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Rezaul Mahmood

University of Nebraska - Lincoln

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Equilibrium Sampling Used to Monitor Malodors in a Swine Waste Lagoon

John H. Loughrin* and Nanh Lovanh USDA-ARS

Rezaul Mahmood Western Kentucky University

The concentrations of malodorous compounds in a 0.4-ha anaerobic lagoon that received waste from approximately 2000 sows were monitored during the late summer to late fall of 2006 to gain insight into the factors influencing their concentrations. Selected malodorous compounds were measured by the use of equilibrium samplers consisting of submersible stir plates and stir bar sorptive sampling with polydimethylsiloxane-coated magnetic stir bars. During the same period, air and water temperatures, suspended solids, total organic carbon and nitrogen content, and wastewater pH were recorded. Concentrations of malodorous compounds were higher at the surface of the lagoon than at the middle or bottom of the lagoon. Skatole concentration, for instance, averaged 54, 24, and 38 $\mu\text{g L}^{-1}$ near the surface, in the middle, and at the lowest sampling depths, respectively. While the lagoon was being pumped down during field application of wastewater, concentrations of malodorous compounds fluctuated widely, increased 16-fold as compared with the sampling period before pumping, and continued to increase as fall progressed and temperatures cooled. Suspended solids, volatile suspended solids, and total organic carbon increased near the bottom of the lagoon during this same period. The increases in the concentrations of malodorous compounds in the wastewater during the fall could have been due to a combination of several factors. These factors include reduced degradation by lagoon bacteria, less wind stripping of volatile compounds from the lagoon surface due to lowering of the lagoon surface after crop application, and/or reduced evaporation of malodorous compounds due to falling temperatures.

AS THE number of animals raised in concentrated animal feeding operations (CAFOs) increases, concerns over potentially adverse environmental impacts from these operations grow. Although there are many important issues that drive these concerns, the emission of malodorous compounds is the foremost factor driving public awareness of this matter. Malodorous compounds are produced from fresh feces and from waste-containment structures. Although the volatile compounds emitted from CAFOs are diverse (Schiffman et al., 2001), a limited number of these may be responsible for malodor (Williams, 1984; Hobbs et al., 1995; Zahn et al., 2001).

Among these, some of the most offensive—*p*-cresol, indole, skatole, and *p*-ethylphenol—are products of the anaerobic metabolism of aromatic amino acids and *p*-coumaric acid (Elsden et al., 1976; Spoelstra, 1977; van Beek and Priest, 2000). They are often cited as being major contributors to malodors in CAFOs (Spoelstra, 1977; Williams, 1984; Hobbs et al., 1995; Gralapp et al., 2001; Schiffman et al., 2001). In addition to having characteristically fecal odors, they also have low thresholds for olfactory detection. For instance, Schiffman et al. (2001) determined the odor thresholds of skatole and indole at 3.09 $\mu\text{g m}^{-3}$ and $1.55 \times 10^{-2} \mu\text{g m}^{-3}$ air, respectively. However, inside a recently cleaned swine house, although they found offensive fecal odors, they found concentrations of skatole and indole of only 0.6 $\mu\text{g m}^{-3}$ and 0.5 $\mu\text{g m}^{-3}$, respectively. Although the concentration of skatole may have been below its odor threshold, they conjectured that swine housing odor offensiveness was due to the cumulative effects of numerous compounds, many of which were present below their individual odor threshold.

Although there is disagreement as to which compounds or combinations thereof are primarily responsible for malodors from CAFOs (Spoelstra, 1980; Williams, 1984; Mackie et al., 1998; Zhu et al., 1999; Schiffman et al., 2001; Zahn et al., 2001; McGinn et al., 2003), it may be important only to monitor the concentrations of a few key contributors to reliably assess the meteorological factors and/or management practices that affect the release of malodors from CAFOs. The aromatic compounds are ideal for this purpose: They are relatively stable compounds (Spoelstra, 1980) without ionizable functional groups and therefore seem likely to persist in the air long enough to facilitate accurate measurements and do not react with other species, such as ammonium or sulfate ions.

