University, Fuzhou 350002, China. E-mail: zgyi@fjau.edu.cn
2. State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

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Abstract

Carbonyl sulfide (COS) and dimethyl sulfide (DMS) fluxes from an urban *Cynodon dactylon* lawn and adjacent bare soil were measured during April–July 2005 in Guangzhou, China. Both the lawn and bare soil acted as sinks for COS and sources for DMS. The mean fluxes of COS and DMS in the lawn (–19.27 and 18.16 pmol/(m^2·sec), respectively) were significantly higher than those in the bare soil (–9.89 and 9.35 pmol/(m^2·sec), respectively). Fluxes of COS and DMS in mowed lawn were also higher than those in bare soils. Both COS and DMS fluxes showed diurnal variation with detectable but much lower values in the nighttime than in the daytime. COS fluxes were related significantly to temperature and the optimal temperature for COS uptake was 29°C. While positive linear correlations were found between DMS fluxes and temperature. COS fluxes increased linearly with ambient COS mixing ratios, and had a compensation point of 336 ppt.

Key words: carbonyl sulfide; dimethyl sulfide; flux; urban lawn

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Introduction

Carbonyl sulfide (COS) and dimethyl sulfide (DMS) both play important roles in atmospheric chemistry. As COS is almost completely inert to photochemical decomposition in the troposphere, most of it is transported into the stratosphere where it is oxidized to H_2SO_4 and condensed to form stratospheric sulfate aerosols (SSA). These aerosols contribute to stratospheric ozone depletion (Fahey et al., 1993) and influence the earth's radiative balance and global climate (Andreae et al., 2001). In the troposphere DMS can be oxidized to sulfate, which acts as cloud condensation nuclei (CCN). Since changes in CCN concentration affect the concentration of cloud droplets, emissions of DMS influence cloud albedo and consequently climate (Charlson et al., 1987; Andreae and Crutzen, 1997). Due to their important roles, comprehensive understanding and quantification of COS and DMS sources and sinks are important.

Atmospheric COS comes from a variety of direct and indirect sources, and is taken up or photo-dissociated by different processes. Some studies have suggested that total global sources and sinks are balanced within estimate uncertainties (Watts, 2000; Kettle et al., 2002), but this balance is still under question (Sandoval-Soto et al., 2005). Uptake of COS by vegetation has been studied for more than three decades (Taylor et al., 1983), but large uncertainty still exists (Sandoval-Soto et al., 2005). Soils have been recognized as COS sinks only recently and understanding is still limited (Kesselmeier et al., 1999; Liu et al., 2010). Additionally, limited data have revealed variations in COS fluxes by a factor of more than ten for different soils (Kesselmeier et al., 1999; Steinbacher et al., 2004; Liu et al., 2010). These uncertainties demonstrate that further investigation of additional soil types is required.

Since oceans are recognized as the dominant source of atmospheric DMS, most DMS fluxes have been carried out in mid-latitude and low-latitude oceans (Kettle et al., 2001; Huebert et al., 2004), with little attention paid to terrestrial ecosystems. While terrestrial ecosystems generally act as a source for atmospheric DMS, large variations have been observed between different ecosystems (Yang et al., 1996; Geng and Mu, 2004, 2006; Yi et al., 2008, 2010).

Urban lawns are an important part of urban ecosystems, which have distinct biogeochemical processes from natural ecosystems (Kaye et al., 2006). Recent studies have been conducted with the aim to explore the role of urban lawns in the urban, regional, and global biogeochemical cycles (Geng and Mu, 2004; Liu et al., 2007; Hall et al., 2008). Current research in China has investigated COS and DMS fluxes in urban lawn located in the temperate zone, which

* Corresponding author. E-mail: wangxm@gig.ac.cn

has indicated that urban lawn and bare soil acted as a source for DMS and a sink for COS (Geng and Mu, 2004; Liu et al., 2007, 2010). In the present study, fluxes of COS and DMS from an urban lawn in subtropical China were investigated to determine flux strength for the two gases and explore the factors influencing these fluxes.

