Emission of volatile organic sulfur compounds from a heavily polluted river in Guangzhou, South China

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Abstract Emissions of five volatile organic sulfur compounds (VOSCs), including methanethiol, carbonyl sulfide, dimethyl sulfide, carbon disulfide, and dimethyl disulfide, from a heavily polluted river, Shijing River in Guangzhou of South China, was studied. The results showed that the amounts of all VOSCs emitted from the river increased from downstream to upstream along the river with increasing magnitude of water pollution. The emission of carbonyl sulfide was the highest among the target analytes, ranging from 23.8 $\mu g\ m^{-2}\ h^{-1}$ to 42.6 $\mu g\ m^{-2}\ h^{-1}$ at the water surface of Shijin River. The concentration levels of VOSCs on the riverbank were lower than those at the water surface either in Shijing River or in Liuxi River. However, the contribution of dimethyl disulfide to the total VOSCs on the riverbank was higher than that at the water surface in most sampling sites, indicating that there might be a point source of dimethyl disulfide on the riverbank besides diffusion from water surface. The 24-h semi-continuous monitoring data revealed that the emissions of VOSCs at the water surface peaked at 9:00 and 21:00, which was consistent with the water quality variability in Shijin River caused by daily tidal variation.

Keywords Volatile organic sulfur compounds · Emission · Odor · Polluted river · Guangzhou

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Introduction

Volatile organic sulfur compounds (VOSCs) play an important role in atmospheric acid–base chemistry and in formation and growth of aerosol particles (Andreae and Crutzen 1997). They originate either from natural processes or from anthropogenic activities (Bates et al. 1992; Hu et al. 2007). Natural sources are thought to contribute a large fraction of the atmospheric sulfur burden (Aneja 1990). For example, marine aquatic systems account for as much as 98% of the natural atmospheric VOSCs (Brasseur et al. 1999).

On the other hand, the presence of VOSCs in certain environmental settings deserves special attention because of their very low odor threshold and high toxicity (Smet et al. 1998). Contrary to natural emissions, anthropogenic emissions may contribute to local concentrations, which could substantially exceed

the odor threshold. Anthropogenic sources include landfill facilities, sewage or wastewater treatment plants, etc. Hydrogen sulfide (H_2S) is the predominant odorant in municipal landfill areas, and VOSCs have been shown to be the second major components as odor stimuli in some landfill facilities (Kim et al. 2006; Kim 2006). The results from Wu et al. (2006) showed that the average concentrations of carbon disulfide (CS_2) and dimethyl sulfide (DMS) in gas samples collected during four different seasons from a wastewater treatment plant were 3.29 ± 1.59 ppbv (12.13 ± 5.88 μg m^{-3}) and 88.72 ± 80.50 ppbv (275.03 ± 249.55 μg m^{-3}), respectively, in excess of their odor thresholds (Smet et al. 1998).

Polluted rivers located in metropolitan areas are also an important source of odors, especially in developing countries where domestic and industrial wastes are often discharged into rivers without adequate treatment. In the city of Izmir, Tukey, DMS and H_2S as well as 2-propane thiol and 2-butane thiol were the major malodor compounds in the emitted and ambient air in polluted creeks (Muezzinoglu 2003). Wu et al. (2006) also found that DMS was one of the major VOSCs downstream of a river connected to a wastewater treatment plant in Taiwan.

Guangzhou, located in South China, is the political, economic, and cultural center of Guangdong Province. There are 231 rivers in Guangzhou, approximately 100 of which run through the urban area, and the total river length is 913 km. Most of these rivers are contaminated with raw sewage due to lack of treatment facilities. The obvious odor from these rivers has been a nuisance to local residents, and studies on the distribution and emission mechanisms of the volatile odorous compounds are critically needed to provide sound data for developing effective measures to control the unpleasant malodor.

The present study focused on the emissions of VOSCs from a heavily polluted river, Shijing River, in Guangzhou. Emissions of VOSCs from a relatively clean river, Liuxi River, were also determined for comparison. The target compounds include methanethiol (MT), carbonyl sulfide (COS), DMS, CS_2, and dimethyl disulfide (DMDS). To understand the temporal variability in the emissions of VOSCs from Shijing River, a 24-h semi-continuous monitoring program was carried out. In addition, the relationship between the emission of VOSCs and water quality in Shijing River was also discussed.

Materials and methods

Study area

Shijing River originates from Longgui Town of the Baiyun District in Guangzhou (Fig. 1). The total length and average width of this river are approximately 27.6 km and 60 m, respectively. The water depth is 0.3−3.5 m, and the thickness of sediment sludge is about 0.2−0.7 m. The height of the riverbanks is 3.6 m. This river is a typical tidal watercourse, and the water is usually dark and odorous because it receives large quantities of domestic sewage, industrial and commercial wastewater daily. Liuxi River locates at the northwest of Shijing River, with a total length and average width of 171 km and 140 m, respectively. The water depth is ~1.0−5.5 m, and the height of riverbanks is 5 m. Liuxi River is the main drinking water source of Guangzhou, but is still lightly polluted, especially in downstream. These two river are basically isolated form one another to minimize pollution to Liuxi River.

