

# Pollution status of volatile organic sulfur compounds causing odor in Xi River and factors influencing spatial distribution

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## ABSTRACT

This study investigated the pollution status of volatile organic sulfur compounds (VOSCs) and the factors influencing their spatial distribution in the Xi River in Shenyang, China. A method for simultaneous determination of 14 VOSCs that cause odor in water samples was developed by using purge and trap coupled with gas chromatography and a flame photometric detector. The results indicated that each target compound could be identified from 15 sampling sites, and the total concentration of 14 VOSCs ranged from 2.575 to 52.981  $\mu\text{g L}^{-1}$ . Dimethyl sulfide (DMS) was the most important contaminant with an average concentration of 4.029  $\mu\text{g L}^{-1}$ , a detection rate of 93.33% and a variation coefficient of 0.72. The VOSCs were primarily distributed in suburban and rural sections, and the suburban section was the worst in regard to pollution by VOSCs. Dimethyl trisulfide was primarily distributed in urban and suburban sections of the Xi River due to industrial emissions. Ethanethiol, DMS, and ethyl methyl sulfide, which are typical by-products of microbial anaerobic decomposition from domestic wastewater, were found in abundance in the suburban section. Diethyl sulfide, diethyl disulfide, methyl propyl disulfide, and 1-propyl disulfide representing agricultural nonpoint source pollution were mostly distributed in the rural section.

**Key words** | odor, pollution status, volatile organic sulfur compounds (VOSCs)

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## INTRODUCTION

The Xi River, with a total length of 52.7 km, is located at the southwest of Shenyang City, China. It is the first-level branch of the Hun River system and one of the major urban rivers. In the past decade, due to the pollution from municipal and agricultural sources, a phenomenon of water blackening and stink has become increasingly serious. Volatile organic sulfur compounds (VOSCs) are major substances that cause odor in the water environment (Wardencki 1998; Hu *et al.* 2007; Zhang *et al.* 2010; Chen *et al.* 2018), and most of them are harmful to the human respiratory system and central nervous system (Jaakkola *et al.* 1999; Jardine *et al.* 1999). No information related to VOSCs in the Xi River has been reported in previous references. Hence, this study aimed to investigate the pollution

status of VOSCs and determine the factors influencing their spatial distribution. This study provides data and theoretical support for the treatment of malodorous black water of the Xi River.

## MATERIALS AND METHODS

### Water sampling

As shown in Figure 1, the Xi River flows from northeast to southwest, and 15 sampling sites were selected along the path of the river. The sampling sites from S1 to S5 are located in the upstream section of the Xi River, which



**Figure 1** | Map of the sampling location of the Xi River.

passes through the urban section. Samples from S6 to S10 belong to the suburban section and the sampling sites from S11 to S15 are distributed in the downstream section, which is classified as the rural section. Each water sample was collected and preserved in a 1.0 L brown glass bottle without air. The samples were then stored at 4.0 °C and analyzed within 72 h. The water sampling was conducted twice, and the sampling dates were November 13–14, 2018, and July 1–2, 2019. The concentration data of the VOSCs from the two samplings were averaged for each sampling site.

### Instruments and reagents

The concentrations of  $\text{COD}_{\text{Cr}}$  (chemical oxygen demand chromium),  $\text{NH}_4\text{-N}$ , total nitrogen, and total phosphorus were determined by a rapid water quality analyzer (HACH DR900, USA). Total organic carbon (TOC) was measured using a TOC- $\text{V}_{\text{CPN}}$  analyzer (Shimadzu, Japan). Volatile organic sulfur compounds (VOSCs) were analyzed by purge and trap (P&T) (EST Encon Evolution, USA) coupled with gas chromatography (GC)–flame photometric detector (FPD) (Shimadzu, Japan). The GC was equipped with a DB-5 capillary column (30 m  $\times$  0.53 mm  $\times$  1.0  $\mu\text{m}$ ). The standards of VOSCs were purchased from Sigma-Aldrich, and their detailed information can be found in Table 1.