J.H. Loughrin and N. Lovanh, USDA-ARS, Animal Waste Management Research Unit, 230 Bennett Ln., Bowling Green KY, 42104. R. Mahmood, Dep. of Geography and Geology, Western Kentucky Univ., Bowling Green, KY 42101.

Abbreviations: CAFO, concentrated animal feeding operations; MTBE, methyl *tert*-butyl ether; SBSE, stir bar sorptive extraction; SPME, solid-phase microextraction; TOC, total organic carbon; VFA, volatile fatty acids.

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*Corresponding author (jloughrin@ars.usda.gov).

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677 S. Segoe Rd., Madison, WI 53711 USA

When conducting measurements of malodorous compounds from CAFOs, it is desirable to obtain concomitant measurement of the concentrations of malodors from their source. In this way, source concentrations of volatiles may be factored in when investigating the factors that influence concentrations and fluxes of malodors from CAFOs. Solid-phase microextraction (SPME) is a common technique for the measurement of malodors in wastewater (Buchholz and Pawliszyn, 1994; Zahn et al., 1997; Loughrin, 2006). In SPME, a polymer-coated fiber is extended into a headspace or liquid sample, and analytes are thermally desorbed in a gas chromatograph injection port. Recently, Loughrin (2006) compared stir bar sorptive extraction (SBSE) with SPME for the quantification of malodors in wastewater. Stir bar sorptive extraction is similar to SPME except that a polymer coating (polydimethylsiloxane) is placed over a glass-coated magnetic stir bar. Compared with SPME, SBSE had comparable accuracy and greater precision for quantifying aromatic malodorous compounds in wastewater. Later, an equilibrium sampler was developed using SBSE for the quantification of these malodorous compounds in wastewater *in situ* (Loughrin and Way, 2006). Using these samplers, it was possible to quantify malodorous compounds in a swine waste lagoon.

In this study, we measured the concentrations of malodorous compounds in a swine waste lagoon from the late summer to late fall of 2006 while monitoring weather conditions and the solids, pH, carbon, and nitrogen (N) content of the wastewater. By doing this, we were able to note seasonal changes in the concentrations of malodorous compounds and note the weather conditions and management practices, such as field application of wastewater, that might have affected the concentrations of the malodorous compounds.

Materials and Methods

Measurement of Odor Compounds

Odor compounds in the lagoon were measured as described previously (Loughrin and Way, 2006). Briefly, waterproof submersible magnetic stir plates were suspended in the lagoon by the means of threaded steel rods attached to floats. Initially, the stir plates were suspended at depths of 10, 50, and 100 cm and later at depths of 10, 100, and 170 cm during the late summer to early fall of 2006 until the lagoon was pumped down during field application of wastewater. Thereafter, water samples were taken at depths of 10 cm. Odor compounds were absorbed onto preconditioned Twister stir bars (Gerstel USA, Baltimore MD) for 3 h, after which the stir bars were placed in autosampler vials and stored at 4°C until analyzed as described below.

Manure was collected underneath slatted flooring in each swine house and gravity drained into the lagoon weekly by removal of a drain plug. Odor compounds in the flushed manure were measured by collecting samples from the outlet end of the pipes and extraction of 40-mL samples of the flush water in the laboratory with preconditioned Twisters as described below.

Gas Chromatography–Mass Spectroscopy

Twister stir bars were desorbed in a Gerstel Model TDSA desorption unit interfaced to a Varian model 3800 gas chromatog-

raph and Varian Star mass spectrometer (Varian Associates, Palo Alto, CA). After an initial time of 0.25 min and an initial temperature of 25°C, the thermal desorption unit was programmed to 225°C and held for 3 min. Compounds were transferred at 240°C in splitless mode to a cooled injector maintained at –55°C with liquid CO₂ and transferred to a 30 m by 0.25 mm VF-23MS column with a film thickness of 0.25 μm (Varian Associates) using a 20:1 split by heating the injector at 10°C s⁻¹ to 300°C. This temperature was held for 3 min.

