Characterization of wastewater and solids odors using solid phase microextraction at a large wastewater treatment plant

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Abstract A simple and reliable technique has been developed and used to detect odorous gases, i.e. propionic and butyric acids, carbon disulfide, dimethyl sulfide, dimethyl disulfide, and trimethylamine, emitted from various materials generated by the wastewater treatment process. The method detection limits are in the low ppb range and comparable to the odor threshold for human detection. In this study solid phase microextraction (SPME) was employed to characterize and quantify odorous compounds in the headspace over samples collected from various unit processes at the District of Columbia Wastewater Treatment Plant, Washington DC, USA. The patterns of odorous chemicals released from wastewater influent, thickened sludge, dewatered sludge and biosolids were evaluated. Volatile reduced sulfurs were more prevalent in samples collected from downstream processes and corresponded with decreased oxidation-reduction potential (ORP) conditions. Volatile fatty acids were consistently identified in the primary gravity thickeners, while trimethylamine could only be detected from biosolids after the post-liming process.

Keywords Biosolids; gas phase analysis; odor; solid phase microextraction; trimethylamine; volatile fatty acids; volatile reduced sulfurs; wastewater

Introduction

Depending on various operating parameters, each wastewater and sludge unit process can contribute to the release of specific odorous compounds. Individual unit processes can not only contribute to on-site process odor emissions, but they can greatly affect the odor quality of the resulting biosolids. Odor intensity from wastewater processes usually increases as the wastewater or sludge flows downstream since more septic or reduced conditions are often developed (WEF, 1995). Therefore, it is important to maintain conditions that minimize odors within a wastewater treatment facility. Typically, odor reduction from unit processes is achieved by collecting the odors and treating them in scrubbers or biofilters. However, this form of treatment is expensive and not always successful. Reduction in odors at the source will not only reduce on-site air quality problems but will also reduce odor emissions from the biosolids produced and distributed for land application.

Relatively few studies have been carried out to evaluate and reduce odors from wastewater treatment facilities, although some studies have evaluated odor emissions from livestock processing and animal manure treatment facilities (Hobbs *et al*., 1995; Persud *et al*., 1996). Prior to identifying methods to control odors, however, it is important to have an easy and reliable method to characterize and quantify these volatile, reactive gases, and

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identify the conditions under which odors are developed in each unit process and in different types of biosolids.

Traditionally, odors have been quantified using olfactometry, where an odor panel consisting of several assessors determines the odor character and intensity of a gas sample (Misselbrook *et al.*, 1993). This method has a major disadvantage of being very subjective and does not provide good reproducibility (Qu *et al.*, 1999; Powers *et al.*, 2000). The use of sorbent tubes to capture volatile gases followed by thermal desorption coupled with gas chromatography is also a popular method (Ma *et al.*, 1997). However, it requires extensive sample preparation, which is impractical for routine use in a wastewater treatment facility. In addition, new electronic nose technologies, which utilize conducting polymer arrays, have been used to generate a signal pattern corresponding to different chemicals (Byun *et al.*, 1997). However, this technique is at preliminary stage, and further investigation is needed to determine whether this technology can be applied to odors emitted from wastewater processing.

In this study, solid phase microextraction (SPME) was used as a gas-phase sampler to measure the concentration of odorous compounds from the headspace over sludge and biosolids samples. SPME utilizes a small, coated fiber that equilibrates with the gas phase prior to direct analysis by gas chromatography. The fibers are relatively inexpensive, reusable, and can be used in ambient and laboratory experiments for analysis of multiple volatile organic compounds. Unlike other conventional methods, where extensive sample preparation is required, SPME is a one-step extraction procedure. A thin polymer film that is bonded to a fused silica fiber absorbs the compounds of interest. SPME is based on an equilibrium process and the mass of analyte adsorbed by the fiber is proportional to its concentration in the sample matrix (Pawlyszin, 1997).

Preparation of gas standards for these reactive chemicals can be problematic due to serious safety hazards in handling. In addition, traditional methods using Tedlar bags can introduce significant errors due to permeability of the bags, adsorption to the walls and degradation occurring in the bag (Brymer *et al.*, 1996; Koziel *et al.*, 2000). In this study, permeation devices were used to generate gas standards introduced into a flow-through Teflon chamber to improve the accuracy of calibration curves (Kim *et al.*, 2001).

