Odorous Volatile Organic Sulfides in Wastewater Treatment Plants in Guangzhou, China

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ABSTRACT: Odorous volatile organic sulfides (VOSs) in headspace atmosphere and wastewaters were identified and quantified synchronously in two municipal wastewater treatment plants (WWTPs) in Guangzhou, China. Dimethyl sulfide (DMS), with concentrations ranging from 0.66 to 5.41 mg/m^3, was the major VOS in air samples. Carbonyl sulfide (COS), carbon disulfide (CS_2), and dimethyl disulfide (DMDS) ranged from 0.01 to 0.21, 0.03 to 0.44, and 0.06 to 1.61 mg/m^3, respectively. Methanethiol was not found in any gas samples. The concentrations of DMS in wastewaters ranged from 23.68 to 308.17 mg/m^3 and were also the highest values compared with other VOSs, for all of the treatment processes. Methanethiol was detected in all wastewater samples, except that from the aeration tank, which ranged from 113.08 to 216.82 mg/m^3. The COS, carbon disulfide, and DMDS in wastewaters ranged from 0.11 to 2.21, 1.37 to 23.29, and 0.24 to 106.75 mg/m^3, respectively. Odors from pollution related to VOS were different in the two plants, and they were strongly associated with the characteristics of incoming wastewater and treatment processes. The VOSs in ambient air samples from nearby residential areas downwind of the plant border were also measured, and the results strongly suggested that control measures are needed for odor pollution in the WWTPs to mitigate malodor in the surrounding neighborhoods. *Water Environ. Res.,* **80,** 324 (2008).

KEYWORDS: odor, volatile organic sulfides, wastewater treatment plants, emission, dynamic chamber.

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Introduction

Emission of chemical compounds from some municipal wastewater treatment plants (WWTPs) may cause odor nuisance and have great effects on the population in the vicinity (Langenhove et al., 1985). Odor control has been of great concern in wastewater collection, treatment, and drainage systems (Wu et al., 2006). Hydrogen sulfide (H_2S) and ammonia (NH_3) are the two principal inorganic odorous compounds from WWTPs, whereas many malodors of an organic nature arise from the anaerobic decomposition of compounds containing nitrogen or sulfur. These malodorants, including mercaptans and other nitrogen or sulfur organics, are often unavoidable because of the nature of the wastewater (Bourgeois and Stuetz, 2002; Hwang et al., 1995). Among the odorous organics, volatile

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organic sulfides (VOSs) are an important class of malodors that should not be ignored.

Volatile organic sulfides, including methanethiol, carbonyl sulfide (COS), dimethyl sulfide (DMS), carbon disulfide (CS_2), and dimethyl disulfide (DMDS), generally have a very negative hedonic value and will contribute to odor pollution, even when emitted in very small amounts. Because of their very low odor thresholds, high toxicity, and potential corrosive effects, the presence of VOSs in waste gases deserves special attention (Smet and Langenhove, 1998; Smet et al., 1998). For their significant contribution to atmospheric sulfur and potential influence to global climate, VOSs distributed in the atmosphere and marine system have been extensively studied (Andreae and Crutzen, 1997; Bates et al., 1987). Other studies investigated VOSs dissolved in freshwater system and heavily polluted creeks (Hu et al., 2007; Muezzinoglu, 2003). The primary concern about these sulfur compounds in WWTPs is their irritating nature, which would cause a nuisance to people in the surrounding neighborhood. Many studies about the malodorants in offgases from WWTPs typically focus on hydrogen sulfide (H_2S) (Al-Shammiri, 2004; Parsons et al., 2000; Stuetz et al., 1999), partly because of a relatively large share of hydrogen sulfide in odorous sulfur-containing compounds. However, hydrogen sulfide seemed not to be a good marker measuring odor concentrations, although it also had a low odor threshold based on dynamic dilution olfactometry (Cheng et al., 2005). Because of the lower odor threshold values and wide concentration ranges of VOSs distributed in WWTPs, it is very difficult to find a well-established analytical procedure using on-line detection with some instruments (Islam et al., 1998). Analysis of these compounds and relevant quality control are quite complicated by factors such as sampling methods, sample storage and transportation, instrument applied, and analytical methods chosen (Wardencki, 1998). For example, losses may occur during storage and analysis, as a result of irreversible adsorption onto surfaces, rearrangements catalyzed by different materials, and reaction with substances the VOSs come into contact with (Nielsen and Jonsson, 2002).

