

Identification of Seasonal Variations in Volatile Sulfur Compound Formation and Release from the Secondary Treatment System at a Large Wastewater Treatment Plant

Kweku Sekyiamah^{1*}, Hyunook Kim², Laura L. McConnell³, Alba Torrents⁴, Mark Ramirez⁵

ABSTRACT: The purpose of this study was to identify, quantify, and determine source locations of significant volatile sulfur compounds (VSCs) associated with the activated sludge treatment process at a large wastewater treatment plant. Flux chamber and wastewater headspace sampling techniques were used to capture odorous gases followed by gas chromatography mass spectrometry analysis. Olfactometric analysis corroborated the results from the chemical analysis. Dimethylsulfide (DMS) and dimethyldisulfide (DMDS) concentrations in wastewater were strongly correlated with sludge blanket depth [DMDS: $r = 0.86$ ($p < 0.001$, $df = 24$) and DMS: $r = 0.72$ ($p < 0.001$, $df = 24$)]. A strong statistical correlation also was established between concentrations of these two odorants in the gas samples and the recognition odor concentration [DMS: $r = 0.85$ ($p < 0.001$, $df = 13$) and DMDS: $r = 0.81$ ($p < 0.001$, $df = 13$)]. Results indicate that settled sludge in the anoxic environment of the secondary sedimentation basin is the most important contributor to the formation of VSCs in the activated sludge treatment system. *Water Environ. Res.*, **80**, 2261 (2008).

KEYWORDS: Reduced sulfur compound, volatile sulfur compound, dimethylsulfide, dimethyldisulfide, odor, wastewater treatment.

doi:10.2175/106143008X304677

Introduction

Volatile sulfur compounds (VSCs) such as sulfides and mercaptans are odorants associated with wastewater treatment processes (Koe and Tan, 1990; Nurul Islam et al., 1999; Van Langehove et al., 1985; Huang et al., 1979). Domestic wastewater typically consists of 3 to 10 mg/L organic sulfur, largely derived from proteinaceous material (e.g., sulfur-containing amino acids) and sulfonates originating from household detergents (Boon, 1995; Harkness, 1980). The organic sulfurs are hydrolyzed or reduced under septic conditions during the wastewater treatment process.

^{1*} PBS&J, 12101 Indian Creek Court, Beltsville, MD 20770; e-mail: ksekiamah@gmail.com.

² Department of Environmental Engineering, University of Seoul, Seoul, Korea.

³ U.S. Department of Agriculture, Agricultural Research Service, Environmental Management and Byproducts Utilization Laboratory, Beltsville, Maryland.

⁴ Department of Civil Engineering, University of Maryland, College Park, Maryland.

⁵ District of Columbia Water and Sewer Authority, Washington, D.C.

Each unit treatment process is a potential source of VSCs (Kim et al., 2002). However, because of its large surface area, the secondary aeration basin is frequently cited as an important source of volatile organic carbon and odor emissions from wastewater treatment plants (WWTPs) (Koe, 1985).

In a previous study performed at the Blue Plains WWTP in Washington, D.C., by Camp Dresser and McKee (2003), aeration basins were identified as a major emission source of VSCs, including hydrogen sulfide (H₂S), methyl mercaptan, dimethylsulfide (DMS), carbon disulfide (CS₂), and carbonyl sulfide (COS). Their study reported that the aeration basin ranked second after grit/screening facilities in odor emissions. Their study also observed that the front-half of the aeration basin released significantly more VSCs than the back-half. This observation was attributed to three potential factors: low aeration efficiency resulting in inadequate transfer of oxygen creating anaerobic zones in the aeration basin; methylation of the HS⁻ from the upstream processes; and stripping of sulfur compounds in the activated sludge recycled from the bottom of the sedimentation basins.

The goal of this study was to determine the most important factors affecting the formation and release of VSCs from primary and secondary treatment. To achieve this goal, wastewater and gas samples from both the aeration and sedimentation basins were collected during all four seasons in 2004. The samples were analyzed for VSC concentration and odor concentration and character. The results were interpreted to establish relationships between the formation and release of VSCs and odor from the secondary treatment process and plant process parameters.

Materials and Methods

All samples were collected at the District of Columbia Water and Sewer Authority (DCWASA), Blue Plains WWTP. The facility is located on the banks of the Potomac River, to the south of Washington, D.C. Blue Plains serves more than 2 million people in the Washington Metropolitan Area and has the capacity to treat 1400 ML/d of wastewater.

Sample Collection. Wastewater and gas samples were collected from predetermined locations in the primary clarifier, secondary aeration basin, and secondary sedimentation basins (Figure 1). Five sampling locations were selected: the primary clarifier (location A);

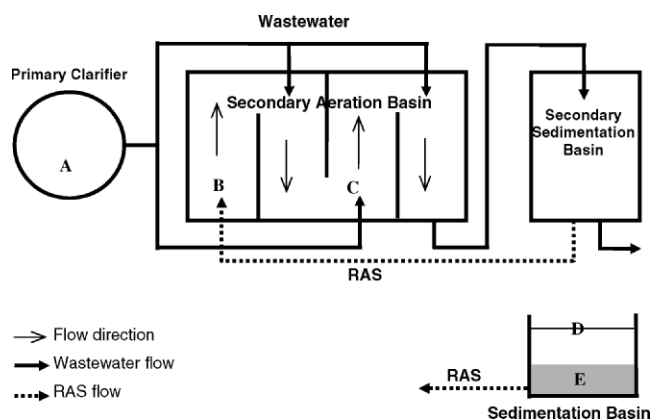


Figure 1—Sample collection locations (RAS = return activated sludge).

the first and third passes of the secondary aeration basin (locations B and C); and the top and bottom of the sedimentation basin (location D and E). Samples were collected on 6 different days for each of the four seasons in 2004 for a total of 24 sampling events (Table 1). Wastewater samples were collected approximately 0.3 m below the water surface at locations A, B, C, and D. A sample also was collected 0.3 m from the bottom of the sedimentation basin at location E. Field measurements for temperature, oxidation-reduction potential (ORP), and pH were recorded during sample collection.