The selected analytes represent odorous compounds that are generated under various conditions in the wastewater treatment process. They are trimethylamine (TMA), carbon disulfide (CS_2), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), propionic acid (PA), and butyric acid (BA). Trimethylamine is typically released with ammonia during and after the liming process (Banwart and Bremner, 1976). Septic conditions in a treatment plant produce reduced sulfurs (WEF, 1995). Propionic and butyric acids occupy more than 50% of volatile acid gases released from a plant (WEF, 1995). These compounds are also frequently detected at biosolids land-application sites (Mosier *et al.*, 1997).

This paper describes the results of a plant wide survey of samples from unit processes from a major WWTP on October 28 2000, and three detailed studies of thickened sludge and limed-biosolids collected from September to November, 2000. The District of Columbia WWTP in Washington DC consists of primary clarification followed by activated sludge treatment. The primary sludge is thickened in gravity thickeners, and the secondary sludge settles in sedimentation tanks and is pumped to dissolve air flotation (DAF) thickeners. The combined sludge is blended and dewatered, prior to being lime stabilized.

The approach used in this project provides a relative comparison between unit processes of a WWTP as a means to determine the factors which may control the odor potential of the sludge and biosolids materials. Results may be used by researchers and operators as a starting point for further studies into controlling odor production at the WWTP. Concentration values do not necessarily correspond to emission rates from a WWTP or ambient levels at a biosolids application site.

Material and methods

Calibration of the SPME fibers

The preparation of gas standards that are used for SPME calibration is an important and challenging component of the method. The odorous gases are very reactive and unstable. Gas standards were generated using certified Teflon membrane permeation devices (NIST traceable, VICI Metronics, Inc., Santa Clara, California, USA) for each compound (Table 1). The permeation devices were placed together in a thermostated glass chamber of a Model 320 Dynacalibrator (VICI Metronics, Inc.). The base flow of high purity (99.99%) nitrogen gas through the permeation chamber was 72 ml/min, and the concentration was varied using additional dilution gas. Two SPME fibers were exposed to the gas standard in a temperature-controlled (20°C), Teflon cylindrical collection chamber (i.d. = 4.1 cm, Savillex, Co., Minnetonka, Minnesota, USA) (Figure 1). The temperature inside the chamber was measured by inserting a temperature probe (Traceable®-4085, Control Com., Houston, Texas, USA) into the chamber. The chamber was equipped with two septa ports with Teflon coated septa through which the needle of the SPME device was inserted so that duplicate measurements could be made for all calibration points. A more detailed description of the calibration process is given elsewhere (Kim *et al.*, 2001).

SPME and gas chromatography conditions

A 75 μm Carboxen-Polydimethylsiloxane (Car-PDMS) coating was used to capture trimethylamine (TMA), carbon disulfide (CS_2), dimethylsulide (DMS) and dimethyldisulfide (DMDS), and an 85 μm Polyacrylate coating was used for propionic acid (PA) and butyric acid (BA) (Supelco, Bellefonte, Pennsylvania, USA). Car-PDMS has been used for the analysis of reduced sulfurs (Abalos *et al.*, 1999; Hill and Smith, 2000). Polyacrylate fibers are often used for polar compounds (Pan *et al.*, 1995). Analysis of propionic and butyric acids was performed using capillary gas chromatography with flame ionization detection using a Hewlett Packard 5890 gas chromatograph. A Hewlett Packard 5890 gas chromatograph coupled to an HP 5970 mass spectrometer was used in selected ion monitoring mode for TMA and the reduced sulfur compounds. Both GC systems were equipped with a Merlin microseal septum (Supelco, Bellefonte, Pennsylvania, USA) designed for SPME to insure reproducibility between injections. Detailed chromatographic conditions are given elsewhere (Kim *et al.*, 2001).

Sample collection and analysis

A sample (600 mg) was collected from each unit process, i.e. influent, primary settling, secondary settling tank, nitrification settling tank, gravity thickener (GT), dissolved air

Table 1 Physical properties, method detection limits, and odor threshold for human detection of target analytes

Compounds	Molecular Weight, g/mol	Boiling point*, °C	MDL**, ppbv	Odor threshold, ppbv
Propionic acid	74	141.4	1.80	28 (Hellman and Small, 1974)
Butyric acid	88	163.5	1.32	0.5 (Fazzalari, 1978)
Trimethylamine	59	2.87	2.38	0.44 (O'Neill and Phillips, 1992)
Carbondisulfide	76	46.5	0.189	16 (Verschueren, 1983)
Dimethylsulfide	62	37.3	0.074	0.11 (Amoore and Hautala, 1983)
Dimethyldisulfide	94	109.7	0.063	6.4 (Fors, 1988)