Devai and DeLaune (1999) studied the amounts and types of sulfur compounds, including methanethiol and DMS, released from a WWTP at various stages of treatment. Smet and Langenhove (1998) examined biotechnological and physiochemical methods for the abatement of VOSs in odorous emissions. Smet et al. (1998) reviewed sources of sulfur compounds and their control methods, including biofiltration, scrubbing, and adsorption. Although there were studies about the identification, quantification, and mutual relationship of odorous VOSs in different environments (Hwang

et al., 1995; Watts, 2000; Winter and Duckham, 2000), most of them only characterized these compounds occurring in air or in water bodies separately; simultaneous determination of VOSs in wastewaters and the above headspace was quite scarce. Langenhove et al. (1985) used a purge and cold trap method with a gas chromatography-mass selective detector (GC-MSD) to identify the odorous volatiles in wastewater. They could detect a number of odorous compounds, but this did not quantify the compounds. Wu et al. (2006) studied the occurrence of VOSs in the different sections of a WWTP, the outlet of both the WWTP and rainfall water, and its downstream area, but only carbon disulfide and DMS were studied, and the relationship between the gas phase (water surface) and liquid phase (water body) was also poorly understood. In the present study, the distribution of VOSs both in wastewater and in the headspace atmosphere (different phases) in different treatment stages were measured successfully and thus benefit the discussion on the mutual relationship of each compound between the air and liquid phases.

Guangzhou is a central city in the Pearl River Delta of south China. In the city, currently most municipal wastewater treatment processes are designed to achieve acceptable removal of organic matter, toxic substances, and various nutrients, but they do not always satisfactorily remove odors. A comparative inquiry of the odor nuisance made by the local environmental protection agency in recent years suggests that complaints about odors from these WWTPs in urban Guangzhou is growing, and this malodor problem has even led some adjacent commercial or recreational institutions to stop their business occasionally or permanently. In this paper, the distributions of VOSs emitted from wastewater and dissolved in water bodies were studied simultaneously in different sections of two WWTPs. Target malodorous compounds in this paper include methanethiol, COS, DMS, carbon disulfide, and DMDS. The possible effects of emission of these odorants on the population dwelling in the vicinity were also primarily assessed.

Materials and Methods

Chemicals and Preparation of Standard Gases. Standards of methanethiol (purity 99.5%), COS (100%), DMS (99%), and DMDS (97.5%) were all purchased from Sigma-Aldrich (Sigma-Aldrich Co., St. Louis, Missouri). Carbon disulfide (97.5%) was purchased from XinHua Chemical Co. Ltd. (Taiyuan, China). Pure air and high-purity nitrogen (99.999%) were purchased from Guangzhou Industrial Gases Co. Ltd. (Guangzhou, China). The calibration was carried out after dilution of methanethiol, COS, DMS, carbon disulfide, and DMDS. These VOSs were first diluted to 4.82 mg/m³ for methanethiol, 2.08 mg/m³ for COS, 5.81 mg/m³ for DMS, 3.02 mg/m³ for carbon disulfide, and 2.56 mg/m³ for DMDS, in nitrogen gas as a primary standard mixture. This primary standard was further dynamically diluted with pure nitrogen to calibration standards, by using mass-flow controllers and a mixing chamber. Calibration curves (area–dose) were obtained by running 250 mL standard gas with methanethiol levels of 0, 1.21, 2.41, 3.62, and 4.82 mg/m³; 0, 0.51, 1.04, 1.56, and 2.08 mg/m³ for COS; 0, 1.45, 2.95, 4.36, and 5.81 mg/m³ for DMS; 0, 0.75, 1.51, 2.66, and 3.02 mg/m³ for carbon disulfide, and 0, 0.64, 1.28, 1.92, and 2.56 mg/m³ for DMDS, respectively. The method detection limit was 0.062 μg/m³ for methanethiol, 0.058 μg/m³ for COS, 0.031 μg/m³ for DMS, 0.048 μg/m³ for carbon disulfide, and 0.055 μg/m³ for DMDS, with air sample volumes of 250 mL. The relative precision of the measurement was <6%, based on the reproducibility of consecutive samples over a 10-day period, with 2.95-μg/m³ (n =

10) and 29.5-μg/m³ (n = 10) COS standards. All operations were conducted at room temperature (25°C). No target compounds were detected in the blanks.

Apparatus and Analytical Procedures. To avoid possible reaction and adsorption, all the materials (air pump, gas flow meters, and other apparatus) used for sample treatment were inert. The silanization stainless-steel canisters were used for collecting air samples. Before sampling, all canisters were cleaned and kept under a high vacuum by an Entech 3100 system (Entech Instruments Inc., Simi Valley, California). The SKC Tedlar sampling bags (3-L, SKC Inc., Covington, Georgia) were used for collecting gas samples purged out from wastewater. Before usage, all bags were flushed three times with pure nitrogen gas.