Gas chromatography–mass spectroscopy was performed as follows: column oven 30°C for 1 min, then programmed at 4°C min⁻¹ to 220°C and then at 20°C min⁻¹ to 225°C and held for 2 min. The column flow rate was held constant at 1 mL min⁻¹ using high-purity helium carrier gas, and, after a delay of 5 min, the mass spectrometer was operated in electron impact mode with a scan time of 0.45 s scan⁻¹, an emission current of 10 μamperes, and a mass range of 45 to 225 amu.

Wastewater Quality Analyses

Wastewater samples were collected at the lagoon surface and above the sludge layer on 31 August, 20 September, and 18 October in a 1.0-L polyethylene vessel. Lagoon depth above the sludge on these three dates was 4.0, 1.8, and 2.6 m, respectively. All analyses were performed according to Standard Methods (APHA, 1998). Total suspended solids (TSS) and volatile suspended solids (VSS) were determined according to Standard Methods 2540 D and 2540 E, respectively. The TSS were that portion of solids retained on a glass microfiber filter with a nominal pore size of 1.5 μm (Whatman grade 934-AH; Whatman, Clifton, NJ) after filtration and drying to constant weight at 105°C, whereas VSS was that portion of TSS that was lost on ignition in a muffle furnace at 500°C for 15 min. Total organic carbon (TOC) and N analyses were performed on an Elementar Vario Max carbon-nitrogen analyzer (Elementar USA, Mt. Laurel, NJ).

Meteorological Data

Data were collected using a 15-channel HOBO weather station (Onset Computer Corp., Bourne, MA) placed approximately 20 m from the southwest corner of the waste lagoon. Wind speed, direction, and gust speed were measured by a sensor mounted at a height of 3 m above the ground. Humidity and air temperature probes were placed in a solar radiation shield at a height of 2 m, and rainfall was measured with a tipping-bucket rain gauge mounted at 3 m. Solar radiation was measured with a silicon pyranometer with a spectral range of 300 to 1100 nm also mounted at 2 m. Barometric pressure was monitored with a sensor mounted inside the case of the data logger. Wastewater temperatures were monitored with HOBO probes. One was floated on the surface of the lagoon, and the other was weighted with lead sinkers and sunk to the bottom of the lagoon. Both probes were moored to an anchor at the edge of the lagoon for retrieval.

In the case of all air measurements, data were collected at 5-s intervals and averaged over 5-min intervals, and water temperatures were recorded every 5 min.

Results and Discussion

When sampling was begun on the 8 August, we collected samples at three depths, starting at 10 cm and varying from 60 to 180 cm. On 14 September, field application of wastewater was begun and continued intermittently over the next 2 wk. Before partial drainage, the lagoon averaged about 4 m in depth and was lowered to less than 1 m thereafter. From 6 October on, all samples were taken at a depth of 10 cm due to the low depth of the lagoon.

For samples taken before 14 September, there was a distinct tendency for malodorous compounds to occur in higher concentrations at the lagoon surface than at the middle or lower depths (Table 1). Concentrations of *p*-cresol, *m*-cresol, *p*-ethylphenol, and skatole were highest at the 10-cm sampling depth; concentrations of the latter three compounds were significantly higher. The concentrations of all compounds were lowest at the middle depth of the lagoon, except for *p*-cresol and indole, which showed no difference. It is possible that differences in concentrations with depth noted in the present study reflect a gradient that is caused by temperature stratification of the lagoon. Baehr and Zapezca (1998), for instance, found that vertical stratification of methyl *tert*-butyl ether (MTBE) occurred in lakes that had undergone temperature stratification in early summer. Therefore, insofar as MTBE is largely introduced into lakes at the surface by spills and the incomplete combustion of gasoline, in a body of water in which little or no vertical mixing of lake water occurs, MTBE concentrations decrease with depth. In the fall, as the lakes became vertically mixed, Baehr and Zapezca (1998) found that MTBE concentration gradients disappeared.