Sampling procedures

The modified flux chamber setup used for sampling of emissions from water surface is shown in Fig. 2. Fresh air was used as inlet air, different from a method reported previously (Muezzinoglu 2003), to avoid adsorption and other negative issues. The emission area was 0.13 m^2 with a headspace of 0.12 m. At the time of sampling, the flux chamber was placed on the river water surface, all sets were connected, the pressure valve of the fresh air cylinder and simple valve were opened, and the air pump and air propeller were switched on at the same time. Two gas flow meters were all adjusted to 2 L/min till the dynamic equilibrium was achieved (in about half an hour), the flow rate was adjusted to 1 L/min (Muezzinoglu 2003), and the cleaned canisters were opened to collect gas samples

Four sampling sites were selected in Shijing River and Liuxi River (Fig. 1) to measure the emissions of VOSCs along the river banks. Sampling was conducted on September 1 and September 8, 2006, respectively, for Shijing River and Liuxi River. All samples were collected from mid-stream by a small boat fixed on the middle of the rivers. To examine the temporal variability in the emissions of VOSCs, gas
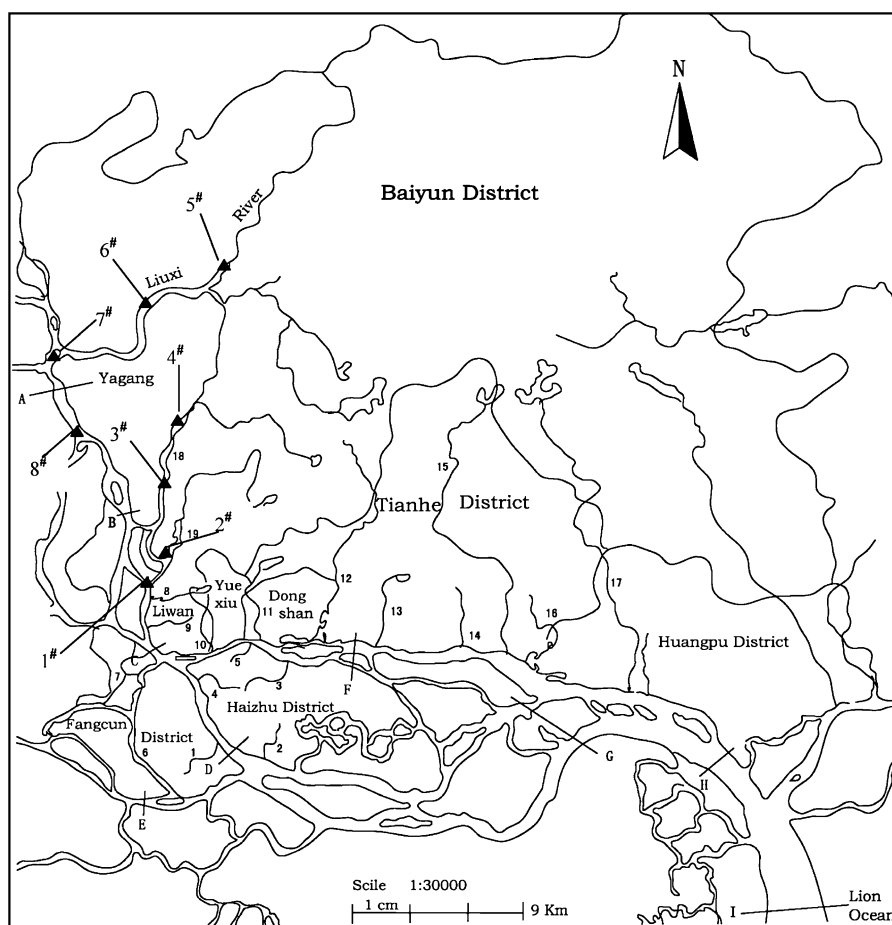
samples were collected at 3-h intervals through a 24-h semi-continuous sampling cycle in Tancun (3#, one of the sampling sites in Shijing River; Fig. 1) on September 12, 2006. Samples were taken from the air at the water surface using a modified flux chamber, and the concentrations of the target compounds were

determined, and emission fluxes of the target compounds from the water surfaces were also calculated. In order to assess the influence of malodor to surrounding residential areas, gas samples were also collected on the position about 5 m from the edge of the riverbank at each sampling site. These samples were collected directly by the 2 L pre-vacuum silanized stainless steel canisters. All gas samples were analyzed in 48 h. In order to examine the relationship between the emission of VOSCs and the river water pollution, water samples were collected simultaneity with gas samples. All water samples were collected from mid-stream at about ~0.2−0.3 m below the water surface, and were kept in icebox and analyzed within 48 h.
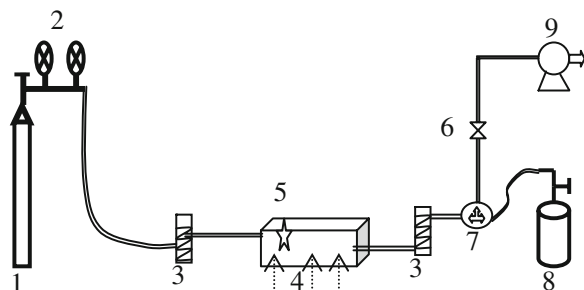
Analysis of VOSCs