Surface wastewater samples were collected with a handheld grab sampler. The wastewater sludge at the bottom of the sedimentation basin was collected with a 4.6-m sludge sampler. Wastewater quickly was transferred to 100-ml polyethylene bottles with zero headspace. Gas samples were collected using a flux chamber (0.6-m diameter) with a stainless steel bottom section and a Plexiglas top dome with a 152-mm open stack as described by Eklund (1992) and U.S. Environmental Protection Agency (U.S. EPA) (1989). This apparatus was used to capture gases released from the first and third passes of the secondary aeration basins (location B and C, respectively). The gas isolated from the chamber was sampled using Teflon tubing at a rate of 4 L/min. Two 1-L Tedlar bags and two 10-L Tedlar bags were filled at each of the two sampling locations using a suction pump (224-PCXR4, SKC, Eighty Four, Pennsylvania). An in-line water-vapor trap filled with a CaCl_2 (4-20 mesh anhydrous, Fisher Scientific Co., Fair Lawn, New Jersey) was used to remove humidity from the gas samples prior to suction into the Tedlar bags.

Sample Processing. Sample processing was carried out as soon as possible, within 1 to 2 h, after collection. A 10-ml aliquot of wastewater or sludge was transferred into 20-ml glass headspace vials and capped with an airtight seal. The VSCs were extracted from the headspace over the sample using solid-phase micro-extraction (SPME) (Supelco, Bellefonte, Pennsylvania). The SPME fiber was coated with an 85- μm film of carboxen/polydimethylsiloxane. The fiber was equilibrated with the headspace for 1 h. The same approach was used for the gas samples, except the fiber was inserted through the 1-L Tedlar bag septum and exposed to the gas inside the bag. After extraction, the fibers were placed in a cooler containing dry ice and transported 30 min to the U.S. Department of Agriculture (USDA), Agricultural Research Laboratory in Beltsville, Maryland. Upon arrival, the SPME fibers were stored

Table 1—Sample Collection Events in 2004.

	Winter	Spring	Summer	Fall
Average aeration rate	45.7 cfm	63.1 cfm	81.1 cfm	77.8 cfm
Average wastewater temperature	14.7°C	22.6°C	25.4°C	22.0°C
Sampling dates	Feb 23 Mar 05 Mar 12 Mar 19 Mar 22 Mar 29	May 13 May 24 May 27 Jun 03 Jun 07 Jun 10	Jul 22 Jul 29 Aug 06 Aug 09 Aug 16 Aug 18	Oct 11 Oct 13 Oct 15 Oct 18 Oct 20 Oct 22

in a freezer (-40°C), until they were analyzed. The maximum holding time for the SPME samples was typically 24 h.

Sulfide-ion concentrations were measured using a silver/sulfide electrode with an Accumet AR60 electrode meter (Fisher Scientific). Oxygen-reduction potential and pH were also measured with appropriate electrodes.

Sample Analysis. The 10-L Tedlar bag samples were shipped immediately to St. Croix Sensory (Lake Elmo, Minnesota) for olfactometric analysis. The detection and recognition threshold concentrations of each sample were determined by an odor panel using a dynamic olfactometer (AC'SCENT). The procedures for sensory evaluation complied with industry standards (ASTM E679, 2004; EN13725, 2003). The odor panel presentation rate was 20 L/min to satisfy both ASTM E679 and the EN13725 standards. Odor descriptors and the hedonic tone of each sample also were reported.

SPME fibers were desorbed and analyzed for VSCs using multi-dimensional gas chromatography-mass spectrometry as described in detail by Arispe (2005). Certified Teflon membrane permeation devices (NIST traceable, VICI Metronics Inc., California) and a gas standard generator (Dynacalibrator-320, VICI Metronics) were used to prepare standard gases for target VSCs, including CS_2 , methyl mercaptan, ethyl mercaptan, propyl mercaptan, butyl mercaptan, DMS, and dimethyldisulfide (DMDS). The method detection limits ranged from 1ppbv for dimethyldisulfide to 13 ppbv for ethyl and methyl mercaptan (Table 2).