Methyl *tert*-butyl ether has a \log_{10} octanol-water partition coefficient (k_{ow}) of 0.94 and a boiling point of 55°C (National Library of Medicine, 2007), whereas the malodorous compounds of the present study have \log_{10} k_{ow} values ranging from 1.46 to 2.60 and boiling points ranging from 182 to 266°C. Although MTBE is considerably more volatile than our study compounds, MTBE and the malodorous compounds are comparatively polar (as indicated by k_{ow} values) and are therefore relatively water soluble. Skatole, the most nonpolar compound in this study, for instance, has a water solubility of 498 mg L⁻¹ (National Library of Medicine, 2007).

In the present study, flush water entered the lagoon from pipes at the surface of the wastewater. It is therefore possible that in a manner similar to that for MTBE, the concentration of malodorous compounds was higher near the surface due to their being introduced at the top of the lagoon

Table 1. Malodorous compounds depth profile in lagoon from 9 Aug. through 14 Sept.†

Compound	Concentration		
	Depth		
	Upper	Middle	Lower
	μg L ⁻¹		
Phenol	2.6 ± 0.8a	2.6 ± 0.9a	5.1 ± 2.5a
<i>p</i> -Cresol	42.1 ± 18.0a	34.5 ± 15.8a	34.6 ± 15.8a
<i>m</i> -Cresol	14.0 ± 15.8a	8.2 ± 3.0ab	4.8 ± 2.7b
<i>p</i> -Ethylphenol	48.7 ± 17.2a	30.2 ± 11.9b	35.7 ± 13.1ab
Indole	0.8 ± 0.1a	0.8 ± 0.1a	0.9 ± 0.3a
Skatole	54.4 ± 14.3a	23.6 ± 6.6b	38.0 ± 13.7ab

† Data represent the mean ± SE of five sampling dates from 8 Aug. through 14 Sept. 2006. Means followed by the same letter are not significantly different at $p = 0.05$ by a Duncan's multiple range test.

and temperature stratification of the wastewater, which prevented vertical mixing.

On bright sunny days, temperatures at the surface of the lagoon were notably higher than air temperatures or wastewater temperatures near the bottom of the lagoon, whereas on cloudier days, air temperatures were higher than those of the lagoon surface (Fig. 1). The dark coloration of the lagoon surface was responsible for the high daytime temperature of the lagoon surface on these days just as the high heat capacity of the water would be responsible for the relatively warm surface overnight lows. It is conceivable that temperature stratification of the lagoon was responsible for the differences seen in the concentrations of malodorous compounds at different depths.

During the previous winter, we sampled another waste lagoon on the same property and found concentrations of malodorous compounds that averaged 3- to 200-fold higher than those presented in Table 1 (Loughrin and Way, 2006). Al-