The analytical method is similar to that described in literature (Yi et al., 2007). Briefly, VOSs were analyzed by an Entech model 7100 Preconcentrator (Entech Instruments Inc.) coupled with an Agilent 5973N GC-MSD (Agilent Technologies, Santa Clara, California). For the preconcentration of VOSs in air samples, there are three stages of trapping in the Entech Preconcentrator. In the first stage, 250-mL (101 kPa [1 atm], °C) air samples were drawn through a liquid nitrogen trap at −160°C, to trap the VOSs. After this, the first-stage trap was heated to 10°C, and the trapped gases were transferred by 40 mL of helium at a flowrate of 10 mL/min to a second-stage trap with Tenax sorbents at −40°C. Most of the carbon dioxide was removed during this stage. Then, the second-stage trap was heated to 150°C, and the thermally desorbed gases were transferred to a third-stage cryofocusing trap at −170°C by 30 mL of helium at a flowrate of 10 mL/min. This cryogenic focusing is necessary to improve the separation in the gas chromatography column and to improve the shapes of the gas chromatography peaks. An HP-1 capillary column (60 m length × 0.32 mm internal diameter, and 1.0 μm film thickness; Agilent Technologies) was used, and the gas chromatography oven temperature was programmed initially at −50°C, holding for 2 minutes, increasing to 100°C at 5°C/min, then to 250°C at 10°C/min, and then holding for 10 minutes. The MSD was used in the scan mode, the ionization method was electron-impacting, and the scan was set from m/z 46 to 300 in 0.45 second. The operating system was controlled by a MS Chemstation software (Agilent Technologies). For determination of the VOSs, target ions (methanethiol: m/z 48; COS: m/z 60; DMS: m/z 62; carbon disulfide: m/z 76; and DMDS: m/z 94) were selected.

Sites Description. Two municipal WWTPs in Guangzhou Economic and Technological Development District were selected for tests in this study—the West Zone WWTP (plant A) and the East Zone WWTP (plant B). They received domestic wastewater and some industrial wastewater after primary treatment. Conventional activated sludge process was used in the plants. Plant A, built in 1994, with treatment capacity of 30 000 m³/d, is a secondary wastewater treatment facility with two sets of primary sedimentation tanks and two sets of secondary sedimentation tanks. Wastewater, after the primary sedimentation tanks, is delivered to the aeration tank for secondary biological treatment, operated in sludge reaeration. Aeration basin selector zones are designated to be anoxic zones in the aeration tank, to allow for the selective growth of facultative bacteria to assist in the wastewater treatment processes. After the aeration tank, wastewater is delivered to the secondary sedimentation tank, then to the effluent. In plant A, all wastewater tanks were exposed to the open air. Sampling sites in this plant were selected in the order of treatment processes. Plant B, built in 2003, with capacity of 25 000 m³/d, adopted sequencing batch reactor treatment techniques; all the tanks were entirely

Table 1—Averaged parameters measured in wastewater (mg/L, except for pH).[a]

	Plant A				Plant B		
	Influent	Primary effluent	Aeration tank	Secondary effluent	Influent	Biological tank	Final effluent[b]
COD_{Cr}	582.8	406	NA	39	183	NA	21
5-day BOD	248.2	179	NA	7.6	56	NA	3.5
Suspended solids	322.6	172	NA	25	167	NA	15
NH_3-N	14.3	11.5	NA	2.6	6.1	NA	0.2
PO_4^{3}-P	2.9	2.3	NA	1.1	0.6	NA	0.2
Mixed liquor suspended solids	NA	NA	3568	NA	NA	5648	NA
Dissolved oxygen	NA	NA	1.5	NA	NA	5.2	NA
pH			6.7			6.6	

[a] NA = not available.
[b] Outflow from biological tank.

covered by two large sheds built with BlueScope Steel (BHP) armor plates (BHP Billiton Limited, Melbourne Victoria, Australia). Plant B is a new WWTP, so the problem of malodor pollution was taken into account, and all wastewater tanks were covered completely when it was built. The first shed, with a volume of 3144.1 m³ (approximately 4 m high), covers the influent tank and grit and grease chamber. Four sets of selective batch reactor tanks were covered by the second shed, with a volume of 15 486.8 m³. Each shed had four glass windows (each with an area of 2.0 m²) in the walls, and there is no other ventilation equipment. The two WWTPs were all located in residential areas, and an obvious unpleasant odor can be noticed near the plants in the downwind direction. In Guangzhou city, plant A is typical among WWTPs built long ago, and plant B represents WWTPs recently built with more advanced treatment processes. Sampling was conducted on sunny days in July 2005. Some conventional water parameters in the two WWTPs during our test period are listed in Table 1.