Error Analysis. The potential errors (both systematic and random) associated with sample collection and extraction were estimated to identify the uncertainty associated with VSC quantification. The errors associated with the gas chromatography/mass spectrometer/headspace solid phase micro extraction (GC/MS/HS-SPME) analytical method can be exemplified by the variance associated with the calibration curves. Each data point on the calibration curve has an associated standard deviation (Arispe, 2005). The mean of the standard deviation may be used to calculate a percent error associated with the analytical method (Berthouex and Brown, 2002). The percent deviation associated with the DMDS and DMS calibration curves was 6.6% and 9.4%, respectively. The combined error associated with the calibration procedure (both extraction and quantification) for the VSCs quantified was approximately 8.0%. The errors associated with field sampling may be estimated by the deviation between duplicate samples. The percent deviation between duplicate wastewater samples for the headspace extraction of DMDS and DMS was 21% and 18.3%, respectively. The percent deviation between duplicate samples for the gas-phase extraction of DMDS and DMS was 17.6% and 18.3%, respectively. The combined errors associated with the field sampling procedure were calculated to be approximately 19.7% for

Table 2—Method detection limits for volatile sulfur compounds in headspace and gas samples.

Compound name	Abbrev.	Detection limit (ppbv)
Butyl mercaptan	BM	4
Carbon disulfide	CS ₂	8
Dimethylsulfide	DMS	2
Dimethyldisulfide	DMDS	1
Ethyl mercaptan	EM	13
Methyl mercaptan ¹	MM	13
Propyl mercaptan	PM	10

¹ Due to the abiotic oxidation of methyl mercaptan to DMDS in the presence of oxygen, light or metal surfaces, the calibration curve for methyl mercaptan was deemed unreliable. Therefore, response factors for ethyl mercaptan were used for methyl mercaptan quantification.

the analysis of wastewater samples and 18.0% for the analysis of gas samples. The total maximum potential for errors in determining the concentrations of VSCs in this study was approximately 28%.

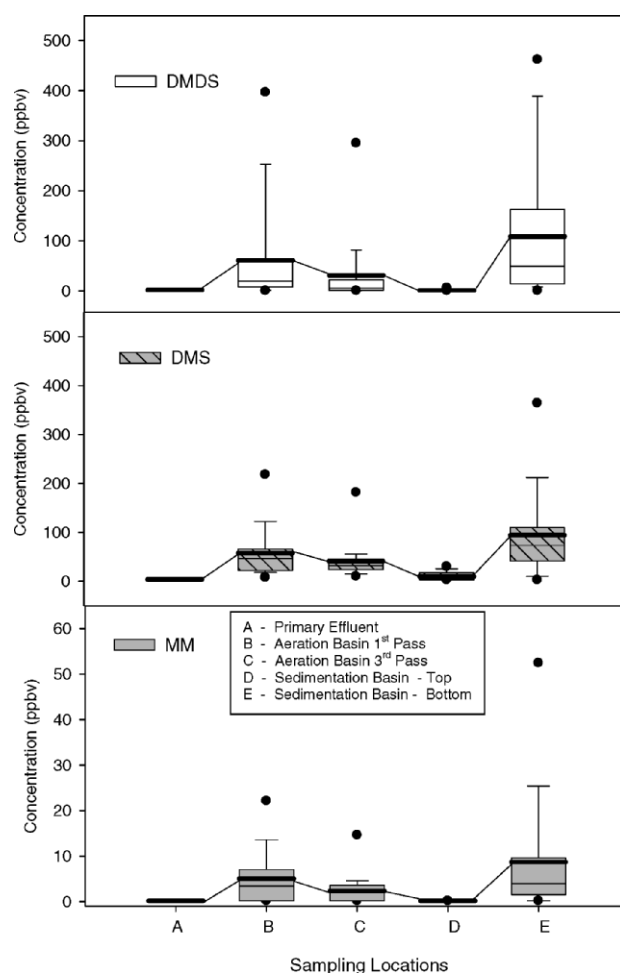
Results and Discussion

The focus of this project was to determine the most important factors affecting the formation and release of VSCs from primary and secondary activated sludge treatment processes. In earlier investigations at Blue Plains, it was found that the front-half of the aeration basin released significantly more VSCs than the back-half. This study investigated potential causes of this increased release. Plant process parameters and chemical measurements also were used to examine overall factors leading to VSC release from the secondary treatment process.

Annual Trends in Volatile Sulfur Compound Wastewater Concentrations. Of the analytes included in this study, DMDS, DMS, and methyl mercaptan were the only VSCs identified in the headspace over wastewater and sludge samples. Methyl mercaptan concentrations were considerably lower than DMDS and DMS (methyl mercaptan concentration was approximately 8.1% of DMDS, 8.5% of DMS, and <5% of total VSC concentration). This observation can be attributed to the fact that methyl mercaptan is readily abiotically oxidized in air to form DMDS (Yarosz et al., 2003; Lomans et al., 2002; Smet et al., 1998).

An examination of annual average trends in DMS, DMDS, and methyl mercaptan concentrations at the five sample collection locations (Figure 2) show that both the highest concentrations and the largest variability in concentration of VSCs were observed at the bottom of the secondary sedimentation basin (mean: DMDS = 110 ppbv; DMS = 83 ppbv). The distinct concentration difference between the samples collected from the top and the bottom of the secondary sedimentation basin is indicative of VSC formation in the activated sludge blanket at the bottom of the basin. The concentration profile across sample collection sites was the same for all three VSCs: the concentration at primary clarifier (A) was almost equal to that at the sedimentation basin surface wastewater (D), which was less than at secondary aeration basin pass 3 (C), which was less than at secondary aeration basin pass 1 (B), which, in turn, was less than the concentration at the bottom of the sedimentation basin (E).

Results of this study confirm earlier investigations because higher VSC concentrations were found in samples from the front half of the aeration basin. The DMDS and DMS concentrations in



Note: the mean value is represented by the thicker line and the median by the thinner line.