### Analysis of VOSCs

The analysis method of VOSCs was analogous to those in other studies (Deng *et al.* 2011; Kabir & Kim 2012). A 25 mL water sample was introduced into the purge chamber with ultra-high purity nitrogen flowing at 55 °C and 40 mL  $\text{min}^{-1}$  for 10 min. The trap was heated to 220 °C to release the VOSCs for 1.0 min, and then baked at 230 °C for 4.0 min.

The injector temperature of GC was at 250 °C and ultra-high purity nitrogen was used as the carrier gas at a constant flow rate of 2.0 mL  $\text{min}^{-1}$  and a split ratio of 0.1. The column oven temperature was controlled as follows: initial hold at 40 °C for 8.0 min, increase at 20 °C  $\text{min}^{-1}$  to 280 °C and hold for 5.0 min. The temperature of the FPD was set to 300 °C, and it was supplied with 40 mL  $\text{min}^{-1}$  of hydrogen and 60 mL  $\text{min}^{-1}$  of synthetic air. The lowest detection limit of VOSCs was 8.0 ng/L.

## RESULTS AND DISCUSSION

### Statistical analysis of VOSCs in the Xi River

The descriptive statistics of VOSCs in the Xi River are listed in Table 2, and each VOSC could be identified

**Table 1** | The detailed information for the VOSCs

VOSCs	Abbreviation	CAS	Molecular weight	Boiling point (°C)	Retention time (min)
Ethanethiol	EtSH	75-08-1	62.13	36.7	5.19
1-Propanethiol	1-PrSH	107-03-9	90.18	67.8	7.80
2-Butanethiol	2-BuSH	513-53-1	90.18	84.6–85.2	9.58
Isobutanethiol	2-Me-1-PrSH	513-44-0	90.18	88.0	9.96
Butanethiol	1-BuSH	109-79-5	90.18	98.2	12.03
Dimethyl sulfide	DMS	75-18-3	62.13	38.0	5.45
Methylthioethane	EMS	624-89-5	76.15	63.2	6.12
Diethyl sulfide	DES	352-93-2	90.18	94.4	10.68
Dimethyl disulfide	DEDS	624-92-0	122.25	152.0	15.94
2,3-Dithiahexane	MPDS	2179-60-4	122.25	154.0	16.10
Dimethyl trisulfide	DMTS	3658-80-8	126.26	165.0–170.0	16.81
Diisopropyl disulfide	2-PrDS	4253-89-8	150.31	178.0	17.41
Diallyl disulfide	DADS	2179-57-9	148.28	180.0	18.17
Propyl disulfide	1-PrDS	629-19-6	150.30	191.0	18.97

**Table 2** | The descriptive statistics for the VOSCs in the Xi River

VOSCs		Average value ( $\mu\text{g L}^{-1}$ )	Range ( $\mu\text{g L}^{-1}$ )	Standard deviation	Variation coefficient	Detection rate (%)
Thiols	EtSH	1.188	n.d.–9.979	0.887	0.747	93.33
	1-PrSH	0.433	0.050–0.799	0.230	0.531	100
	2-BuSH	0.160	0.027–0.260	0.068	0.422	100
	2-Me-1-PrSH	0.029	0.016–0.048	0.014	0.486	100
	1-BuSH	0.157	0.062–0.321	0.079	0.503	100
Sulfides	DMS	4.029	n.d.–9.522	2.895	0.719	93.33
	EMS	2.740	0.180–7.488	2.227	0.813	100
	DES	1.013	0.021–2.853	1.074	1.059	100
	DEDS	0.285	0.011–0.749	0.218	0.766	100
	MPDS	0.110	n.d.–0.285	0.099	0.898	86.67
	DMTS	1.287	0.058–3.762	1.148	0.892	100
	2-PrDS	0.082	n.d.–0.620	0.087	1.060	80
	DADS	0.149	n.d.–0.943	0.174	1.171	86.67
	1-PrDS	0.096	n.d.–0.228	0.087	0.908	80