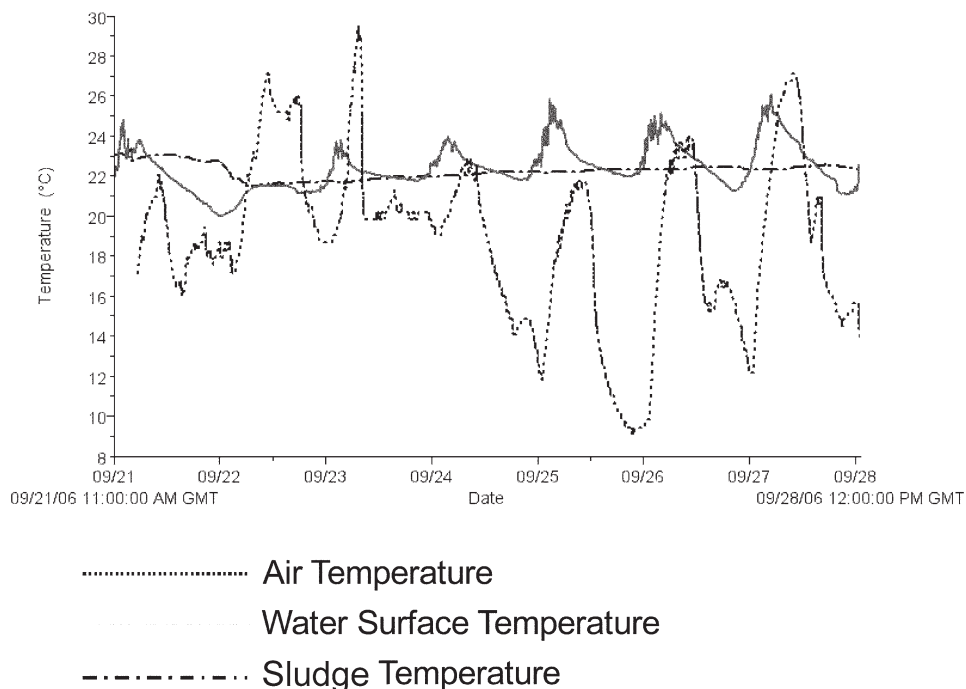


Fig. 1. Temperatures in the air, at the lagoon surface, and in the lagoon sludge during a 1-wk period.

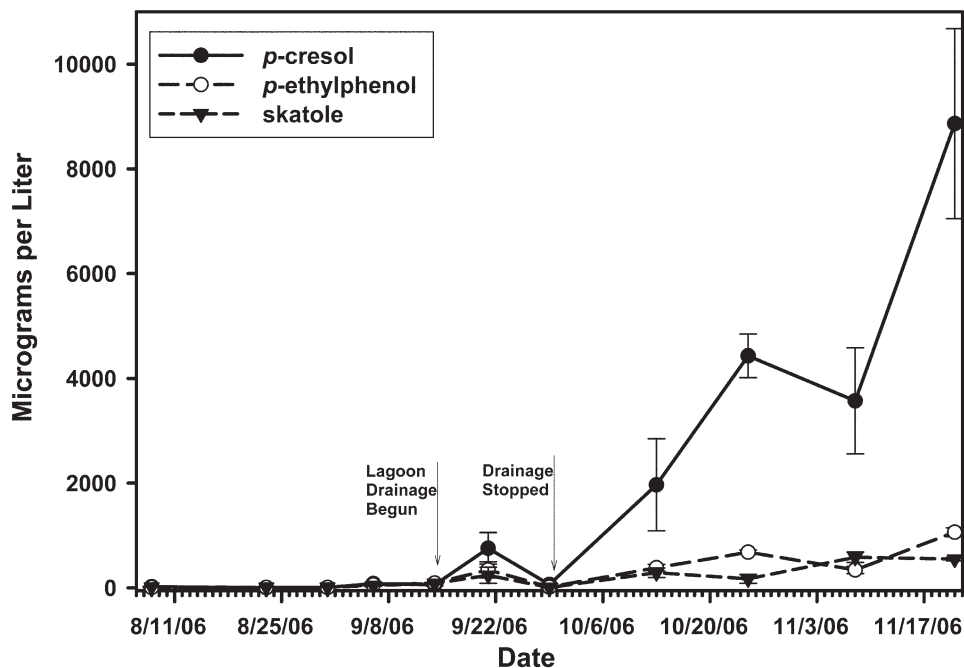


Fig. 2. Concentration of skatole, *p*-cresol, and *p*-ethylphenol in swine waste lagoon from late August to mid-November 2006.

though this lagoon was much smaller than the lagoon sampled here and received proportionally more waste, we feel that the higher concentrations found in the other lagoon largely reflect a seasonal difference in the concentration of malodorous compounds rather than a difference in management practice.