Figure 2—Annual concentration of volatile sulfur compounds in wastewater across the secondary activated sludge treatment system (DMS = dimethylsulfide; DMDS = dimethyldisulfide; MM = methyl mercaptan).

the first pass (location B) ranged from 470 to 0.37 ppbv and 250 to 2.6 ppbv, respectively (Figure 2). Annual average VSC concentrations in the first pass of the aeration basin were greater than in the third pass. The DMDS made up approximately 46% and DMS made up approximately 51% of the total VSC concentration identified in the aeration basin (i.e., first and third pass combined) on an annual average basis.

The VSCs measured from the secondary treatment system were similar in compound type and concentration range to values determined from previous studies. Cheng et al., (2005) measured DMS (approximately 1200 to 5 $\mu\text{g/L}$) and DMDS (approximately 40 to 5 $\mu\text{g/L}$). Kim et al., (2002), measured DMDS (approximately 3 ppbv) and DMS (approximately 2 ppbv) in return activated sludge (RAS) samples from the Blue Plains WWTP. Nurul Islam et al., (1999), measured methyl mercaptan (approximately 2500 to 30 ppbv) and DMS (approximately 1200 to 20 ppbv) concentrations from secondary aeration and sedimentation basins at four WWTPs. Jenkins et al. (1980) likewise measured methyl mercaptan (approximately 44 ppbv) from mixed liquor sampled at the head of an activated sludge aeration basin.

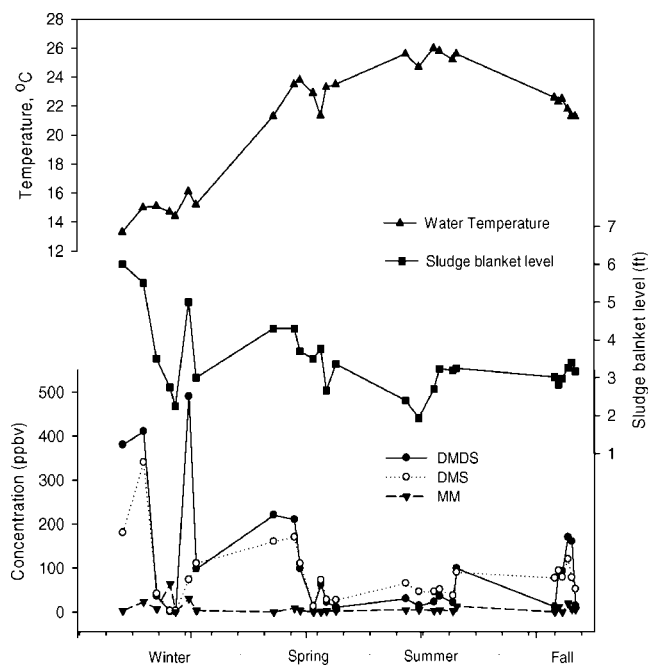


Figure 3—Volatile sulfur compound concentration compared with activated sludge blanket level and wastewater temperature at the bottom of the secondary sedimentation basin (DMS = dimethylsulfide; DMDS = dimethyldisulfide; MM = methyl mercaptan).

At the Blue Plains WWTP, primary clarifiers feed wastewater in step-feed mode into each of the four passes in the secondary aeration basin (Figure 1). During this study, however, no primary effluent was introduced into the first pass of the aeration basin because of a malfunctioning sluice gate. RAS from the bottom of the sedimentation basin was, however, fed to the head of the first pass. Therefore, the higher concentrations of VSCs in samples collected from the first pass of the aeration basin were not influenced by any VSCs or VSC precursors from the primary clarifier effluent.

Changes in VSC concentrations during the year did not vary with wastewater temperature as expected (Figure 3). Concentrations were higher in winter than summer samples from the bottom of the sedimentation basin. In winter, DMDS averaged 200 ppbv; DMS, 110 ppbv; and methyl mercaptan, 19 ppbv. The average winter wastewater temperature was 14.7°C. The seasonal mean during summer was 37 ppbv DMDS; 56 ppbv DMS; and 5.5 ppbv methyl mercaptan. Average summer wastewater temperature was 25.4°C (Figure 3). Typically, microbial activity increases as temperatures rise, so higher VSC concentrations would have been expected in summer. This observation suggests that factors other than temperature govern formation of VSCs in the secondary treatment system.

Recent reports have found that dimethyl sulfoxide (DMSO) in WWTP influents may be reduced to DMS during the secondary activated sludge treatment process (Glindemann et al., 2006). The reduction of DMSO to DMS can be carried out by a variety of micro-organisms (Alef and Kleiner, 1989). Reduction of DMSO occurs in anoxic/anaerobic zones in the activated sludge system, such as poorly mixed and selector zones. In our study, the DMSO concentration in the plant influent was not measured, and, there-