from water samples at the 15 sampling sites. Dimethyl sulfide (DMS) was the most important contaminant with an average concentration of  $4.029 \mu\text{g L}^{-1}$ , a detection rate of 93.33% and a variation coefficient of 0.72. Methylthioethane (EMS) was also abundant with an average concentration of  $2.740 \mu\text{g L}^{-1}$ , a detection rate of 100% and a variation coefficient of 0.81. The variation coefficients and average concentrations of thiols were lower than those of sulfides in the Xi River. The statistical data of VOSCs in the Xi River were relatively higher than

those previously reported in other rivers (Gerbersmann *et al.* 1995; Ginzburg *et al.* 1998; Noblet *et al.* 1999). Prior to this study, we investigated the concentrations of VOSCs in two other rivers (the Baitapu River and Pu River) in Shenyang. The average concentrations of DMS, DES, and EtSH in the Baitapu River were  $3.361 \mu\text{g L}^{-1}$ ,  $1.002 \mu\text{g L}^{-1}$ , and  $0.840 \mu\text{g L}^{-1}$ , respectively. In the Pu River, DMS, EtSH, and 1-BuSH were the most important VOSCs, with average concentrations of  $0.114 \mu\text{g L}^{-1}$ ,  $0.064 \mu\text{g L}^{-1}$ , and  $0.051 \mu\text{g L}^{-1}$ , respectively. The above

two rivers were polluted in recent years with black water and an obvious peculiar smell was present in some river sections. However, the concentrations of VOSCs in the Xi River were even higher than those in the above two rivers. These results indicate that when compared with other municipal rivers, the Xi River is more heavily polluted and the malodor phenomenon is even more evident.

### Spatial distribution of VOSCs in the Xi River

As shown in Figure 2, the total concentration of the 14 VOSCs,  $\rho(\Sigma\text{VOSCs})$ , ranged from 2.575 to 52.981  $\mu\text{g L}^{-1}$  along the path of the Xi River, and sulfides accounted for a predominant part of the VOSCs in most of the sampling sites. The  $\rho(\Sigma\text{VOSCs})$  in the sites from S1 to S5 were much lower than those in other sites, and the highest  $\rho(\Sigma\text{VOSCs})$  were detected in sites S8 to S10, which indicated that the degree of the malodor phenomenon in the suburban section of the Xi River was more serious than that in the urban section. The  $\rho(\Sigma\text{VOSCs})$  in the sites from S11 to S15 decreased probably due to the reaeration effect of the river in the rural section. However, they were still higher than 25.0  $\mu\text{g L}^{-1}$ . The high concentration of VOSCs observed in the Xi River is consistent with the high organic and nutrient concentrations. The average concentrations of  $\text{COD}_{\text{Cr}}$  and TOC measured in the Xi River were 90.03  $\text{mg L}^{-1}$  and 11.65  $\text{mg L}^{-1}$ , respectively. The decomposition of organics

by aerobic microorganisms consumed most of the dissolved oxygen in the water and promoted substantial breeding of anaerobic bacteria. Then, the decomposition of organics by anaerobic microbes resulted in a large production of VOSCs (Caron & Kramer 1989). In addition, the average concentrations of total nitrogen and total phosphorus in the Xi River were 3.37  $\text{mg L}^{-1}$  and 1.18  $\text{mg L}^{-1}$ , respectively. The high level of nutrient concentrations could induce water eutrophication and the rapid propagation of algae. The anaerobic decomposition of dead algal cells can also release a large quantity of VOSCs into the water body (Fritz & Bachofen 2000).

### Factors influencing the spatial distribution of VOSCs

The evolutions in concentrations of eight characteristic VOSCs along the river are illustrated in Figure 3. It was observed that the concentration of dimethyl trisulfide (DMTS) was higher in the sites from S1 to S8 than those from S9 to S15 (Figure 3(a)). DMTS is a typical contaminant from industrial emission (Watson & Jüttner 2017; Jana & Sarkar 2018; Yu *et al.* 2019); therefore it can be rich in the urban and suburban sections where effluent from factories is discharged. The decrease of DMTS concentration from S9 was probably the decomposition of DMTS because its chemical structure is relatively unstable among VOSCs. The concentrations of DMS and EMS significantly