When the data on the concentrations of the three main malodorous compounds were pooled for all depths, the trend was for their concentrations to slowly increase from 31 August until 14 September (Fig. 2). On 14 September, the lagoon was partially emptied over a period of approximately 2 wk and, when sampled on 21 September, the concentrations of these compounds had increased by about fourfold (from approximately 300 µg L⁻¹ to about 1200 µg L⁻¹). On 29 September, their concentrations had returned to concentrations comparable to that found at the beginning of the application period, increased when sampled again on 13 October, and continued to increase through the fall season. Additional changes were noted in other wastewater quality parameters during this same period. The pH of the lagoon had dropped from approximately 8.0 to 7.2 during lagoon pumping (Table 2), whereas TSS, VSS, TOC, and N content increased during this period and remained elevated thereafter.

It seems certain that the marked rises in malodor concentrations that occurred on 21 September and on 13 October were

a direct result of lowering of the lagoon that occurred intermittently over the 2-wk span. It is possible that, by removing a large portion of the lagoon's volume, freshly discharged waste entering into the lagoon accounted for a higher percentage of the total volume, which was then reflected in the relatively high concentration of malodorous compounds. Support for this deduction is given by the relatively high concentration of malodorous compounds and other organic matter in raw flushed manure (Table 3). *Meta*-cresol and *p*-cresol were not separated on the VF-23MS column at these high concentrations and so are reported as a single peak. It is also possible that agitation of the sludge during the lagoon pumping served to increase concentrations of malodorous compounds.

We feel that the increases in TSS,

VSS, N, and TOC seen at the bottom of the lagoon during this period are probably related to the agitation of the sludge layer that occurred during pumping of the lagoon.

The decline in the concentrations of malodorous compounds seen on 29 September could be due to further pumping of the lagoon that occurred between then and 14 September and the removal of the recently added waste. When sampling was conducted on 21 September and 13 October, large volumes of wastes were being discharged into the lagoon over a period of at least several hours. This probably contributed to the relatively high concentrations of malodorous compounds seen on these dates as opposed to the previous sampling dates of 14 and 29 September.

Although both of the marked increases in the concentrations of malodorous compounds (i.e., on the 21 September and 13 October) seem to be due to the partial emptying of the lagoon, the overall trend for the concentrations of malodors to increase after pumping down of the lagoon also seems likely to be related directly or indirectly to declining temperatures. In early August, when chemical analyses were begun, daily air temperature highs were in the mid-thirties, and lows were in the upper twenties. By mid-November, when the last collection was performed, daily highs were variable, ranging from about 20 to about 10°C, and

lows ranged from about 15 to near -5°C. Lagoon surface highs generally approximated air temperature highs except that they were higher on bright sunny days, lower on cloudy days, and, due to water's high heat capacity, overnight lows were considerably warmer than were overnight air temperatures

Table 2. Liquid analyses performed on the samples collected at lagoon surface and above sludge layer.†

Date	pH		TSS‡		VSS		Total N		TOC	
	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
	mg L ⁻¹									
21 Aug.	7.96	7.89	1850	9080	850	5000	610	800	1100	3600
20 Sept.	7.96	7.22	4320	24,500	1700	7100	637	4130	1185	22,300
18 Oct.	8.03	7.55	1630	32,100	13,100	13,100	765	3820	1850	19,300

† Data represent the mean of three determinations.

‡ TOC, total organic carbon; TSS, total suspended solids; VSS, volatile suspended solids.

(Fig. 1). Sludge temperatures, on the other hand, were not variable and declined slowly, lagging a number of days behind those of the average air temperature. In early August, sludge temperatures were nearly constant at slightly above 30°C, had dropped only 5°C in 1 mo, and had dropped only about 15°C during the 3.5 mo, during which we performed our measurements. Figure 3 shows air and sludge temperatures averaged over 24-h periods from early September through mid-November 2006.