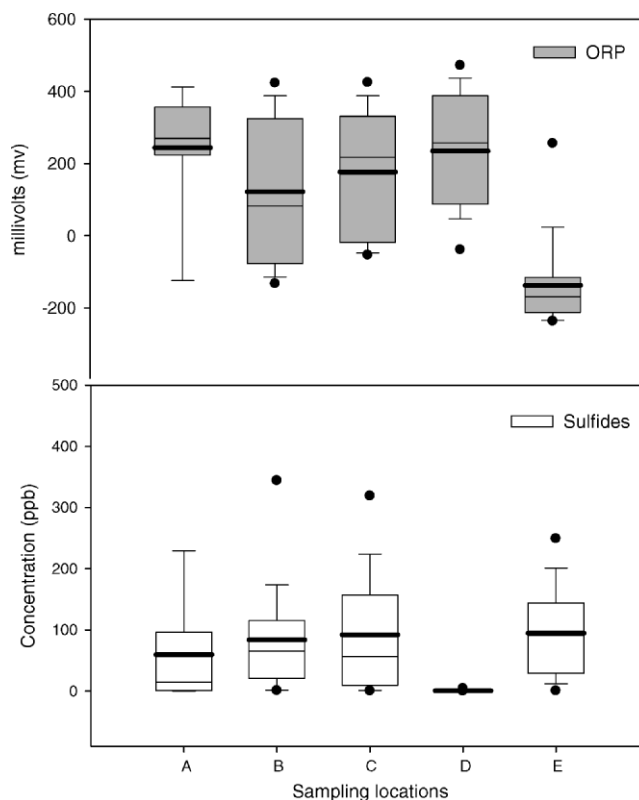


Figure 4—Annual oxidation-reduction potential (ORP) and sulfide concentrations within the secondary activated sludge treatment system.

fore, DMSO reduction to DMS in the aeration basin cannot be completely ruled out. However, DMSO reduction would not be possible in the first pass of the aeration basin because primary effluent was not introduced. Of the five locations sampled in the secondary activated sludge treatment system, only location C, third pass of the aeration basin, could have been influenced by DMSO reduction.

Hydrogen Sulfide Ion Concentration in Wastewater. The HS^- ion is in equilibrium with H_2S in water and is formed in septic environments characterized by low ORP and high concentrations of sulfur-containing compounds. Average sulfide concentrations were similar in the primary clarifiers, the aeration basin, and at the bottom of the sedimentation basin at approximately 60 to 100 ppb (Figure 4). However, ORP conditions were lowest in the secondary sedimentation basin, averaging -131 mV (Figure 4). The difference in the concentration of HS^- between the top and bottom of the secondary sedimentation basin (98 ppb versus 0.73 ppb), indicates the activity of anaerobic, sulfur-reducing bacteria in the activated sludge blankets at the bottom of the sedimentation basin. The presence of similar average sulfide concentrations at locations B and E (84 ppb and 98 ppb, respectively) suggest that RAS is a significant source of sulfides to the secondary aeration basin because there was no primary effluent introduced into the first pass of this basin. The primary clarifiers are a significant additional source of sulfides as indicated by the slightly higher average sulfide concentration at location C (92 ppb) as compared to location B (84 ppb).

Effect of Activated Sludge Blanket Depth on Volatile Sulfur Compound Concentration. There is a distinct relationship

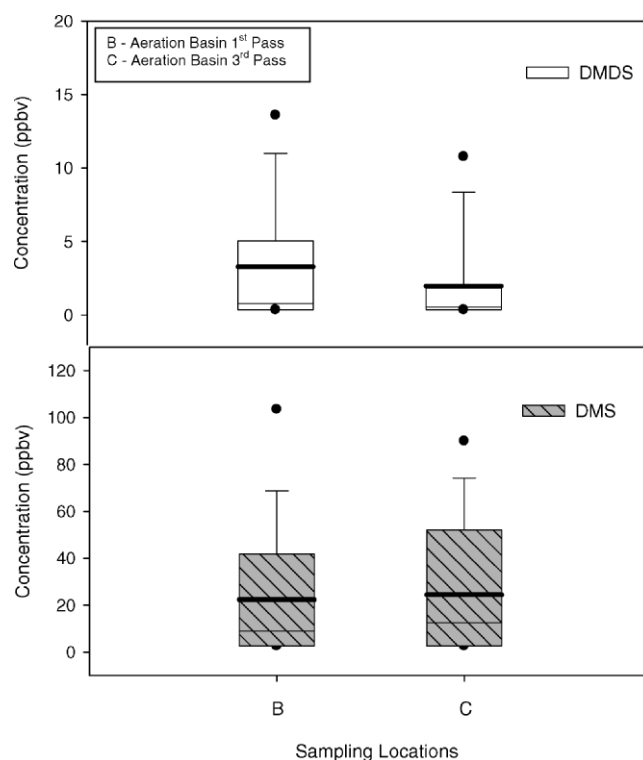
Table 3—Statistical analysis of headspace volatile sulfur compound concentrations and plant parameters (DMS = dimethylsulfide; DMDS = dimethyldisulfide).

	DMDS	DMDS	DMS	DMS
	Correlation	P-value	Correlation	p-value
Sludge blanket depth	0.86	<0.001	0.72	<0.001
Water temperature	-0.45	<0.001	-0.26	<0.001
df	24	24	24	24

between activated sludge blanket depth and the concentration of VSCs at the bottom of the secondary sedimentation basin: The higher the blanket depth, the higher the concentration of VSCs (Figure 3). Visual inspection also reveals that wastewater temperature has less of an influence on the concentration of VSCs than sludge blanket depth (Figure 3). Statistical analysis corroborates this observation. There is a strong positive correlation between the concentrations of DMS and DMDS at this location and sludge blanket depth [DMDS: $r = 0.86$ ($p < 0.001$, $df = 24$) and DMS: $r = 0.72$ ($p < 0.001$, $df = 24$)] (Table 3). The correlation between wastewater temperature and VSC concentration did not follow the expected trend. A strong positive correlation between water temperature and VSC concentration was not established [DMDS: $r = -0.45$ ($p < 0.001$, $df = 24$) and DMS: $r = -0.26$ ($p < 0.001$, $df = 24$)] (Table 3). Any influence of wastewater temperature on VSC formation seems to have been masked by the greater influence of other plant parameters (e.g., sludge blanket depth), which should be further investigated.