The target analytes were measured with an Entech 7100 Preconcentrator (Entech Instruments Inc., CA,

Fig. 2 Modified flux chamber setup used for emission sampling. *1* Fresh air cylinder; *2* pressure valve; *3* gas flow meter; *4* flux chamber; *5* air propeller; *6* simple valve; *7* Teflon valve with three exits; *8* silanized stainless steel vacuum canisters; *9* air pump

USA) coupled to an Agilent 5973N gas chromatography-mass selective detector (GC-MSD, Agilent Technologies, USA). Pre-concentration of VOSCs in air samples was conducted with three stages of trapping in the Entech Preconcentrator. Two hundred fifty milliliters of air samples (1 atm, 0°C) were drawn through a liquid nitrogen trap at −160°C to obtain VOSCs in the first stage. The trapped VOSCs were heated to 10°C to transfer to a second-stage trap with Tenax sorbents at −40°C by 40 ml helium at a flow of 10 ml min^{-1}. Most of CO_2 was removed during this stage. The second-stage trap was heated to 150°C and the thermally desorbed gases were transferred to a third-stage cyro-focusing trap at −170°C by 30 ml helium at a flow of 10 ml min^{-1}. This cryogenic focusing was necessary to optimize the separation in GC column and improve the shapes of GC peaks. A HP-1 capillary column (60 m × 320 μm × 1.0 μm, Agilent Technologies, USA) was used, and the GC oven temperature was programmed initially at −50°C, held for 2 min, ramped to 100°C at 5°C min^{-1}, and finally increased to 250 at 10°C min^{-1} where it was held for 10 min. The MSD was operated in the selected ion monitoring and electron impact modes. The target ions used to quantify COS, DMS, CS_2, DMDS and MT were m/z 60, 62, 76, 94 and 48, respectively.

The calibration was carried out after dilution of MT, COS, DMS, CS_2 and DMDS. They were diluted to 2,400 μg m^{-3} for MT, 3,000 μg m^{-3} for COS, 1,045 μg m^{-3} for DMS, 1,513 μg m^{-3} for CS_2 and 1,277 μg m^{-3} for DMDS in nitrogen gas (>99.999%) as primary standard mixed gas. This primary standard was further dynamically diluted with pure nitrogen to calibration standards by using mass flow controllers and a mixing chamber. Calibration line (area-dose) was obtained by running 250 ml standard gas with MT levels of 0, 1.2, 2.4, 24, 60, 120 μg m^{-3}, and 0, 1.5, 3, 30, 75, 150 μg m^{-3} for COS, 0, 2.64, 26.4, 52.39, 78.43, and 104.47 μg m^{-3} for DMS, 0, 1.85, 3.7, 37, 75.85, and 113.59 μg m^{-3} for CS_2, and 0, 1.58, 3.17, 31.7, 63.9, and 96.1 μg m^{-3} for DMDS, respectively. The detection limit was 62.4 ng m^{-3} for MT, 60 ng m^{-3} for COS, 31 ng m^{-3} for DMS, 48.1 ng m^{-3} for CS_2, and 55.2 ng m^{-3} for DMDS with a sample volume of 250 ml. The relative precision of the measurement was <6%, based on the reproducibility of consecutive analyses of 300 ng m^{-3} ($n=10$) and 3,000 ng m^{-3} ($n=$ 10) COS standards over a 10-day period. All the operations were conducted at 27°C.

Ancillary parameters

Measurements of dissolved oxygen (DO) in water were conducted in situ with a YSI550A handheld DO system (TechTrend International Limited, USA). Suspended solid (SS), chemical oxygen demand (COD_{Cr}), biochemical oxygen demand (BOD_5), sulfide, ammonia nitrogen (NH_3–N), total nitrogen (TN) as well as total phosphor (TP) were measured with standard methods (APHA 1998).

Chemicals

Standard gases of MT (99.5%) and COS (100%) were kept in the 10-1 aluminum cylinders. DMS (99%) and DMDS (97.5%) were all in liquid form. These standards were purchased from Sigma-Aldrich Chemical. CS_2 (97.5%) was purchased from XinHua Chemical. Liquidfacient nitrogen used as refrigerant for operation, fresh air and high purity nitrogen (99.99%) kept in high-pressure stainless steel cylinders were all purchased from Guangzhou Industrial Gases Co.