Sampling Methods. Because of the limitation in sampling management, all the values in this study were from single analysis. To understand the spatial pattern of VOS concentrations in the plant, air samples (grab) were collected (on water surface) at various treatment stages with the pre-evacuated 2 l silanization stainless-steel canisters. Wastewater samples were collected simultaneously from the same sampling points. The intervals of samples collected between two different units were decided considering the corresponding hydraulic retention time (HRT) of each treatment process.

Wastewater Sampling. The sampling locations were designed to reflect VOSs occurring in the different units as references. Grab samples were collected in 250-mL amber screw cap glass bottles with no headspace, to avoid alteration of organic compounds by chemical reactions or microbial action. The water samples taken from the field studies were immediately placed in an adiabatic cold box with ice and then delivered to the laboratory and stored in a refrigerator (4°C). No sample preservatives were used to adjust the pH or affect the chemical nature of the samples. All wastewater samples were analyzed in 48 hours. For the determination of VOSs, 25 mL of wastewater was injected to a purging vessel (capacity is 50 mL), and VOSs in wastewater were purged out by a flow of pure nitrogen gas. The detailed purging assembly is illustrated in Figure 1. The purging nitrogen flowrate was 160 mL/min, and the purging time was 11 minutes (Wardencki, 1998). After the stripping step, the gas sample was immediately connected to a preconcentration system followed by GC-MSD, and 250 mL of air mass was drawn for chemical analyses. Before the next stripping, the purging vessel was flushed three times with deionized water. A blank test with this deionized water was also conducted the same way, to find if there is any interference from the ambient conditions.
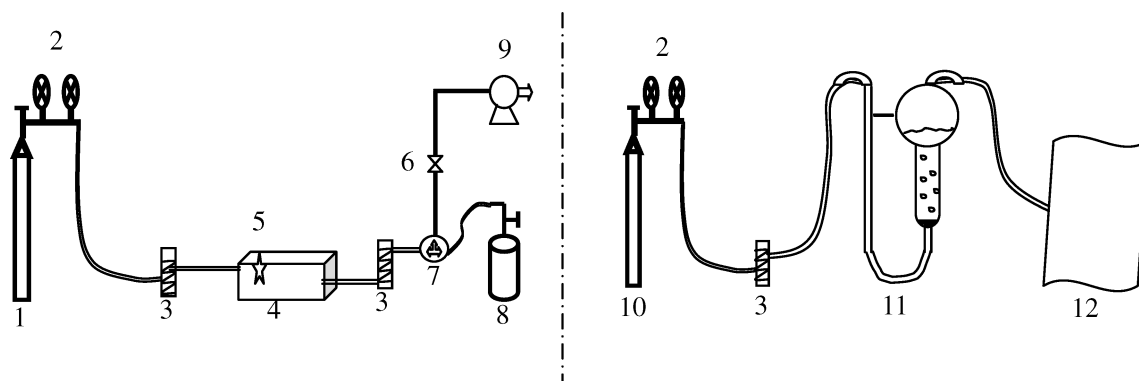