Odorous Gas-Release from the Secondary Activated Sludge Aeration Basin. Results of the odorous gas-release measurements using flux chambers over the first and third pass of the aeration basin support results from headspace analysis. Only DMDS and DMS were detected above quantification limits in the gas samples. Odorous gas release is expected to be influenced by concentration, wastewater temperature, aeration rate, and Henry's law constant of the odorants. The annual average concentration of DMDS was considerably lower than that of DMS in both the first and third passes of the aeration basin. The annual average gas-phase concentration of DMS and DMDS for the first pass of the aeration basin was 24 ppbv and 3.3 ppbv, respectively (Figure 5). This observation could be related to the volatility of these compounds. Air-water partition coefficient ($\log K_{H}$) for DMS is 0.25 L-atm/mole and DMDS is 0.02 L-atm/mole (Schwarzenbach et al., 1993). Because DMS is more volatile than DMDS, the former will tend to strip out of the wastewater in greater quantities than the latter.

The gas-phase VSC concentrations measured in winter were the lowest of the four seasons (winter mean: DMDS = 0.9 ppbv and DMS = 5.2 ppbv). The highest concentrations were observed in the fall (mean: DMDS = 9.3 ppbv and DMS = 66 ppbv). The concentrations of VSCs measured in the summer were less than that of the fall (summer mean: DMDS = 2.5 ppbv and DMS = 20 ppbv). The odor detection threshold of DMS is about 0.4 ppbv (Glindemann et al., 2006) and that of DMDS is about 1 ppbv (Nurul Islam et al., 1999). This represents a calculated dilution threshold concentration for DMS and DMDS of 50 dilution thresholds and 2.5 dilution thresholds, respectively. Since an odor problem is assumed to exist at approximately 10 dilution threshold or 10 odor units/m³, DMS can be assumed to cause an odor problem. In addition, most odor control strategies at WWTPs

**Figure 5—Annual volatile sulfur compound concentrations in gas samples from the secondary activated sludge aeration basin (DMS = dimethylsulfide; DMDS = dimethyldisulfide).**

attempt to meet a fence-line odor concentration of less than 7 dilution thresholds. Although the concentrations of DMS and DMDS are relatively small, the large surface area of the secondary aeration basins (3×10^4 m²), i.e., six basins each with four passes at 8.8 m \times 140 m) coupled with the air flow rate through this system (Table 1), has the potential to cause odor problems in the neighboring communities. The role of DMS and DMDS as primary odor-causing compounds also was verified in the olfactometric evaluation of the gas samples as described below.

Figure 6 illustrates annual temporal trends in recognition odor concentration (odor units/m³) along with the concentrations of DMS, DMDS, water temperature, and sludge blanket depth. As with the VSCs, the highest mean recognition odor concentrations were observed in the fall samples (2254 odor units/m³) and the lowest in winter (33 odor units/m³). A strong statistical correlation was established between VSC concentration and recognition odor concentration [DMS: $r = 0.85$ ($p < 0.001$, $df = 13$) and DMDS: $r = 0.81$ ($p < 0.001$, $df = 13$)] (Table 4). Because more than 80% of the variation in odor can be explained by variations in VSC concentration, it is likely that VSCs are an important class of odorants released from the aeration basins. A significant correlation between wastewater temperature and recognition odor concentration was not established. If the fall sampling data are excluded, then a good correlation between wastewater temperature and odor concentration is established (Table 4).

Further evidence of a positive correlation between analytical and olfactometric measurements is provided by odor character descriptors (Figure 7). Each gas sample was scaled on the strength of the perception of various odor descriptors, including floral, fruity,

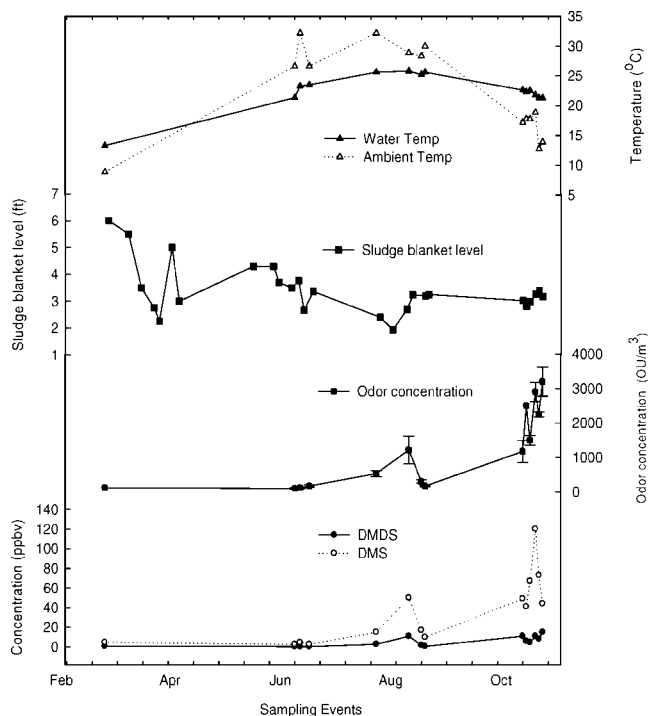


Figure 6—Seasonal gas volatile sulfur compound/odor concentrations for the secondary activated sludge aeration basin (first pass) (DMS = dimethylsulfide; DMDS = dimethyldisulfide; MM = methyl mercaptan).