1 Materials and methods

1.1 Site description

The investigated lawn covered an area of 30 m × 50 m on the campus of the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (23°08′56″N, 113°21′30″E). *Cynodon dactylon*, a multi-year common grass species in south China, was planted there in 2002. The lawn was mowed every 2–3 months and watered regularly, but no additional fertilizer as added. In March 2005, grass from one third of the lawn was removed to plant other species later. This section was regarded as the bare soil area for the present study. The experiment was conducted before and after mowing to determine the role of the aboveground plant compartments on COS and DMS fluxes.

The study area experiences a low subtropical monsoon humid climate. Mean annual temperature is 21.8°C with the maximum temperature experienced in July and minimum in January. The mean annual rainfall is 1694 mm, with April to September being the rainy season and November to January the dry season.

The soil type is lateritic red earth, which is typical in subtropical China. Soil properties in the top 15 cm of surface soil were analyzed according to our previous study (Yi et al., 2008). Soil pH averaged 7.4 (extracted with KCl solution). Contents of organic carbon, total nitrogen, total sulfur, and available sulfur were 22.5 g/kg, 1.4 g/kg, 305.7 mg/kg, and 45.9 mg/kg, respectively.

1.2 Field sampling and laboratory analysis

The static chamber technique was adopted and has been previously described in details (Yi et al., 2008). Briefly, the chambers (60 cm × 60 cm × 60 cm, H × L × W) were made of Teflon film supported by a stainless steel frame. Teflon-lined collars (60 cm × 60 cm, L × W) were inserted to a depth of 10 cm two weeks before the first measurement. Field sampling was carried out on 15 April, 14 May, 26 June, and 14 July before mowing and 15 July after mowing. On each sampling day, three measurements were conducted every three hours during 10:00–17:00, except on 14 May when flux measurements were conducted every three hours to determine diurnal variation with three duplicates for lawn but only one plot selected for bare soil.

Sample collection and laboratory analysis of COS and DMS, and flux calculation and data analysis have been described in our previous studies (Yi et al., 2007, 2008, 2010). Briefly, four air samples inside the chamber were collected in 0.5 L Tedlar sampling bags (SKC Inc., USA) at 0, 5, 10 and 20 min after the chamber was placed onto the collars. Both COS and DMS were analyzed by a 6890/5973N GC-MSD (Agilent Technologies, USA) coupled with an Entech 7100 Preconcentrator (Entech Instruments Inc., USA). Fluxes were calculated by measuring temporal change in the concentration inside the chamber. One-way ANOVA with a post hoc LSD test or *t*-test were performed to compare the difference between the campaigns or treatments.

2 Results and discussion

2.1 Fluxes of COS and DMS

The averages and ranges of COS and DMS fluxes in each campaign are shown in Table 1. The COS fluxes in the lawn ranged from –4.84 to –33.87 pmol/(m^2·sec), with an average of –19.27 pmol/(m^2·sec) (positive flux values indicate emission source and negative values indicate sink). Unlike COS, urban lawn acted as a source for DMS, and fluxes ranged from 7.18 to 31.78 pmol/(m^2·sec), with an average of 18.16 pmol/(m^2·sec). The greatest COS uptake in June was 3.91 times the lowest in April, while the greatest DMS emission in May was 1.56 times the lowest in July.

For bare soil, average COS and DMS fluxes were –9.64 pmol/(m^2·sec) (range of –1.57 to –18.26 pmol/(m^2·sec)) and 10.37 pmol/(m^2·sec) (range of 3.26 to 18.70 pmol/(m^2·sec)), respectively (Table 1). The greatest COS uptake rate in June was 3.91 times the lowest in April and the greatest DMS emission in April was 1.74 times the lowest in June.