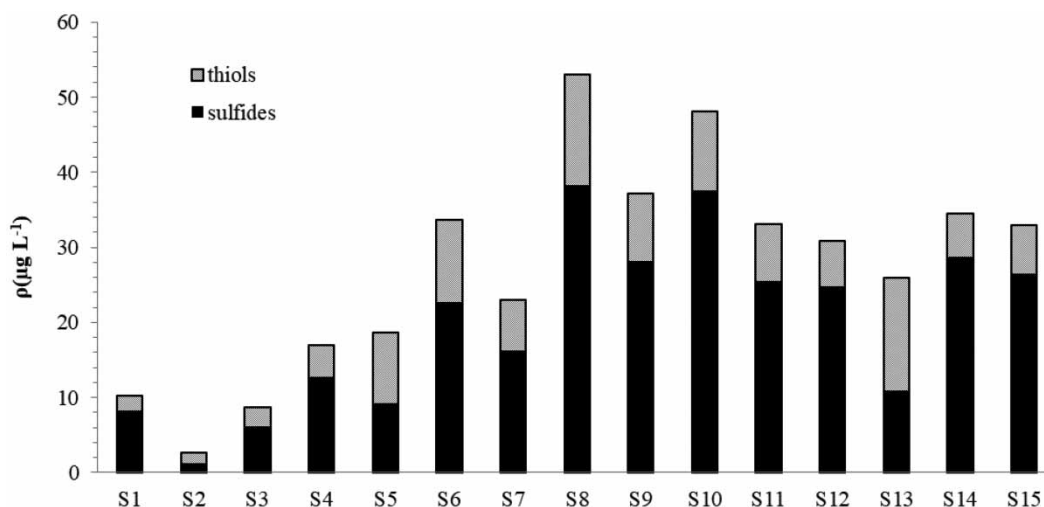
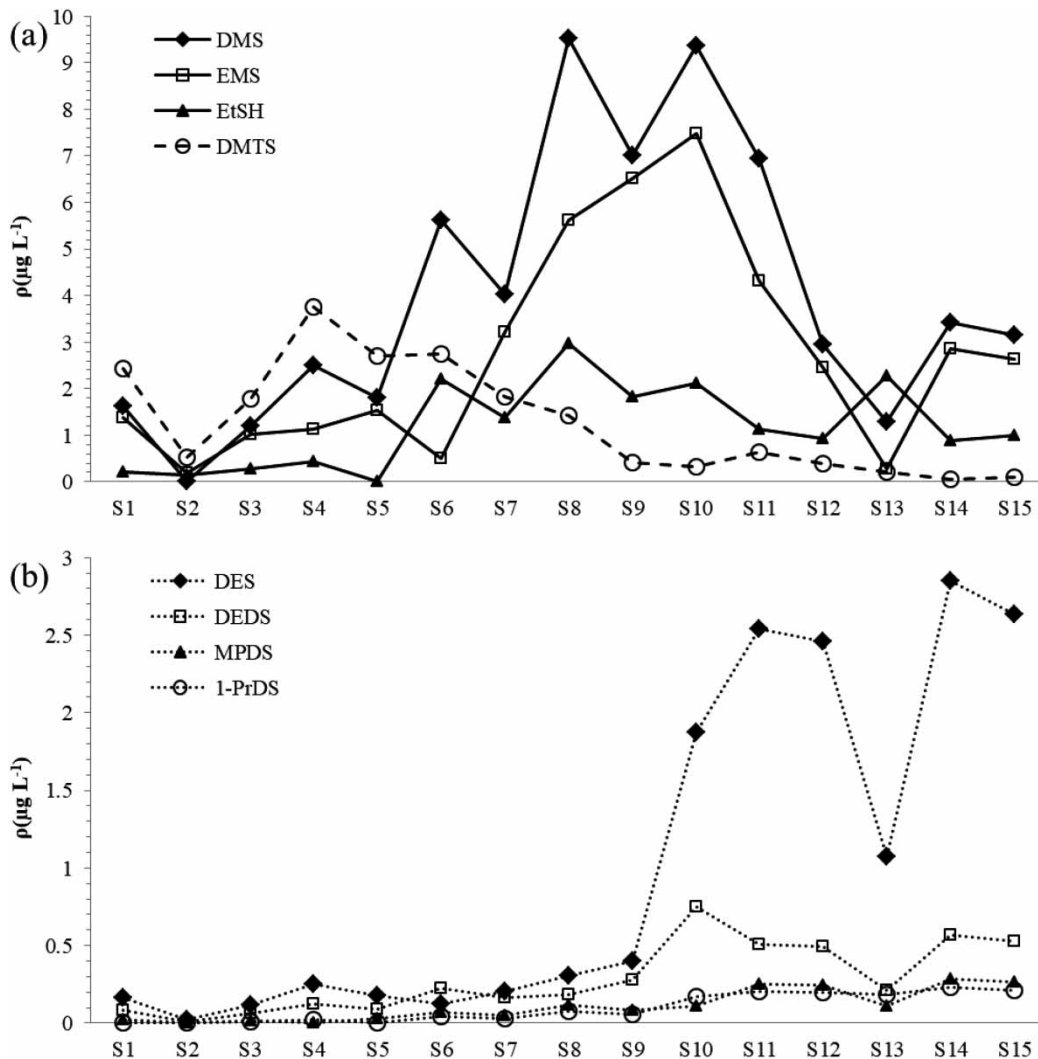