Result and discussion

Variability of VOSCs emissions

The water quality parameters for Shijing River and Liuxi River are shown in Table 1. The parameters of water quality in Shijing River ranged from 120 to 197 mg l^{-1} for COD_{Cr}, 46.1 to 76.0 mg l^{-1} for BOD_5, 25.2 to 42.4 mg l^{-1} for NH_3–N, 199 to 249 mg l^{-1} for SS, 0.27 to 0.94 mg l^{-1} for sulfide, 27.3 to 48.0 mg l^{-1} for TN, 1.12 to 2.40 mg l^{-1} for TP, and 0.09 to 0.83 mg l^{-1} for DO, respectively. It is obvious that Shijing River has been heavily polluted, as all water quality parameters were far higher than the local standards. In addition, the extent of water pollution increased from downstream to upstream of Shijin River except for a few locations, which can be attributed to the dilution effects from tidal water in downstream of Shijing River. The water quality parameters in Liuxi River ranged from 9.02 to 58.0 mg l^{-1} for COD_{Cr}, 1.22 to 12.1 mg l^{-1} for BOD_5, 1.31 to 8.72 mg l^{-1} for NH_3–N, 33.0 to 63.2 mg l^{-1} for SS, 0 to 0.02 mg l^{-1} for sulfide, 2.72

Table 1 Measured water quality parameters (mg L^{-1}) in Shijing River and Liuxi River

Sites	COD$_{Cr}$	BOD$_5$	NH$_3$–N	SS	Sulfide	T–N	T–P	DO
1[#]	120	46.0	25.0	199	0.27	27.1	1.12	0.83
2[#]	197	70.1	35.2	248	0.82	42.0	2.30	0.21
3[#]	189	74.4	41.0	206	0.94	46.3	2.10	0.17
4[#]	188	76.0	42.4	249	0.86	48.0	2.40	0.09
5[#]	9.02	1.22	1.31	33.0	ND	2.72	3.92	4.39
6[#]	12.1	4.62	4.52	41.1	ND	3.63	4.22	4.21
7[#]	31.3	5.11	4.91	56.1	0.01	5.62	4.41	3.67
8[#]	58.0	12.1	8.72	63.2	0.02	9.83	4.71	2.59
Local standard	20	4	1	/	0.05	1	0.2	5

ND = not determined

to 9.83 mg l^{-1} for TN, 3.92 to 4.71 mg l^{-1} for T–P, and 2.59 to 4.39 mg l^{-1} for DO, respectively. The degree of pollution was higher in downstream than in upstream of Liuxi River, probably due to the unregulated discharge of wastes from businesses along the river. In general, the water quality of Liuxi River is better than that of Shijing River; however, a majority of the water quality parameters with Liuxi River still exceed the local standards, especially in the downstream (7[#], 8[#]). It should be noted that the mean value of TP in Liuxi River was twice as much as that in Shijin River, but the reason remains unknown presently.

Table 2 shows the concentration levels of VOSCs at the water surface and on the riverbank of Shijing River and Liuxi River. The concentration levels of VOSCs at the water surface in Shijing River ranged from 51.6 to 92.2 μg m^{-3} for COS, 17.8 to 64.1 μg m^{-3} for DMS, 11.6 to 14.8 μg m^{-3} for CS$_2$, and 8.10 to 59.7 μg m^{-3} for DMDS. MT was not found in any sample. Previous studies also reported the occurrence of VOSCs in air of other regions. For example, the maximum concentrations of DMS and DMDS were 61,000 and 1,125 mg m^{-3}, respectively, in Kraft pulp mill operations (Bordado and Gomes 2001). The maximum concentration of DMS was 39.9 μg m^{-3} in ambient air around a chemical fiber factory in Taiwan (Lin 2001). The mean concentrations of DMS, CS$_2$, and DMDS were 395 ppbv (1,225 μg m^{-3}), 106 ppbv (392 μg m^{-3}), and 82.1 ppbv (378 μg.m^{-3}) in a new landfill, whereas they were 1.22 ppbv (3.78 μg m^{-3}), 0.88 ppbv (3.26 μg m^{-3}), and 0.45 ppbv (2.07 μg m^{-3}) in an old landfill of Don Hea city, Korea (Kim 2006). The mean concentrations of DMS and CS$_2$ were 88.72 ppbv (275 μg m^{-3}) and 3.29 ppbv (12.17 μg m^{-3}), respectively, in a wastewater treatment of Taiwan (Wu et al. 2006). Finally, the concentrations

of DMS ranged from 11.8−59.2 mg m^{-3} in the air at the deltas of the polluted creeks in the city of Izmir (Muezzinoglu 2003). The concentration levels of VOSCs at the water surface in Shijin river were much lower than those in the air at the deltas of the polluted creeks in the city of Izmir, but close to those in air samples at wastewater treatment plant. The concentration levels of DMS, CS$_2$, and DMDS in all air samples collected near the water surface of Shijin river were much higher than their odor thresholds.