Table 1 Fluxes of COS and DMS in lawn and bare soil[a]

Date (dd-mm)	COS (pmol/(m^2·sec))			DMS (pmol/(m^2·sec))		
	Lawn	Bare soil	ΔF[b]	Lawn	Bare soil	ΔF
15-Apr	–9.05 ± 5.51 (–5.80~–15.41)	–3.73 ± 2.98 (–1.57~–7.12)	–5.32 ± 2.59 (–3.46~–8.28)	17.83 ± 10.46 (11.10–29.89)	9.80 ± 5.00 (5.67–15.36)	8.03 ± 5.66 (4.14–14.52)
14-May	–22.17 ± 12.75 (–4.84~–33.87)	–10.69 ± 6.55 (–2.37~–18.26)	–11.48 ± 6.60 (–2.47~–17.13)	23.23 ± 9.51 (10.91–31.78)	13.59 ± 6.24 (5.20–18.70)	9.65 ± 3.33 (5.70–13.08)
26-Jun	–25.58 ± 7.37 (–17.08~–30.11)	–14.57 ± 3.96 (–10.27~–18.07)	–11.01 ± 3.79 (–6.81~–14.18)	15.01 ± 11.16 (7.18–27.79)	7.79 ± 6.51 (3.26–15.25)	7.22 ± 4.65 (3.92–12.54)
14-Jul	–19.32 ± 6.24 (–15.12~–26.49)	–9.22 ± 3.86 (–6.41~–13.62)	–10.10 ± 2.69 (–7.49~–12.86)	14.89 ± 8.97 (8.27–25.10)	9.24 ± 7.03 (4.04–17.24)	5.65 ± 1.94 (4.23–7.86)
15-Jul[c]	–13.58 ± 6.49 (–9.47~–21.07)			11.52 ± 7.43 (6.48–20.05)		

[a] Data are daily mean values, positive values indicate source and negative values indicate sink; data in the parentheses were the range of the fluxes;
[b] ΔF denotes the difference between the lawn and the bare soil; [c] lawn was mowed on the afternoon of 14 July.

Recent field experiments under ambient COS concentrations indicate that soils act as a sink rather than a source for COS, and the uptake rates differ significantly (Kesselmeier et al., 1999; Kuhn et al., 1999; Geng and Mu, 2004, Steinbacher et al., 2004; Yi et al., 2007; Liu et al., 2010). Steinbacher et al. (2004) found that COS uptake rates ranged from 0.23 to 1.38 pmol/(m^2·sec) with an average of 0.81 pmol/(m^2·sec) in a temperate spruce forest in central Germany, while rates varied from 1.22 to 11.82 pmol/(m^2·sec) in subtropical forests in China (Yi et al., 2007). Liu et al. (2010) measured the COS fluxes of 18 soils from 12 provinces in China and found that rates ranged from –4.90 to 12.9 pmol/(m^2·sec), with all but three paddy soils shown to be a sink for COS. Results from the present study indicate, however, that urban lawn soil consumed relatively more atmospheric COS than the previous studies.

To our knowledge, DMS fluxes between soil and atmosphere are quite limited. Geng and Mu (2004) reported that no obvious DMS emission was observed in bare soil in Beijing, while Yi et al. (2007) found that DMS fluxes varied from –0.07 to 5.63 pmol/(m^2·sec) in subtropical forests in China. Compared with these studies, DMS emission rates in the bare soil investigated in the present study were unexpectedly high.

Studies on the exchange of COS and/or DMS between lawn and the atmosphere are quite scarce. Due to the lack of data from this biome, some researchers have used COS fluxes from wheat as a surrogate to estimate COS inventory in grassland (Watts, 2000). To date, only a few studies have been conducted on urban lawns in Beijing, which demonstrated that COS uptake rates ranged from 3.24 to 94.52 pmol/(m^2·sec) and DMS emission rates from 0 to 3.14 pmol/(m^2·sec) (Geng and Mu, 2004, Liu et al., 2007). Compared to their field data, COS fluxes in the present study were relatively lower and DMS fluxes were substantially higher.

2.2 Diurnal variation of COS and DMS fluxes

As shown in Fig. 1, diurnal variation of COS and DMS fluxes differed significantly, but diurnal patterns for both COS and DMS fluxes in the lawn were similar to those in the bare soil. For COS, two flux peaks were observed during the daytime, while only one peak was observed for DMS.