Figure 2 | The distribution of  $\rho(\Sigma\text{VOSCs})$  along the path of the Xi River.



**Figure 3** | The concentrations of eight VOSCs in the sampling sites along the Xi River.

increased in the sites from S6 to S10, and the concentrations of ethanethiol (EtSH) were higher in the sites from S6 to S10 than those from S1 to S5 (Figure 3(a)). Under anaerobic condition, DMS and EMS can be generated from the microbial decomposition of sulfur amino acid, which is a major component of proteins in domestic sewage (Sreekumar *et al.* 2009; Du & Parker 2012; Liu *et al.* 2015; Fisher *et al.* 2018). DMS and EtSH may also be derived from the anaerobic decomposition of sulfur-containing surfactants, which commonly exist in laundry detergent (Sugiura *et al.* 2004; Dzialowski *et al.* 2009; Yin & Wu 2016). In the suburban section, sewage treatment facilities and drainage pipe networks were very deficient, and much domestic sewage was directly

discharged into the Xi River, which led to an increase in DMS, EMS, and EtSH. The concentration of diethyl sulfide (DES) was much higher in the sites from S11 to S15 than in the other sites (Figure 3(b)). Diethyl disulfide (DEDS), methyl propyl disulfide (MPDS), and 1-propyl disulfide (1-PrDS) also increased in the sites from S11 to S15, but they were not as prominent as DES (Figure 3(b)). The above four substances are stable VOSCs with large molecular weights, and they are microbial by-products of carbamate pesticides from paddy fields (Lu *et al.* 2015; Jing *et al.* 2018). Therefore, the distributions of DES, DEDS, MPDS, and 1-PrDS in the rural section can be attributed to agricultural non-point source pollution.

The above results indicated that artificial remediation measures should be taken to control VOSCs in the Xi River. In urban and suburban areas, the building of enough decentralized facilities for wastewater treatment is required to treat domestic wastewater and decrease organics and nutrients that are discharged into the river. In rural areas, relevant policies and measures should be adopted to limit the use of pesticides and fertilizers and control agricultural non-point source pollution. The construction of ecological wetlands along the river could be a supplementary solution. Furthermore, the release of pollutants from the river sediments should be considered and further investigation is needed.

## CONCLUSION

Dimethyl sulfide (DMS) was the most important contaminant among the VOSCs and the malodor phenomenon can be serious in the Xi River. The VOSCs were primarily distributed in the suburban and rural sections, and the suburban section was the worst polluted by the VOSCs. Industrial emissions in urban and suburban sections, the discharge of domestic wastewater in suburban areas, and agricultural nonpoint source pollution in the rural downstream were the main factors influencing the spatial distribution of VOSCs in the Xi River.

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