The concentrations of total VOSCs (TVOSCs, COS+DMS+CS$_2$+DMDS) at the water surface of Shijing River increased from 89.1 μg m^{-3} in downstream to 229.2 μg m^{-3} in upstream, and those of COS and DMDS increased from 51.6 μg m^{-3} to 92.2 μg m^{-3} and from 8.10 μg m^{-3} to 59.7 μg m^{-3}, respectively. The concentration of DMS also increased from downstream to upstream except for sampling site 3[#], whereas the concentration of CS$_2$ showed little change from downstream to upstream.

The concentrations of COS, DMS, CS$_2$, and DMDS at the water surface of Liuxi River increased from 0.10 μg m^{-3} in upstream to 3.21 μg m^{-3} in downstream, from 0.21 to 3.12 μg m^{-3}, from 0.10 μg m^{-3} to 1.23 μg m^{-3}, and from 0.10 μg m^{-3} to 1.71 μg m^{-3}, respectively, which were concordant with the variation in the extent of water pollution. Compared to Shijin River, the amounts of VOSCs emitted from Liuxi River were quite small. However, the levels of DMS at site 7[#] and DMDS at 7[#] and 8[#] also exceeded odor thresholds.

Table 2 also indicates that the concentrations on the riverbank of Shijing River ranged from 0−1.00 μg m^{-3} for COS, 0.41−1.00 μg m^{-3} for DMS, 0−0.71 μg m^{-3} for CS$_2$, and 0−0.92 μg m^{-3} for DMDS. On the riverbank of Liuxi River, the concentrations were 0 −0.42 μg m^{-3} for COS, 0−0.41 μg m^{-3} for DMS, 0

Table 2 Concentrations ($\mu g\ m^{-3}$) of VOSCs at the water surface and on the riverbank of Shijing River and Liuxi River

Sites	COS		DMS		CS$_2$		DMDS		TVOSCs	
	Water surface	River-bank	Water surface	River-bank	Water surface	River-bank	Water surface	River-bank	Water surface	River-bank
1[#]	51.6 (57.9%)	ND	17.8 (20.0%)	ND	11.6 (13.0%)	ND	8.10 (9.1%)	ND	89.1	0
2[#]	59.1 (38.6%)	1.00 (43.5%)	43.8 (28.6%)	1.00 (43.5%)	14.8 (9.7%)	0.10 (4.4%)	35.4 (23.1%)	0.20 (8.7%)	153.1	2.30
3[#]	89.4 (40.9%)	0.41 (16.9%)	69.7 (31.9%)	0.50 (20.6%)	13.9 (6.4%)	0.60 (24.7%)	45.6 (20.9%)	0.92 (37.9%)	218.6	2.43
4[#]	92.2 (40.2%)	0.42 (17.9%)	64.1 (28.0%)	0.42 (17.9%)	13.2 (5.8%)	0.71 (30.2%)	59.7 (26.0%)	0.80 (34%)	229.2	2.35
5[#]	0.10 (19.6%)	ND	0.21 (41.2%)	ND	0.10 (19.6%)	ND	0.10 (19.6%)	ND	0.51	0
6[#]	0.40 (39.2%)	0.10 (25%)	0.30 (29.4%)	0.10 (25%)	0.20 (19.6%)	0.10 (25%)	0.12 (11.8%)	0.10 (25%)	1.02	0.40
7[#]	1.31 (29.3%)	0.31 (25%)	1.41 (31.6%)	0.41 (33.1%)	0.62 (13.9%)	0.22 (17.7%)	1.12 (25.1%)	0.30 (24.2%)	4.46	1.24
8[#]	3.21 (34.2%)	0.42 (28.6%)	3.12 (33.7%)	0.41 (27.9%)	1.23 (13.3%)	0.22 (15.0%)	1.71 (18.4%)	0.42 (28.6%)	9.27	1.47
OT[a]	NDA		1.66–111		32.5		0.42–15.1			
H$_{25°C}$[a]	1.94		0.07		0.65		0.04			
ALF[a] (days)	730		1		12–40		0.2			

Data in parentheses are the contributions to TVOSCs

ND = not determined; NDA = no data available; OT = odor threshold value; H$_{25°C}$ = dimensionless henry coefficient at 25°C(mol/m^3)$_{air}$/(mol/m^3)$_{water}$; ALF = atmospheric life time; TVOSCs = the total concentration of VOSCs(COS + DMS + CS$_2$ + DMDS)

[a] Refer to references: Smet et al. (1998)

−0.22 $\mu g\ m^{-3}$ for CS$_2$, and 0−0.42 $\mu g\ m^{-3}$ for DMDS. The concentrations of VOSCs on the riverbank were markedly lower than those at the water surface along either Shijing River or Liuxi River.