vegetable, earthy, offensive, fishy, chemical, and medicinal. The scale represents the degree to which odor panel members recognized a specific odor descriptor, with lower values representing less intense perception. To show the degree of pleasantness or offensiveness of the samples, the 8 descriptors were reduced to 4 by combining similar descriptor values: floral and fruity, vegetable and earthy, offensive and fishy, and chemical and medicinal. The top right quadrant of the diagram in Figure 7 indicates the intensity of a floral earthy scent and the bottom left quadrant indicates the intensity of an offensive medicinal scent. Each sample is represented in both quadrants. It is clear from the diagram that panelists rated the winter and spring samples as the least offensive and the fall samples as the most offensive.

Water temperature does not appear to govern gas-phase VSC concentrations or odor during the fall. The larger sludge blanket depth observed during the fall as compared to the summer may have led to increased release of VSCs from the aeration basin. This larger sludge blanket depth combined with relatively high water

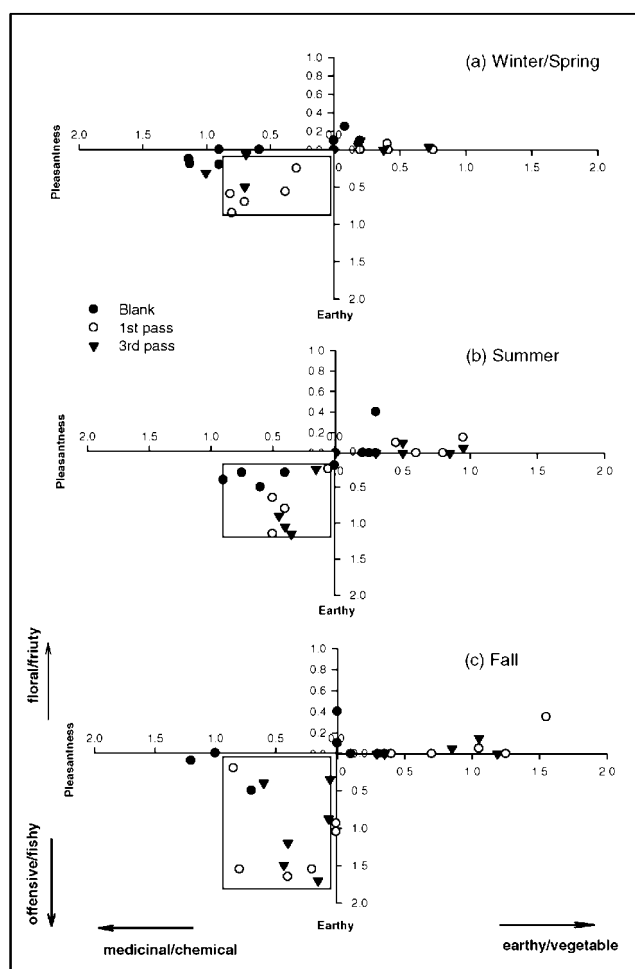


Figure 7—Seasonal variations in scaled odor descriptors of gas samples from the activated sludge aeration basin.*

temperature and aeration rates (Table 1) may have led to a greater-than-expected release of VSCs and their associated odor.

Conclusions

Volatile sulfur compounds in wastewater and gas samples were analyzed to better understand the formation and release of VSCs from the primary settling and secondary activated sludge treatment system at Blue Plains WWTP. The results from this study have

Table 4—Correlation between volatile sulfur compound release and plant parameters in the activated sludge aeration basin for the first pass (DMS = dimethylsulfide; DMDS = dimethyldisulfide).

	Odor concentration		Water temperature		Water temperature (excluding fall data)	
	Correlation	p-value	Correlation	p-value	Correlation	p-value
DMDS	0.85	<0.001	0.04	0.047	0.35	0.36
DMS	0.81	<0.001	<0.001	<0.001	0.43	0.001
Odor concentration	—	—	−0.074	<0.001	0.43	<0.001
df	13	13	13	13	7	7

established that DMS and DMDS are formed in the sludge blanket at the bottom of the secondary sedimentation basins. The VSCs formed in the sludge blankets are returned by RAS pumps to the secondary aeration basin where the intense interaction with compressed air strips the VSCs from the wastewater. A strong correlation between VSC concentration at the bottom of the sedimentation basin and sludge blanket depth was established. DMS formation in the aeration basin from DMSO reduction could potentially contribute to odor generation, although this mechanism was not examined.

Recognition odor and VSC concentrations in gas samples from the secondary aeration basin also were strongly correlated. Odor panelist descriptions of the odor support the conclusion that VSCs are a major contributor. Wastewater temperature was found to be an important factor in predicting VSC release. In the fall sampling period, however, it appears that sludge blanket depth combined with water temperature amplified VSC release. Effective management of activated sludge inventory in the secondary sedimentation basins potentially could minimize formation of VSCs in the secondary activated sludge treatment system, thereby mitigating the odor problem associated with this process.