* Obtained from Budavari *et al.* (1996)
** Method detection limit. MDL determined with 8 samples; EPA standard procedure for MDL calculation was followed (Longbottom and Lichtenberg, 1982)

flotation (DAF) thickener, belt press, and post-liming, of the Wastewater Treatment Plant, and transferred into a 1L Teflon jar (Figure 2). The pH (Mattler Toledo Type 405-SC-DPAS, Woburn, Massachusetts, USA) and ORP (oxidation/reduction potential; Mattler Toledo Type Pt4805-DPAS-SC, Woburn, Massachusetts, USA) of each sample were recorded prior to odor sampling. The headspace was flushed with pure N_2 gas at a constant rate (72 mL/min). Odorous compounds in the headspace were extracted by exposing SPME fibers to the off gas for 1 hr in an on-site laboratory, where the room temperature is controlled at $20 \pm 2°C$. After extraction, the fibers were immediately transferred into a cooler with dry ice, and transported to the USDA laboratory, where GC analysis was performed the same day. Fibers were stored on dry ice until just before analysis to minimize losses.

Results and discussion

Odors from plant-wide survey

Results from the survey of unit processes illustrate how odorous compounds may develop through an entire plant (Figure 3). In the influent, the major reduced sulfur form was carbon disulfide. In the downstream processes, more reduced sulfurs were detected. Interestingly,
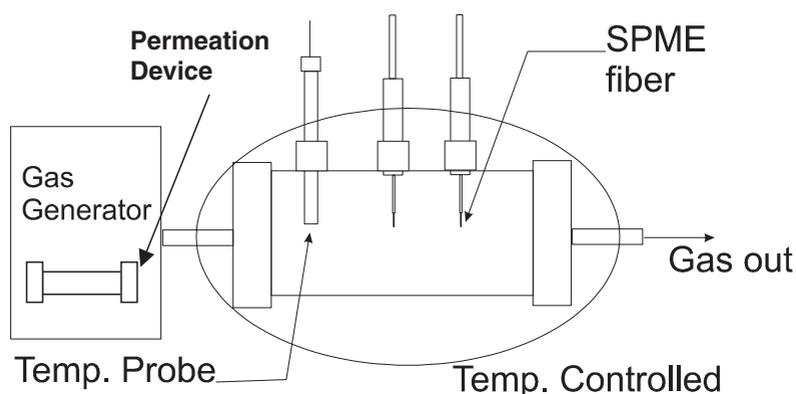

Figure 1 Schematic diagram of experimental set up for SPME calibration
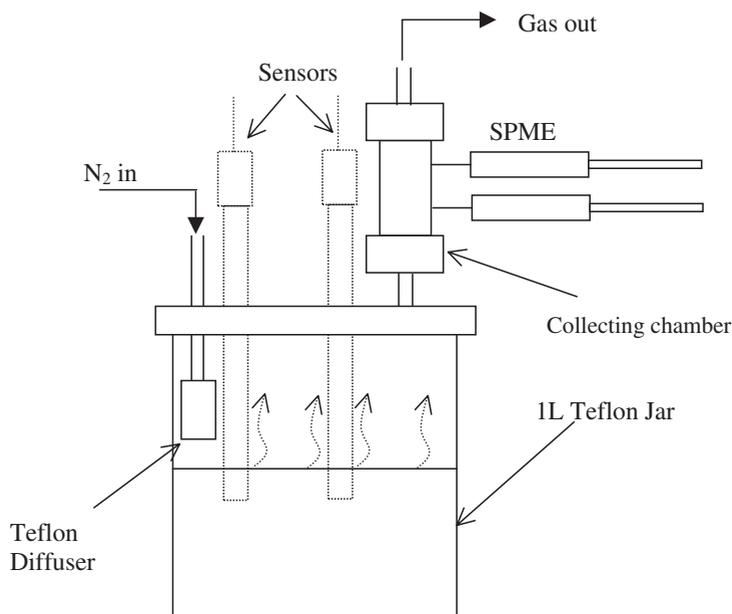