The highest COS uptake rate was observed at 17:00 or 20:00, not at 14:00 when the highest temperature was recorded. This was probably due to the fact that temperature at noon exceeded the optimal temperature for enzyme carbonic anhydrase (CA) activity, a key enzyme for the uptake of COS in higher plants (Protoschill-Krebs et al., 1995, 1996; Blezinger et al., 2000; Haritos and Dojchinov, 2005) and the partial closure of stomata. The optimal temperature for CA in the present study was about 29°C. The temperature inside the chamber at 14:00 was 35.7°C, much higher than the optimal temperature and the likely cause of CA activity reduction (Kesselmeier et al., 1999). In addition, high temperature would cause the partial closure of the stomata, which would also decrease

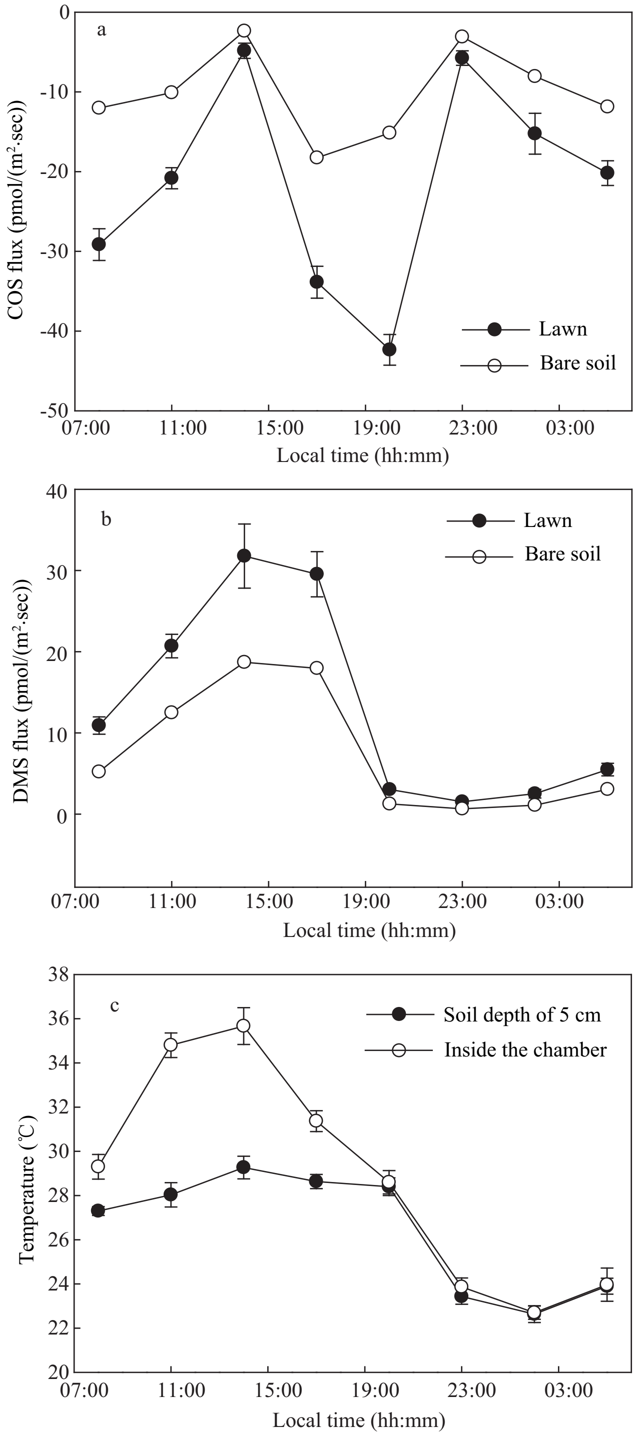

Fig. 1 Diurnal variation of COS (a), DMS fluxes (b), and temperature (c) on 14 May, 2005.