The contributions of COS, DMS, CS2, and DMDS to TVOSCs in all samples are shown in Table 2. The concentrations of VOSCs at the water surface followed the order of COS > DMS > DMDS > CS$_2$, either in Shijing River or Liuxi river (except for sampling site 1[#], 5[#], and 6[#]), and the ratio of COS–DMS–DMDS–CS$_2$ was about the same at sampling site 2[#], 3[#], 4[#], 6[#], and 7[#] at the water surface. The concentration of COS at the water surface was the highest among all target analytes at each sampling site. One of the reasons may be that COS has the highest dimensionless Henry coefficient among the target analytes, and therefore possesses highest volatility (Smet et al. 1998). The ratios of COS–DMS–CS2–DMDS on the riverbank were different from that at water surface in almost all sampling sites. For example, the ratio of COS–DMS–CS2–DMDS was 40.9:31.9:6.4:20.9 on the riverbank at site 3[#], and was 16.9:20.6:24.7:37.9 at the water surface at the same sampling site. It should be noted that the relative abundance of DMDS was higher on the riverbank than at the water surface. Because l COS has a longer atmospheric life time than DMDS, there was probably an emission source of DMDS on the riverbank at site 3[#] besides diffusion from water surface. There may be two reasons for this. The first reason is that the polluted sediment near the riverbank would be easy to expose in the air while ebb-tide, which result in emission of DMDS because higher oxidation-reduction potential on the surface of naked sediment sludge on riverbed. This was consistent with the results reported by Langenhove et al. (1985), who found that higher oxidation-reduction potential favored the formation of DMDS. Another reason is that some factories located near the river use or produce DMDS, resulting in high DMDS concentrations.

The emissions of VOSCs at the water surface of Shijing River and Liuxi River are presented in Table 3. The emissions of COS, DMS, CS$_2$, and DMDS ranged from 23.8−42.6 $\mu g\ m^{-2}\ h^{-1}$, 8.22−32.2 $\mu g\ m^{-2}\ h^{-1}$, 5.32−6.83 $\mu g\ m^{-2}\ h^{-1}$, and 3.74−27.6 $\mu g\ m^{-2}\ h^{-1}$ at the water surface of Shijing River and ranged from 0.046−1.48 $\mu g\ m^{-2}\ h^{-1}$, 0.097−1.44 $\mu g\ m^{-2}\ h^{-1}$, 0.046−0.568 $\mu g\ m^{-2}\ h^{-1}$, and 0.046 −0.798 $\mu g\ m^{-2}\ h^{-1}$ at the water surface of Liuxi

Table 3 Emissions ($\mu g\ m^{-2}$ h^{-1}) of VOSCs at the water surface of Shijing River and Liuxi River

Sites	COS	DMS	CS$_2$	DMDS
1[#]	24.0	8.22	5.35	3.74
2[#]	27.0	20.2	6.83	16.3
3[#]	41.4	32.2	6.42	21.1
4[#]	42.6	29.6	6.09	27.6
5[#]	0.046	0.097	0.046	0.046
6[#]	0.185	0.138	0.092	0.055
7[#]	0.605	0.651	0.286	0.517
8[#]	1.48	1.44	0.568	0.789

River. Clearly, the emissions were much higher in Shijing River than in Liuxi River.

There are many previous reports on the emissions of VOSCs in oceanic environments. For instance, the mean COS emission ranged from 0.23 to 1.05 μgS m^{-2} h^{-1} in a Danish estuary (Jørgensen and Okholm-Hansen 1985) and from 0.44 to 1.25 $\mu gS\ m^{-1}\ h^{-1}$ in the Coline Estuary, Great Britain (Harrison et al. 1992). The emissions of CS$_2$ varied between 0.3 and 2.23 $\mu gS\ m^{-2}\ h^{-1}$ in Kõnigshafen (Bodenbender et al. 1999) and ranged from 0.19 to 14.2 $\mu gS\ m^{-2}\ h^{-1}$ in salt marshes (Aneja 1990). The emissions of DMS ranged from 0.12 to 2.32 $\mu gS\ m^{-2}\ h^{-1}$ in Kõnigshafen and varied between 2.3 and 328 $\mu gS\ m^{-1}\ h^{-1}$ in salt marshes (Aneja 1990). H$_2$S and DMS appear to be the most important sulfur gases in coastal marine environments (Steudler and Peterson 1984). However, the emission of COS in Shijin River was the highest among all target analytes and much higher than that in marine environments. On the other hand, the emissions of VOSCs in Liuxi River were similar to those in marine environments.