It is likely that slowly declining temperatures were at least in part responsible for the slight rise in the concentrations of malodorous compounds that was seen before partial pumping down of the lagoon. From 31 August to 14 September, lagoon sludge temperatures had declined from 27.7 to 23.9°C, whereas total measured malodors had increased from approximately 30 $\mu\text{g L}^{-1}$ to approximately 330 $\mu\text{g L}^{-1}$. It is likely that cooler weather retards evaporation of volatile compounds from the lagoon and allows for their accumulation. The large increases seen on 14 September and especially on 29 September seem to be a direct consequence of the lowering of the lagoon. We estimate that the volume of the lagoon was lowered about fivefold during field application: A large part of the solids remaining afterward consisted of recently added manure, which had very high concentrations of malodorous compounds (Table 3). Concentrations of malodors increased about fourfold from 14 September to 21 September and 16-fold by 25 October. After lagoon pumping, the continually dropping temperatures could have retarded evaporation of malodors from the lagoon and allowed for their accumulation to a degree not seen during warmer weather. However, sludge temperatures had only declined to 14.8°C by 25 October. This relatively modest temperature decline would seem to be insufficient for the large increase in the concentrations of malodors. It is likely that a seasonal decline, related to shorter days or falling temperatures, in the populations of organisms such as photosynthetic bacteria (Wenke and Vogt, 1981) and/or methanogenic consortia (Wang et al., 1988; Gu and Berry, 1991) were at least partially responsible for increases in the concentrations of malodors.

Do et al. (2003), for instance, found that the population of photosynthetic purple nonsulfur bacteria peaked in the late summer to early fall and that *Rhodobacter sp.* strain PS9 was capable of growth on phenol, *p*-cresol, and skatole. Gu and Berry (1991) found that a methanogenic consortium from sewage sludge was capable of degrading indole, and DeSutter and Ham (2005) found that methane production from a swine waste lagoon in Kansas varied greatly during the year, peaking in June. Perhaps the accumulation of solids, N, and TOC that we noted after partial pump-down of the lagoon (Table 2) is due to a seasonal decline in the population of catabolic organisms in the lagoon and a consequential inability to effectively degrade the recently added wastes.

Table 3. Selected characteristics of raw flushed manure.

Parameter	Concentration†
	$\mu\text{g L}^{-1}$
Phenol	7780 \pm 1345
<i>p</i> -Cresol + <i>m</i> -Cresol	57,600 \pm 6870
<i>p</i> -Ethylphenol	6060 \pm 702
Indole	1100 \pm 331
Skatole	2750 \pm 369
	mg L^{-1}
TSS‡	24,400 \pm 6400
VSS	6020 \pm 1670
Total N	3180 \pm 911
Total organic carbon	11,560 \pm 6690

† Data represent the mean of five determinations \pm SEM.

‡ TSS, total suspended solids; VSS, volatile suspended solids.

On the other hand, after field application of lagoon wastewater, the lagoon surface was considerably lower and consequently seemed to receive less wind. Bajwa et al. (2006) found that wind is an important factor driving volatilization of ammonia from anaerobic waste lagoons. It seems likely that, as for ammonia, volatilization of odor compounds should also be influenced by wind.

More research needs to be conducted to establish the relative importance of physical and biotic factors in controlling malodor concentrations in anaerobic lagoons. Regardless of the cause, when we stopped sampling, the concentrations of malodorous compounds in the lagoon were over 100-fold higher than when sampling was begun in early August (Table 4).