COS uptake rates (Yonemura et al., 2005). The fact that COS uptake rates in the lawn approximated those in the bare soil at 14:00 also supported the finding that COS uptake by grass was greatly inhibited at noon.

Kuhn et al. (1999) assumed that COS uptake by higher plants was completely under stoma control and considered nighttime COS exchange to be negligible. However, considerable COS fluxes were detected in both the lawn and the bare soil during nighttime in the present study (Fig. 1a). It is understandable that COS uptake occurred in the lawn and bare soils during the night given suitable soil temperature and water content, which are two important factors influencing soil biota activity (Liu et al., 2010). In regards to plant leaves, the existence of considerably high COS uptake rates during the night could be attributed to incomplete stomata closure (Sandoval-Soto et al., 2005).

Some studies have shown that DMS emissions from plants are light-dependent in addition to the influence of temperature (Kanda et al., 1995; Yonemura et al., 2005). According to these studies, DMS emissions under dark conditions are negligible. While light intensity data were not available in the present study, the diurnal trends of DMS fluxes appeared consistent with that of light intensity in this region (Fig. 1b). Also consistent with previous studies (Geng and Mu, 2004; Yang et al., 1998; Kanda et al., 1995), the DMS fluxes during nighttime were significantly lower than those during daytime. For lawn, DMS fluxes were 10.91–31.78 pmol/(m^2·sec) in daytime and 1.52–5.48 pmol/(m^2·sec) in nighttime; while for bare soil, DMS fluxes were 5.20–18.70 pmol/(m^2·sec) in daytime and 0.65–3.05 pmol/(m^2·sec) in nighttime. Further studies are needed to evaluate the influence of light intensity on the diurnal variation of DMS emission.

2.3 Effects of grass on COS and DMS fluxes

Campaign-based mean COS and DMS fluxes in lawn were 1.76–2.43 and 1.61–1.93 times that in bare soil, respectively, and their differences were statistically significant ($p < 0.01$ for COS and $p < 0.05$ for DMS).

The role of vegetation as a major global tropospheric sink for COS has been studied for more than two decades and is undisputed (Sandoval-Soto et al., 2005). Steinbacher et al. (2004) found that only about 1% of the total downward flux of COS was taken up by the soil, with the bulk assimilated by plants. According to the present study, COS uptake by bare soil accounted for 50% of COS uptake by the urban lawn. Given that the investigated lawn was a representative, COS uptake by the soil was comparable to that of grass in the subtropical urban lawn.

Although COS uptake rates by the newly-mowed lawn were much lower than before mowing, they were still higher than those of bare soil (Table 1). These results were partly consistent with those reported by Geng and Mu (2004), who observed much lower COS uptake rates or even occasional COS release after mowing. The differences in COS uptake for the lawn before and after mowing could be attributed to the aboveground grass, while the differences between newly-mowed lawn and bare soil could be largely attributed to the underground rhizosphere. Our results indicate that the aboveground grass, the underground rhizosphere, and free-living soil microorganisms were all involved in COS uptake.

The pathways of primary enzymatic production of DMS in higher plants are not yet well understood. Yonemura et al. (2005) found that only one among four plant species could emit DMS, and they concluded that the ability of plants to emit DMS seemed species-specific. If the difference between lawn and bare soil was attributed to the grass (including aboveground grass and underground rhizosphere), then the strength of DMS emission from grass would be 7.79 pmol/(m^2·sec). The gap of DMS fluxes before and after mowing, 3.37 pmol/(m^2·sec), was mainly attributed to the aboveground grass. This also implies that both aboveground grass and the underground rhizosphere play important roles in DMS emission in the urban lawn ecosystem.