The temporal variability of emissions of VOSCs from Shijing River

The variations of water quality in 24 h at Tancun (3[#], one of sampling sites in Shijing River as shown in Fig. 1) were marked in Fig. 3a, b. It is interesting to note that the variation of river water quality variation followed an oscillation trend, and there were two noticeable peaks at 9:00 and 21:00 except for DO and sulfide. This phenomenon was probably resulted from tidal cycles of the Pearl River at the frequency of twice a day. Large quantities of domestic sewage and commercial wastewater are emptied into Shijing

River, while almost no clean water is recharged in upstream of this river. As a result, the water pollutants in Shijing River is diluted as tides come in, and make recovery while tide going out.

Figure 4a and b show the concentrations and emissions of VOSCs from Tancun (3[#]) during a 24-h period, which also featured two marked peaks at
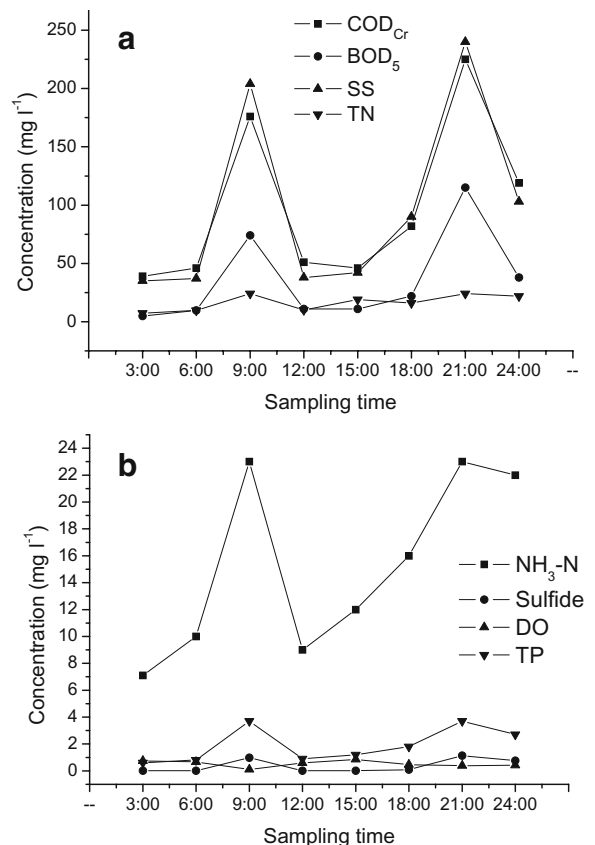

Fig. 3 Variability of water quality parameters at Tancun (3[#]) in Shijin River during a 24-h period: **a** COD$_{cr}$, BOD$_5$, SS, and TN and **b** NH$_3$–N, sulfide, DO, and TP
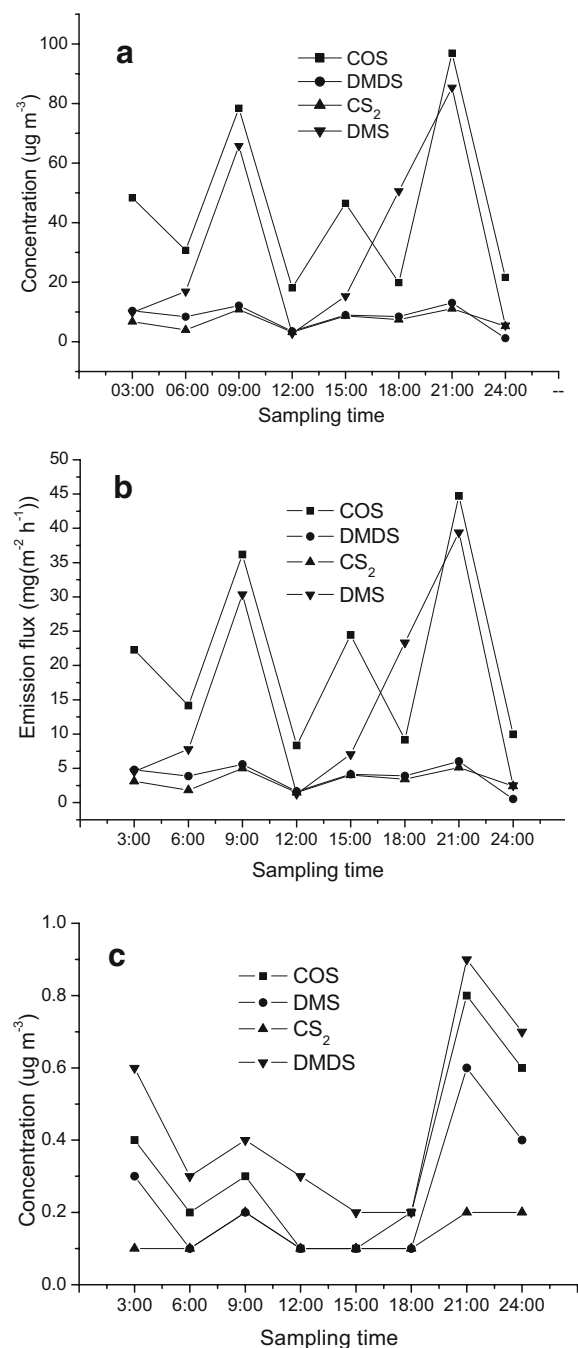
Fig. 4 Variability of emissions of VOSCs at Tancun (3[#]) in Shijin River during a 24-h period: **a** concentrations at the water surface; **b** emissions at the water surface; and **c** concentrations on the riverbank