Malodors emitted from CAFOs are complex mixtures of compounds, and there is considerable difference in opinion as to the compounds that are important contributors to swine waste malodor (Spoelstra, 1980; Williams, 1984; Mackie et al., 1998; Zhu et al., 1999; Schiffman et al., 2001; Zahn et al., 2001; McGinn et al., 2003). In this study, we used SBSE to measure a selected subset of malodorous compounds from a lagoon in situ. Other compounds, such as volatile fatty acids (VFA) (Yo, 1999; Zahn et al., 2001) and sulfides (Yasuhara, 1980), are thought to be important components of swine waste malodor. However, at

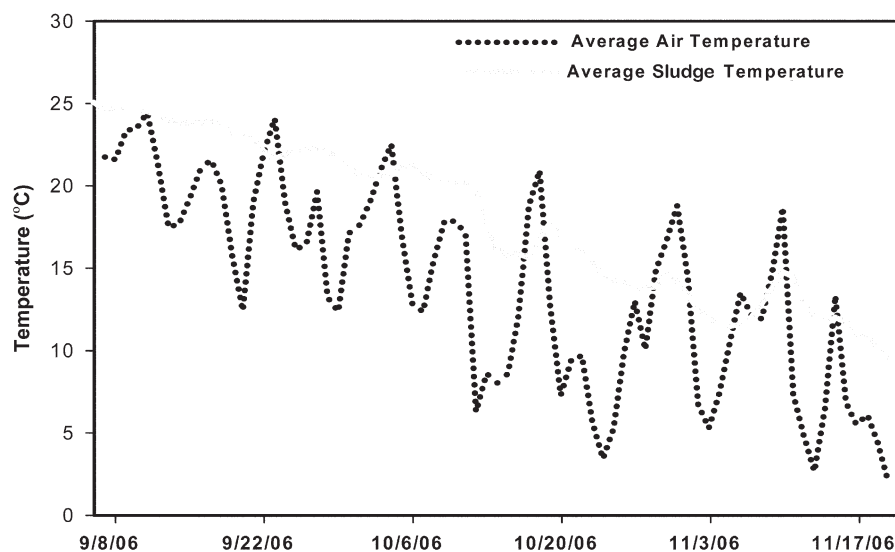


Fig. 3. Average daily air and sludge temperatures from early September to late November 2006.

Table 4. Concentrations of volatile compounds measured in the swine waste lagoon in early August and mid-November 2006.†

Compound	Concentration	
	8 Aug.	21 Nov.
	— $\mu\text{g L}^{-1}$ —	
Phenol	2.0 ± 0.2	330 ± 113
<i>p</i> -Cresol	23.8 ± 8.5	8870 ± 1810
<i>m</i> -Cresol	4.3 ± 1.9	—‡
<i>p</i> -Ethylphenol	8.0 ± 2.3	1060 ± 86.4
Indole	0.7 ± 0.3	76.8 ± 10.2
Skatole	16.8 ± 5.5	551 ± 33.0

† Data represent the mean ± SE of six determinations.

‡ Compound not separated from *p*-cresol.

the high pH of this waste lagoon (about 8.3), VFA and sulfide exist in their ionized forms and are not amenable to this technique, with the exception that, in the relatively high concentrations of malodors found in anaerobic pits, VFA may be measured using Twister stir bars (Loughrin, 2006). In any case, the aromatic amino acids are ideal candidates for monitoring malodorous plumes from CAFOs. Because they are relatively unreactive, they are likely to persist in the air longer than are sulfides and VFA. This makes their measurement less problematic. Their relatively low concentrations (Schiffman et al., 2001), however, make measurement of these compounds at any distance from an odor source challenging. In the future, we need to develop sensitive air monitoring methods for the measurement of these compounds from swine waste lagoons.

Conclusions

We found that the equilibrium samplers may be used to monitor malodorous compounds in a swine waste lagoon and track changes in their concentrations due to season, management practice, and depth. Given the large changes in the concentration of malodors that occurred within a relatively short period, no meaningful study of malodor fluxes can be done without concomitant measurements of the source of these emissions. These samplers, used in conjunction with air monitoring methods, should allow us to better evaluate the environmental factors influencing the emission of malodors from waste lagoons.

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