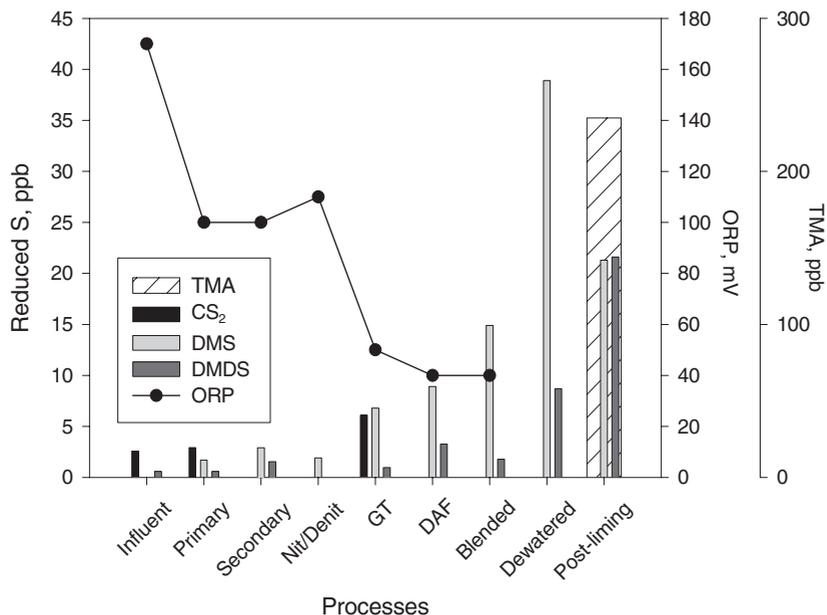**Figure 2** Schematic diagram for experimental set up for sample analysis

Figure 3 Gas-phase concentrations of target analytes (ppb) and measured ORP (mV) in plant-wide survey of District of Columbia Wastewater Treatment Plant

dimethyl sulfide and dimethyl disulfide could hardly be detected in the influent. However, in the downstream processes, carbon disulfide was seldom detected. Instead, dimethyl-mono and disulfides, which are the more reduced sulfur forms, were the major components. This phenomenon corresponds to the ORP of the samples (Figure 3). As the redox potential drops in the downstream processes more dimethyl mono and disulfides are produced.

PA and BA could be detected mainly from GT samples (PA = 23.4 ppbv), and blending processes (PA = 26 ppbv). The relatively high concentrations of acids correspond to sample pH; pH of the GT and blending sludges were 5.7 and 6.5, respectively, while others were neutral or higher. The septic conditions or lack of oxygen that develop in these downstream processes could cause acid to be generated, which results in the lower pH.

TMA was only detected from biosolids collected after the post-liming process. Cationic polymer and protein are known to be major sources of TMA odor at wastewater treatment plants (Murthy *et al*., 2001). Since, polymer is added to enhance DAF thickening and to facilitate the sludge dewatering process, TMA should be detected in both DAF thickened sludge and post limed biosolids. However, results showed that only the post-liming process produced significant amounts of TMA (typical fishy smell) at this wastewater treatment plant. The extremely high pH (>12.5) and temperature (>40°C) that resulted from the lime addition to the biosolids appears to have forced the release of TMA. The pH of the limed biosolids exceeded the pKa of TMA (9.81), and the heat from the exothermic reaction of the liming process combined to cause TMA volatilization.

Odor characteristics of DAF and GT sludge and final biosolids

Since the highest concentrations were observed in the final stages of processing, more detailed sampling of these processes was carried out. Thickened sludge from gravity thickeners (GT) and dissolved air flotation (DAF), which were fed with sludge from primary settling tanks and secondary settling tanks, respectively, were collected on three dates from September to November, 2000. Samples were collected from the outflow of each thickener. Biosolids were collected just after the post-liming process. The pH and ORP

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(oxidation/reduction potential) of each sample were recorded immediately after sample collection.

As shown in Table 2 GT sludge had higher ORP and lower pH than DAF thickened sludge. The feed sludge for the DAF is from a high rate activated sludge tank (SRT of 1.5 d) with high biological activity, which consumes oxygen rapidly, resulting in lower ORP conditions. Figure 4 shows the ORP values of the GT and DAF sludges and temperature profiles from July, 2000 to December, 2000. The ORP of DAF sludge is always lower (more negative) than that of the GT. Sludges both from DAF and gravity thickeners show low ORP values during the summer. While during the winter season, the ORP is higher. This is logical since the lower temperatures limit microbial activity, and the mass transfer rate of oxygen into water also might increase with decreasing temperature.