2.4 Effects of temperature on COS and DMS fluxes

The uptake of COS by higher plants occurs exclusively through the stomata and has a strong correlation with CO_2 assimilation (Sandoval-Soto et al., 2005). Studies have also found that CA in many soil microorganisms is one of the dominant factors controlling soil COS uptake (Kesselmeier et al., 1999). As enzyme activity increases under optimum temperatures and decreases outside of optimum temperatures (Kesselmeier et al., 1999), strong correlations between COS fluxes and temperature are often encountered (Geng and Mu, 2004; Steinbacher et al., 2004; Liu et al., 2010). As illustrated in Fig. 2a, when all the data were pooled together, COS uptake rates increased with temperature increased from 21 to 33°C during the experimental period. On 14 May, COS fluxes were found to be significantly related to temperature inside the chamber and the optimum temperature for COS uptake was about 29°C (Fig. 2b). According to previous studies, the optimum temperatures for COS uptake by different soil types varied greatly in the range of 8–9°C in a spruce forest soil in central Germany (Steinbacher et al., 2004), 25°C in a lawn soil in Beijing (Liu et al., 2007), and 15–20°C in wheat and forest soils in Beijing and Shandong (Liu et al., 2007, 2010). Compared with previous studies, the optimum temperature in the present study was relatively high. This may be a result of acclimation of plants or soil microorganisms to climate, and the optimum temperatures for COS uptake by tropical/subtropical plants or soils is probably higher than for their temperate counterparts.

For both the lawn and the bare soil, similar diurnal DMS flux trends to that of temperature suggest that temperature played a significant role in DMS emission (Fig. 1b, c). The DMS fluxes in both the lawn and the bare soil were significantly correlated to temperature inside the chamber on 14 May (Fig. 2c). Nevertheless, no significant correlation between DMS fluxes and temperature was found when all the data were combined, which was probably due to the influences of some other factors in different months.

2.5 Correlation between COS fluxes and the ambient mixing ratios

Ambient COS mixing ratios exhibited seasonal variations, with means of 573, 527, 501, and 534 ppt in April, May, June, and July, respectively. These values were in the range of those reported in China by Geng and Mu (2004), and were comparable to the globally averaged mixing ratio (500 ± 50 ppt) (Johnson et al., 1993).

According to previous research, gas exchange could be considered a result of simultaneously operating production and consumption processes (Remde et al., 1989; Conrad, 1994). The consumption rate is assumed to be a function of ambient mixing ratios of a trace gas, whereas the