Figure 1—Corresponding assembly of sample collection and preparation. Left: field-flux-chamber sampling setup for emissions; right: laboratory gas-sample-stripping assembly. Numbers denote the following: (1) compressed air cylinder, (2) pressure valve, (3) gas-flow meter, (4) flux chamber, (5) air propeller, (6) gas valve, (7) three-port valve, (8) vacuum canisters, (9) air pump, (10) nitrogen cylinder, (11) purging vessel, and (12) gas bag.
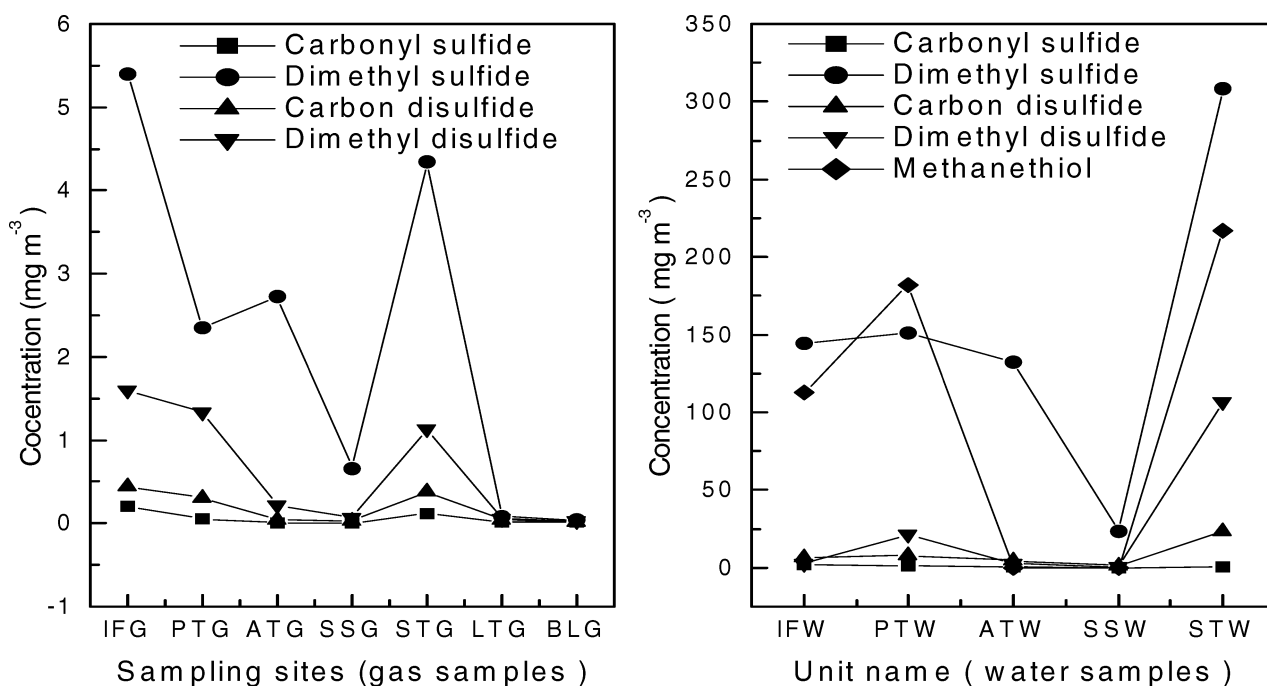
Figure 2—Change of VOS levels in each treatment process in plant A, including gas samples and water samples. Left: IFG = influent, PTG = primary sedimentation tank, ATG = aeration tank, SSG = secondary sedimentation tank, STG = sludge thicker tank, LTG = lawn and woody area, and BLG = borderline of plant. Right: IFW = influent, PTW = primary sedimentation tank, ATW = aeration tank, SSW = secondary sedimentation tank, and STW = sludge thicker tank water.

Air Sampling. A modified dynamic flux chamber was used for measuring VOS emission from the water surface (Figure 1, left). Pure air (in cylinder) was used as a flush gas, and silanization stainless-steel canisters were used as sample collectors, to avoid adsorption and other interferences (Leyris et al., 2005; Muezzinoglu, 2003). This modification ensured the sampling of emissions only from the water surface, without contamination from surrounding ambient air possibly containing the same compound at a different concentration. The dynamic flux chamber covers an area of 0.13 m², with a headspace height of 0.12 m. During sampling, two gas-flow meters were adjusted to 1 L/min. This flowrate was chosen on the basis of ambient-air-sampling procedures applied for many VOSs. If a higher flowrate was used, the air current would enhance diffusion of VOSs from the water surface. However, a lower flowrate would take more time and, considering the warmth of the day, this could have increased the risk of losses resulting from chemical or biochemical reaction and evaporation (Muezzinoglu, 2003). During the sampling time, steady flush gas flowrates (two flow meters were fixed on 1.0 L/min until dynamic equilibrium was achieved in the flux chamber) were maintained, to keep the pressure inside the chamber steady. The samples downwind of the WWTPs were collected with canisters 1 m above the ground.

Results and Discussion

Volatile Organic Sulfides in Wastewater Headspace and in Ambient Air. *Volatile Organic Sulfides in Wastewater Headspace.* Results for air samples from wastewater headspace in the two plants are shown in Figures 2 and 3. The concentration of COS ranged from 0.01 to 0.21 mg/m³ in different treatment processes and were the lowest compared with other VOSs. The DMS levels (0.66 to 5.41 mg/m³) were the highest among VOSs. The concentrations of carbon disulfide and DMDS ranged from 0.03 to 0.44 and 0.06 to 1.61 mg/m³, respectively. On the whole, all compounds presented higher concentrations in the headspace of influent than those from other processes. Methanethiol was not detected in all gas samples analyzed.