Acknowledgments

Funds provide by the District of Columbia Water and Sewer Authority, the U.S. Department of Agriculture, and the University of Maryland – College Park to perform this research are greatly appreciated.

Submitted for publication January 9, 2007; revised manuscript submitted December 3, 2007; accepted for publication April 28, 2008.

The deadline to submit Discussions of this paper is March 15, 2009.

References

- Alef, K.; Kleiner, D. (1989) Rapid and Sensitive Determination of Microbial Activity in Soils and in Soil Aggregates by Dimethylsulfoxide Reduction. *Biol. Fertil. Soils*, **8**, 349–355.
- Arispe, S. Measuring and Developing a Control Strategy for Odorous Gases from Solids Handling Processes of a Large Wastewater Treatment Plant. M.S. Thesis, University of Maryland, 2005.
- ASTM E679-04 (2004) *Standard Practice for Determination of Odors and Taste Thresholds by Forced-Choice Ascending Concentration Series Method of Limits*; Annual Book of ASTM Standards; ASTM International: West Conshohocken, Pennsylvania.
- Berthouex, P.; Brown, L. (2002) *Statistics for Environmental Engineers*; Lewis Publishers: New York.
- Boon, G. (1995) Septicity in Sewers: Causes, Consequences, and Containment. *Water Sci. Technol.*, **31**, 237–253.
- Camp Dresser & McKee (CDM), (2003) *Comprehensive Odor Study – Odor Control Master Plan*; District of Columbia Water and Sewer Authority, Washington, D.C.; CDM Engineering Consultants, Cambridge, Massachusetts.
- Cheng, X.; Peterkin, E.; Burlingame, G. (2005) A Study on Volatile Organic Sulfide Causes of Odors at Philadelphia's Northeast Water Pollution Control Plant. *Water Res.*, **39**, 3781–3790.
- Eklund, B. (1992) *Practical Guidance for Flux Chamber Measurements of Fugitive Volatile Organic Emission Rates Manual*; Air & Water Management Association: Pittsburgh, Pennsylvania.
- EN 13725, (2003) *Air Quality Determination of Odor Concentration by Dynamic Olfactometry*. BSI British Standards: London, England.
- Glindemann, D.; Novak, J.; Witherspoon, J. (2006) Dimethyl Sulfoxide (DMSO) Waste Residues and Municipal Wastewater Odor by Dimethyl Sulfide (DMS): the North-East WPCP plant of Philadelphia. *Environ. Sci. Technol.*, **40**, No. 1, 202–207.
- Harkness, N. (1980) Chemistry of Septicity. *Effluent Water Treat. J.*, **20**, 16–23.
- Huang, J.; Wilson, G.; Schroepfer, T. (1979) Evaluation of Activated Carbon Adsorption for Sewer Odor Control. *Water Pollut. Control*, **51**(5), 1054–1062.
- Jenkins, R. L.; Gute, J.; Krasner, S. (1980) The Analysis and Fate of Odorous Sulfur Compounds in Wastewaters. *Water Res.*, **14**, 441–448.
- Kim, H.; Nochetta, C.; McConnell, L. (2002) Gas-Phase Analysis of Trimethylamine, Propionic and Butyric Acids, and Sulfur Compounds using SPME. *Anal. Chem.*, **74**, 1054–1060.
- Koe, L. C. C. (1985) Ambient Hydrogen Sulphide Levels at a Wastewater Treatment Plant. *Environ. Monit. Assess.*, **5**(1), 101–108.
- Koe, L. C. C.; Tan, N. C. (1990) GC-MS Identification of Gaseous Volatiles in Wastewater. *Environ. Monit. Assess.*, **15**(1), 13–24.
- Lomans, B. P.; Pol, A.; Op den Camp, H. J. M. (2002) Microbial Cycling of Volatile Organic Sulfur Compounds in Anoxic Environments. *Water Sci. Technol.*, **45**(10), 55–60.
- Nurul Islam, A.; Hanaki, K.; Matsuo, T. (1999) Fate of Dissolved Odorous Compounds in Sewage Treatment Plants. *Water Sci. Technol.*, **38**(3), 337–344.
- Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. (1993). *Environmental Organic Chemistry*; Wiley International: New York.
- Smet, E.; Lens, P.; Langenhove, H. V. (1998) Treatment of Waste Gases Contaminated with Odorous Sulfur Compounds. *Crit. Rev. Environ. Sci. Technol.*, **28**(1), 89–117.
- U.S. Environmental Protection Agency, (1989) *Air/Superfund National Technical Guidance Study Series, Volume II – Estimation of Baseline Air Emissions at Superfund Sites*; EPA – 450/1-89-002; U.S. Environmental Protection Agency: Washington, D.C.
- Van Langenhove, H.; Roelstraete, K.; Schamp, N.; Houtmeyers, J. (1985) GC-MS Identification of Odorous Volatiles in Wastewater. *Water Res.*, **19**(5), 597–603.
- Yarosz, D. P.; Chen, Y.; Murthy, S. (2003) Mechanisms of Volatile Sulfur Compounds and Odor Production in Digested Biosolids. *Proceedings of the Water Environment Federation, American Water Works Association, and Chesapeake Water Environment Association Joint Residual and Biosolids Management Conference 2003*; Baltimore, Maryland, Feb 19–22; Water Environment Federation: Alexandria, Virginia.