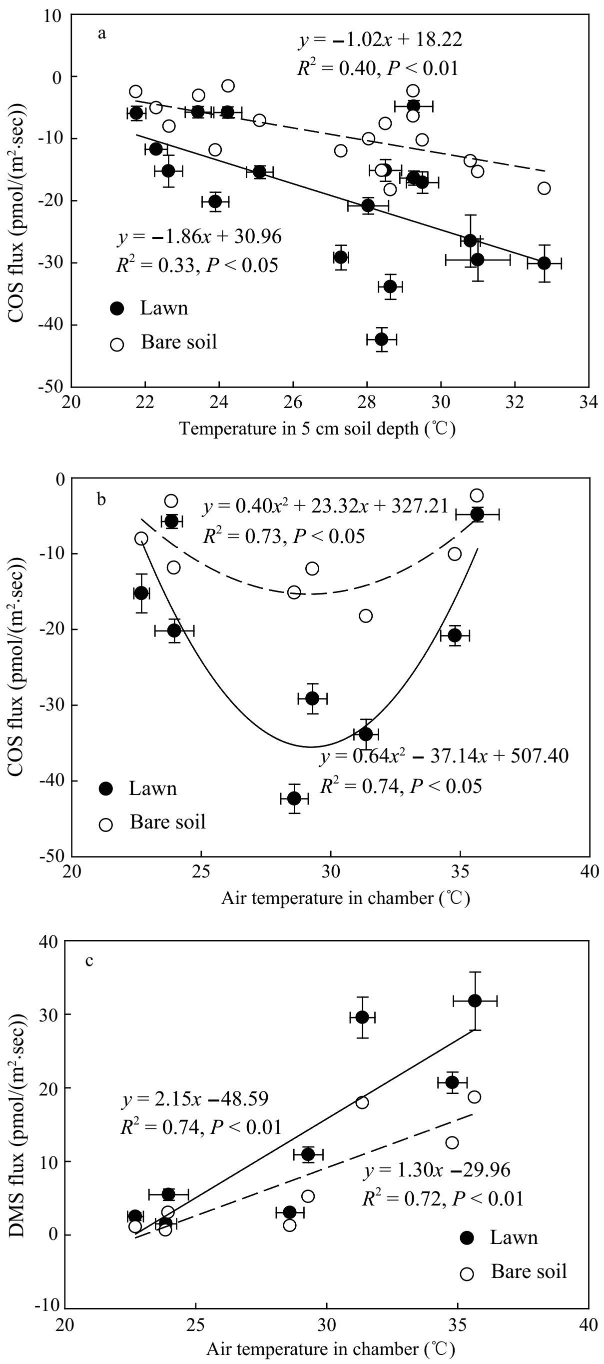

Fig. 2 Correlation analysis for COS fluxes and soil temperature at a depth of 5 cm (a) and temperature inside the chambers (b), and DMS fluxes and temperature inside the chambers (c) on 14 May, 2005.

production rate is not. This implies the existence of a so-called compensation point, at which the net flux is zero (Kesselmeier et al., 1999). Previous studies have shown that COS fluxes strongly depend on ambient COS mixing ratios (Kesselmeier et al., 1999; Kuhn and Kesselmeier, 2000; Geng and Mu, 2004; Yi et al., 2007; Liu et al., 2010). Geng and Mu (2004) reported that the compensation point of urban lawn in Beijing was 291 ppt. In the present study, however, urban lawn in Guangzhou showed significant correlation ($P < 0.01$) between COS fluxes (F_{COS}) and ambient COS mixing ratios (R_{COS}) (Fig. 3), with a fitted regression equation of F_{COS}= 28.226–0.084R_{COS} and a compensation point of 336 ppt. Both these compensation

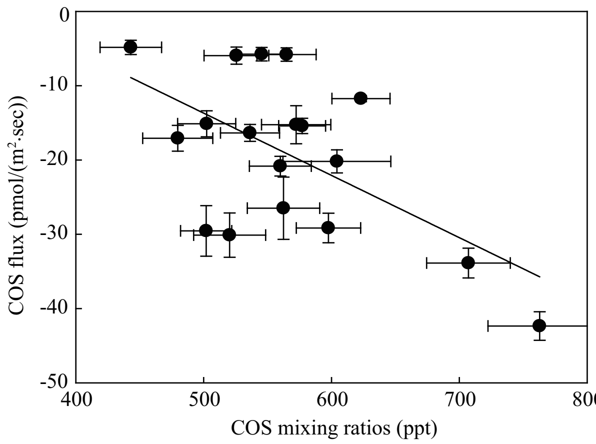

Fig. 3 Correlation between COS fluxes and ambient mixing ratios of COS.

points are lower than the global average concentration of 500 ppt, indicating that urban lawn can be considered a COS sink.

3 Conclusions

Fluxes of COS and DMS were investigated in an urban lawn and an adjacent bare soil. Both the lawn and the bare soil acted as sinks for COS and sources for DMS. In the lawn, fluxes of COS and DMS were –19.27 and 18.16 pmol/(m^2·sec), respectively, while those in the bare soil were –9.64 and 10.37 pmol/(m^2·sec), respectively. The differences in fluxes among lawn, newly mowed lawn, and bare soil indicated that aboveground grass, underground rhizosphere, and free-living soil microorganisms all played important roles in the soil-atmosphere exchange of COS and DMS in the lawn.

Diurnal variation revealed that the highest COS uptake rates did not appear at noon when temperature and light density were the highest, but at 20:00 in the evening. This might be explained by the temperature at noon exceeding the optimum temperature of 29°C (observed in May), and by the partial closure of stoma at noon. The diurnal trend of DMS emission rates was similar to that of temperature. The highest DMS emission rates occurred at 14:00, and DMS emission rates were linearly correlated with temperature inside the chamber. The COS fluxes increased linearly with ambient COS mixing ratio and the compensation point was 336 ppt.

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