Due to the lower ORP range, more reduced sulfur compounds could be detected from the headspace of DAF sludge sample for the 1st (Sept. 13th) and 2nd (Sept. 22nd) study. In the last study (Nov. 9th), similar levels of reduced sulfur could be detected in both the GT and DAF; ORP of each system was 50 and 30, respectively. Also, when ORP was lower (1st and 2nd study), the amount of reduced sulfur from DAF sludge was higher. This result indicates that the generation of reduced sulfur odor depends on the system's oxidation state, which varies with season.

Volatile fatty acids were detected only from the sludge of the gravity thickener. Also, the concentrations of VFAs were different depending on the pH of the system. At pH 5.6, 159 ppb of VFA were detected and 25 ppb of VFA at pH 6.1. The DAF samples did not produce VFAs above our limits of detection. Unlike the GT, the DAF samples do not contain easily degradable products for hydrolysis and acidogenesis in the short SRT of the thickeners.

Results from biosolids were more variable. Trimethylamine and DMDS were consistently detected on all three occasions, but DMS, CS_2 and PA were found in some samples. More sample collections under different conditions are needed to determine the factors controlling odorous chemical release from biosolids.

Conclusions

The recently developed method using SPME has been applied to the analysis of odorous gases from wastewater, sludge and biosolids. In comparison to traditional methods, e.g. olfactometry, this method was considerably more convenient and inexpensive. The method can be used to capture odorous compounds on-site and has the potential for continuous monitoring with some modification as suggested by Eisert *et al*. (1997). SPME was able to absorb both low molecular weight odorous compounds such as carbon disulfide and heavier compounds such as dimethyl mono and disulfide. The heavier compounds were found to increase in intensity as the solids content of the waste flow increased. Gravity thickeners

Table 2 pH, ORP, and odor compound results from sludge under various conditions

	Sampling date	pH	ORP	TMA, ppb	CS_2, ppb	DMS, ppb	DMDS, ppb	Propionic, ppb	Butyric, ppb
GT sludge	Sept. 13, 2000	6.0	10		7.8 (2.2)			45 (6.9)	29
	Sept. 22, 2000	5.6	−10		5.6 (1.4)	6.7 (1.5)		130 (53)	30 (13)
	Nov. 9, 2000	6.1	50		3.3 (0.4)	5.6 (1.1)	4.6 (1.8)	25 (2.2)	
DAF sludge	Sept. 13, 2000	6.8	−40			16 (4.6)	21 (8.4)		
	Sept. 22, 2000	7.2	−50		3.8 (0.2)	11 (2.5)	12 (3.7)		
	Nov. 9, 2000	7.2	30			8.9 (2.1)	6.2 (0.5)		
Post-limed	Sept. 13, 2000			290 (12)			18 (1.4)		
	Sept. 22, 2000			170 (11)		11 (3.1)	19 (7.5)		
	Nov. 9, 2000			360 (17)	3.2 (0.5)	3.6 (1.7)	14 (0.7)	4.0 (0.7)	

* ( ): standard deviation of triplicates
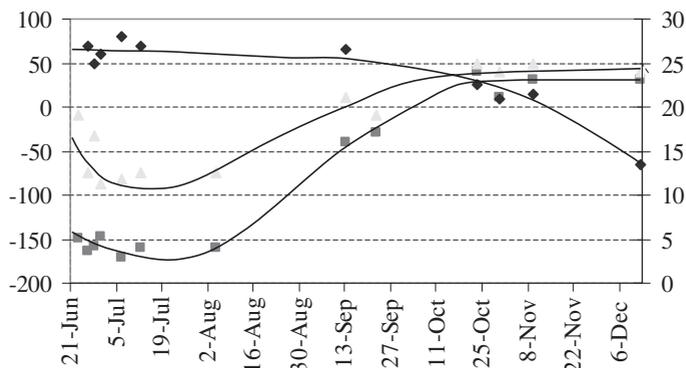
Figure 4 ORPs of GT and DAF sludges and atmospheric temperature

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were the major generators of volatile fatty acids, resulting in lowering of pH. TMA was released only from lime-amended biosolids. The extremely high pH and temperature that resulted from the lime addition to the biosolids appears to have caused the release of TMA. It should be emphasized that much more study is needed under different pH, ORP, temperature and flow conditions to effectively predict the character of gases released from the WWTP unit processes. Studies of aged biosolids are also needed to determine the most persistent odorous chemicals released over time to limit odor complaints from land application sites.

Acknowledgement

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