In this study, the levels of some VOSs were close to data reported by Wu et al. (2006) in a WWTP in Taiwan. Because the chemical composition of wastewater will change after some treatment processes, here individual species are discussed separately. Properties of studied VOSs are listed in Table 2. Similar to the results of Cheng et al. (2005), methanethiol was not observed in all gas samples. The reason perhaps is that methanethiol is only a transient VOS in the atmosphere, with a half-life of approximately 0.2 day, so it would rapidly decay before analysis (Smet and Langenhove, 1998). Furthermore, thiol methylation potential also should not be neglected, because methanethiol may change into DMS through a biological methylation reaction (Stets et al., 2004). As the most abundant VOSs detected, DMS shared nearly 70% of the total VOSs. The DMS is generated principally via the degradation of some sulfur-containing matrix in the anaerobic digestion process caused by some microorganisms (Smet et al., 1998). Moreover, it is believed that DMS can be generated from dimethyl sulfoxide (DMSO), a major solvent used for photo-resistant stripping and cleaning in the electro-optical industry in Guangzhou, because of the chemical oxidation–reduction reactions caused by some reducing agents or because of the biological treatment carried out under anaerobic conditions (Bentley and Chasteen, 2004; Glindemann et al., 2006; Wu et al., 2006). Among all processes, DMS presented the highest concentrations (nearly 5.5 mg/m³) at influent units. This perhaps indicated that the characteristics of influent directly influenced the formation of DMS. Furthermore, most influent
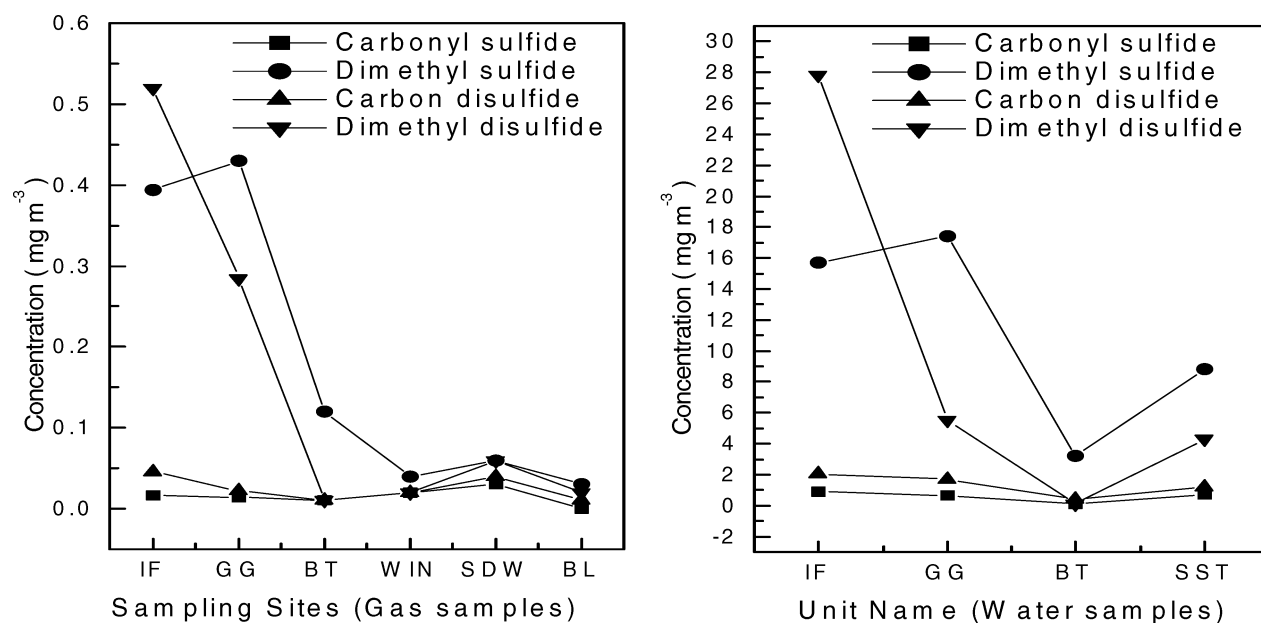
Figure 3—Change of VOS levels in each treatment process in plant B. Both gas samples and water samples are included; IF = influent, GG = grit and grease chamber, BT = biology treatment tank, WIN = windows on shed, BL = borderline of plant, SLD = sludge dewater workshop, and SST = sludge storage tank.