9:00 and 21:00. The concentrations of COS, DMS, CS_2, and DMDS were 78.4, 65.8, 10.8, and 12.1 μg m^{-2} h^{-1} at 9:00, and were 6.9, 85.4, 11.1, and 13.1 μg m^{-2} h^{-1} at 21:00. In addition, the mean concentrations

of COS, DMS, CS_2, and DMDS were 46.8, 37.8, 7.62, and 8.28 μg m^{-2} h^{-1} at nighttime (18:00−3:00), and were 43.4, 25.2, 6.67, and 8.25 μg m^{-2} h^{-1} at daytime (6:00−15:00). Overall, the concentrations and emissions of VOSCs at nighttime were higher than those in daytime, which were coincident with the variability of water pollution. Besides relatively low river water pollution in daytime, photo-degradation was perhaps also a mechanism lowering the concentrations of VOSCs. The concentration of COS was the highest among the target analytes at the water surface at each sampling time.

The variation of VOSCs concentrations with time on the riverbank also followed an oscillation trend (Fig. 4c); however, the pattern differed from that at the water surface. There were marked concentration peaks of COS, DMS and DMDS at 21:00, whereas the concentration of CS_2 remained relatively constant during the entire sampling period. The concentration of DMDS was the highest among the target analytes on the riverbank at each sampling time. This result again suggested that an emission source of DMDS was present on the riverbank at site 3[#] besides diffusion from the water surface.

The mechanism for generation or production of VOSCs has been extensively studied in marine and freshwater environments because of its importance in relation to global warming and acid rains. COS is formed by biogenic decomposition, chemical photolysis of organic sulfur compounds, or chemical oxidation of CS_2 and DMS (Ferek and Andreae 1984; Kelly and Smith 1990). Interaction of H_2S with organic matter has been demonstrated to result in the formation of CS_2, MT and DMS (Bak et al. 1992; Drotar et al. 1987). Another pathway for production of CS_2, MT and DMS in natural waters is the decomposition of sulfur-containing organic compounds (Caron and Kramer 1994). The main source of DMS is considered to be the enzymatic cleavage of dimethylsulfonium propionate (DMSP) from phytoplankton and macroalgae in marine environments (Aneja and Overton 1990). DMDS also could result from the decomposition of sulfur-containing organic compounds (Lomans et al. 1997). In addition, MT can be oxidized easily to form DMDS in the presence of an oxidant (e.g., oxygen) (Adewuyi 1989).

On the other hand, few published reports are available on the mechanism of formation and emission of VOSCs in wastewater environments. Due to

the different characteristics of incoming wastewater and biogeochemical process, the mechanism of VOSCs production in wastewater environments can be significantly different from natural environments, and can vary in different wastewater environments (Cheng et al. 2005). There are at least three possible pathways for the production of VOSCs in aquatic environments: (1) microbial decomposition of sulfur-containing amino acids; (2) methylation of H_2S; and (3) chemical and biological degradation of biochemical precursors. In Shijin River a dark appearance and bursting bubbles were observed during sampling, and no planktonic algae bloom was found. Therefore, VOSCs could not mainly result from the enzymatic cleavage of biochemical precursor DMSP which is an osmolyte of algae and phytoplankton. VOSCs in Shijin River are probably resulted from the decomposition of sulfur-containing amino acids and the methylation of H_2S. However, further evidence is needed to validate the formation mechanism of VOSCs in Shijin River.

Conclusions

The following conclusions can be drawn based on the results of the present study:

- The emissions of VOSCs in Shijing River, a heavily polluted river, were much larger than those from Liuxi River, a slightly polluted river. The emissions of VOSCs increased from downstream to upstream of Shijing River, accompanied by the increasing extent of river water pollution. The emission of COS was the largest among the target analytes in Shijing River, ranging from 23.8 to 42.6 $\mu g\ m^{-2}\ h^{-1}$ at the water surface.
- The concentrations of VOSCs on the riverbank were lower than those at the water surface in either Shijing River or Liuxi River; however, the contributions of DMDS to TVOSCs on the riverbank were higher than those at the water surface at most sampling sites. An additional emission source of DMDS might be present on the riverbank besides diffusion from the water surface.
- The 24-h semi-continuous monitoring data indicated that the emissions of VOSCs at the water surface of Shijing River showed two significant peaks at 9:00 and 21:00, conhesive with the

change of water quality caused by daily tidal variation.

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