wastewater is transported to the plant mainly by pipes underground, which are under pressure and gravitation. The residence time of wastewater in the pipes is longer than 6 hours, which is long enough to deplete oxygen in wastewater and induce the formation of anaerobic conditions; such a condition greatly contributes to the production of VOSs (Hwang et al., 1995). The perturbation of wastewater head is deemed to be the major cause of volatilization of the organic compounds, and the fugitive VOS concentrations at influent units were higher because of more serious perturbation of wastewater (Wu et al., 2006). In the aeration tanks, DMS increased slightly, mainly because of the vaporization of DMS strengthened by strong turbulence of the aquatic system in the aeration process. In plant A, DMS presented relatively high concentrations in the sludge storage tanks. Because of the long HRT (21 hours) in the sludge storage tank, DMS formation would be strongly enhanced by the presence of oxygen-deficient zones stimulating the activity of anaerobic microorganisms during the anaerobic digestion process (Islam et al., 1998). It should be noted that DMS is originally formed in this unit, and since DMS has very low boiling point (37.3°C) and relatively high Hrney's law coefficient, it does not enter the sludge or gets adsorbed by suspend solids; instead it will

come right out of the basin (Wu, 2006). In plant B, however, the headspace concentrations of DMS and DMDS in the sludge storage tank were lower than those in the influent. This could be partly explained by the long HRT (19.4 hours) in biological and aeration processes in the aeration tanks, which caused most organics in the wastewater to be mostly oxygenated and mineralized and hence left very few organics decomposed in the sludge storage tank.

The COS had the lowest concentrations in each unit, though it has the highest dimensionless Henry's law coefficient (1.94 at 25°C) and the longest atmospheric half-life (730 days) among the studied VOSs (Smet and Langenhove, 1998; Table 2). Possibly, there were some unknown factors that restrained the formation of COS in the wastewater environment, and the detailed mechanisms need further investigation. Carbon disulfide also presented concentrations relatively lower in air samples at different units. This can be explained that carbon disulfide could be consumed greatly by various bacteria using it as an energy source for growth (Plas et al., 1993). In plant A, it was observed that the concentration of DMDS is lower than that of DMS in the influent. However, in plant B, DMDS had the highest concentration among the studied VOSs in the influent. This phenomenon was perhaps the result of much more DMDS in the

Table 2—Properties of studied VOSs (Smet and Langenhove, 1998).*

	Boiling point (°C)	Odor threshold value (mg m^{-3})	$H_{25°C}$ (−)	MAK (mg/m^3)	Odor quality	Atmospheric life time (days)
Methanethiol	6.2	0.0022	0.10	1.2	Decayed cabbage	1
DMS	37.3	0.0019	0.07	62	Decayed vegetables	0.2
DMDS	109.7	0.0046	0.04	< 92	Putrification, foul	n.d.a
CS$_2$	46.2	0.0355	0.65	37	Vegetable sulfide, aromatic	12 to 40
COS	−50.0	n.d.a.	1.94	n.d.a.	Pungent	730

* Note: $H_{25°C}$ = dimensionless Henry coefficient at 25°C [(mol/m^3)$_{air}$/(mol/m^3)$_{water}$]; MAK = maximum concentration value in workplace conditions; n.d.a. = no data available.

Table 3—Contrast of odor threshold value, state emission limit and tested WWTPs (mg/m³).

	Methanethiol	DMS	Carbon disulfide	DMDS
Odor threshold value	0.0022	0.0019	0.0355	0.0046
Emission standard	0.007	0.07	3.0	0.06
Plant A	Not detected	0.042	0.021	0.031
Plant B	Not detected	0.032	0.011	0.026

wastewater, because DMDS is widely used as an edible additive in delicatessen factories and as an activation reagent in the local oil refining industry. The studied WWTP might receive some industrial wastewater without efficient removal of DMDS, as can be seen from the high levels of DMDS in the influent wastewater. On the whole, the headspace concentrations of DMDS presented an obvious decreasing tendency with the serial treatment processes.

Volatile Organic Sulfides in Ambient Air Downwind from the Plants. To explore the effects of VOS emissions from plant A on the nearby residential area, samples were taken at the downwind lawns and woody lands, in addition to the border of the plant, when the wind blew towards the residential area (wind velocity is approximately 1 m/s). The DMS had the highest concentrations— 0.081 mg/m³ at the woody land and 0.042 mg/m³ at the border. With the dilution and oxidation, the levels had an obvious decay at the lawn and woody lands. Although they were lower than the local emission standard (0.07 mg/m³, Table 3) at the border, they were still higher than its odor threshold (0.0019 mg/m³). Therefore, obvious malodor can be sensed in the residential area near both WWTPs, so the treatment facilities should be optimized to avoid this effect.

Because there was no ventilation equipment in the shed of plant B, air inside the shed almost had no exchange with the outside, except for the air exchange through the windows. Levels of almost all odorous VOSs at the sampling site near the window were higher than their limits in the workplace (maximum concentration value in workplace conditions [MAK], Table 2). It is well-known that, although the levels of these VOSs were low, long-term exposure to such levels may cause respiratory problems and other symptoms. So, the health effects on staff working in this plant (especially those working inside the shed) should be given attention.

Among all target compounds, the most prevailing compounds were DMS, methanethiol, and DMDS, followed by carbon disulfide and COS. The emission standards of these five odorous VOSs in this study were described in the *Emission Standards for Odor Pollutants* (State Environmental Protection Administration, 1993), except for COS. One problem is that VOS emission from the plants may have levels below this emission standard, but much higher than their odor thresholds, except for carbon disulfide (Table 3). Therefore, obvious malodor existed downwind from the borders of these plants, although the plants had met the emission standards.

Volatile Organic Sulfides in Wastewaters. For wastewater samples, concentrations of DMS were also relatively high at all treatment processes and ranged from 23.68 to 308.17 mg/m³. Concentrations of COS were the lowest, ranging from 0.11 to 2.21 mg/m³ in different treatment processes. Carbon disulfide and DMDS ranged from 1.37 to 23.29 and 0.24 to 106.75 mg/m³, respectively. Variation of VOSs in wastewaters was different from that in the headspace samples. As illustrated in Figures 2 and 3, almost all the highest levels of VOSs were found in the sludge

storage tank, not in the primary sedimentation tank. Unlike the headspace air samples, methanethiol was detected in wastewaters at the units of influent, primary sedimentation tank, and sludge storage tank, with concentrations ranging from 113.08 to 216.82 mg/m³. The reason is that for wastewater analysis, methanethiol was purged out from the wastewater by pure nitrogen gas, and there was not enough oxygen for the degradation of methanethiol, so the possible losses resulting from chemical or biological reactions were largely avoided. The units in which methanethiol can be detected are all anoxic, with no or limited dissolved oxygen in the wastewaters; in the aeration tank and secondary sedimentation tank, where oxygen in the wastewaters is excessive, no methanethiol was detected.

In wastewater, VOSs had higher concentrations in the sludge storage tank than in any other units. One reason is that HRT (21 hours) is long enough in the sludge storage tank of plant A for anaerobic conditions to occur easily, and a great deal of odorous compounds are produced while the sludge is composting. Another reason is that there are large numbers of microorganisms and organic compounds (typically with high molecular weight) condensed in this tank, and VOSs could be produced by biological or chemical reactions during the decomposition of sludge under anaerobic conditions (Smet et al., 1998). A noticeable phenomenon was that the wastewater concentrations of VOSs in sludge storage tank were higher than those in the influent, indicating that the sludge storage tank was one of the main sources producing VOSs. More than 95% of these VOSs were eliminated after the subsequent activated sludge process with biodegradation or chemical reactions. This considerable removal efficiency of the VOSs was the result, not only of biological degradation, but also of the air stripping.

As far as different plants are concerned, different treatment techniques applied resulted in differences in the emission of VOSs. In plant A, the concentrations of all target compounds were approximately 10 times higher than those in plant B for the same treatment process. The pollution degree of influent in plant A was far higher than that in plant B, as can be seen from the influent COD in plant A (248 mg/L) and plant B (56 mg/L) (Table 1). Some studies indicated good correlation between wastewater odors and their corresponding biochemical oxygen demand (BOD) values (Onkal-Engin et al., 2005). As a consequence, it could be predicted that VOS production was strongly associated with the characteristics of incoming wastewater. On the other hand, a longer HRT (19.4 hours) in the biological and aeration processes resulted in lower odorous compounds produced in plant B. Plant A was clearly anaerobic, while plant B had excessive oxygen; thus, higher levels of VOSs were produced in plant A.

Conclusions

Odors from WWTPs are of increasing concern in China's densely populated urban areas. However, partly because of limited analytical facilities, only inorganic odor gases, such as hydrogen sulfide and ammonia, have been considered and tested, although organic compounds, like VOSs, are present in the emission from WWTPs and contribute to malodors in the vicinity. In the present study, VOSs, including methanethiol, COS, carbon disulfide, DMS, and DMDS, were measured both in wastewaters and in the headspace atmosphere in two typical WWTPs with different treatment techniques, in urban Guangzhou. The VOS-related malodor pollution was different in the two plants, and it was strongly associated with the characteristics of the incoming wastewater and treatment processes. Techniques with strong deep-seated aeration and longtime biological reaction with excess oxygen would restrain anaerobic

conditions and therefore can effectively reduce the emission of VOSs. Although covering the tanks or building an isolation belt with trees could reduce the emitted odorous compounds, to some extent, malodor is still a problem for the people dwelling near the WWTPs. Results from this study strongly suggested that a green strategy for odor-pollution control in the WWTPs should be developed, especially for organic odorous gases, such as VOSs, to lower the adverse effects on surrounding neighborhoods.

Credits

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