

AN EQUILIBRIUM SAMPLER FOR MALODORS IN WASTEWATER

J. H. Loughrin, T. R. Way

ABSTRACT. An apparatus for the *in situ* quantification of malodorous compounds from animal wastewater was developed that employed a submersible magnetic stir plate and stir bar sorptive extraction using polydimethylsiloxane-coated stir bars. Prior to deployment of the apparatus in a swine waste lagoon, experiments were conducted to determine minimum equilibration time as well as the minimum volume of sample needed for external standard calibration of samples. Minimum equilibration time was determined by monitoring loss of preloaded standards from the stir bars, while minimum calibration volume was based on the criterion that solutions used for calibration would not be significantly depleted. Based on these experiments, samplers were deployed in a swine waste lagoon for 3 h, and the amount of analytes retained on the stir bars was determined by external standards calibration using a volume of 40 mL. Afterwards, the samplers were preloaded with standards of compounds that approximated the physical characteristics of the target analytes and deployed in the lagoon with, and without, stirring. Significantly higher levels of some key malodorous compounds were found in stirred than in unstirred samples, while loss of preloaded analytes from stirred samples indicated that these samplers had more nearly reached equilibrium with the environment.

Keywords. Absorption, Odor, Octanol-water partition coefficient, SBSE, Stir bar sorptive extraction, Volatile.

Malodor from concentrated animal feeding operations (CAFOs) is due to the anaerobic decomposition of wastes, which produces low-molecular weight, offensive smelling compounds (Elsden et al., 1976; Spoelstra, 1977, 1980; Williams, 1984). In many CAFOs, animal manure is flushed from the housing with large amounts of water, and the wastes are stored in anaerobic pits or treated in anaerobic lagoons (Lim et al., 2004). Because they are a major source of malodor in CAFOs, it is desirable to measure the concentration of these compounds in wastewater.

The most common method for the measurement of volatile organic compounds in wastewater is solid-phase microextraction (SPME) (Zahn et al., 1997). Typically, a sample of wastewater is collected, and the sample is extracted in the laboratory. However, in many situations, it is preferable to measure compounds in the field without disturbing the sample and so that a time-weighted average of compound concentration may be obtained. A number of passive sampling devices have been developed that allow for equilibrium measurement of compounds *in situ* and that in general require no specialized equipment for sample collection (Vrana et al., 2001). Although there is considerable variation in the construction of passive samplers (Mayer et

al., 2003; Vrana et al., 2001), they have certain aspects of their design and behavior in common.

Most passive samplers consist of a receiving phase separated from the environment by a semi-permeable membrane (Vrana et al., 2001). Receiving phases employed have included volatile solvents (Luellen and Shea, 2003), triolein (Lu et al., 2002), and poly(dimethylsiloxane) (PDMS) (Vrana et al., 2001). Regardless of receiving phase, passive samplers exhibit three phases of uptake (fig. 1): kinetic, intermediate, and near equilibrium (Mayer et al., 2003). In the kinetic phase, uptake of analytes is nearly linear, and the amount of analyte absorbed on the sampler cannot be used to infer concentration in the environment without knowledge of the uptake rate of the sampler. When a sampling device is at or near equilibrium, however, the amount of analyte retained on the sampler may be used to calculate concentration in the environment so long as the sampler does not significantly deplete samples used for calibration and fluctuations in analyte concentration take longer than the response time of the sampler. Determination that the sampler is actually in equilibrium with the environment may be difficult, however.

Chen and Pawliszyn (2004) recently studied the kinetics of absorption and desorption for a benzene, toluene, ethylbenzene, and *o*-xylene (BTEX) mixture on PDMS SPME fibers. With the use of deuterated toluene, they were able to demonstrate that the absorption of analytes from solution onto the SPME fiber was isotropic with its desorption back into solution, that is, the kinetics of uptake and loss of analytes were “mirror images” of one another. This is illustrated in figure 1, where idealized absorption and desorption profiles for a passive (equilibrium) sampler are shown.

Preloading of a sampler with labeled analogs of the compounds of interest, or compounds that model the behavior of these compounds, therefore, may offer a convenient means for determining if a sampler has equili-

Submitted for review in March 2006 as manuscript number SE 6413; approved for publication by Structures & Environment Division of ASABE in July 2006.

The authors are **John H. Loughrin**, Research Chemist, USDA-ARS Animal Waste Management Research Unit, Bowling Green, Kentucky; and **Thomas R. Way**, ASABE Member, Agricultural Engineer, USDA-ARS National Soil Dynamics Laboratory, Auburn, Alabama. **Corresponding author:** John H. Loughrin, USDA-ARS Animal Waste Management Research Unit, 230 Bennett Lane, Bowling Green, KY 42104; phone: 270-781-2579, ext. 235; fax: 270-781-7994; e-mail: jloughrin@ars.usda.gov.

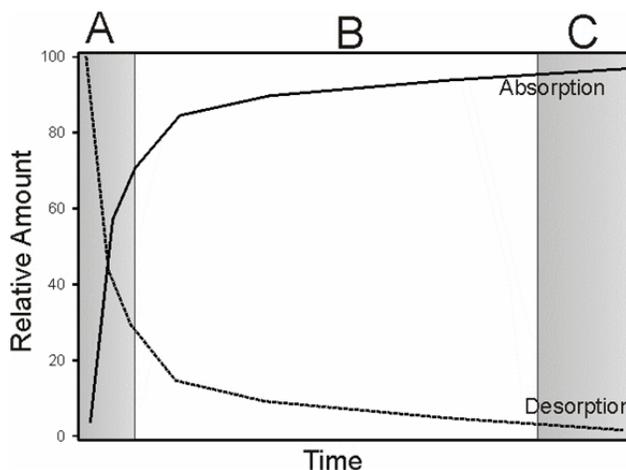


Figure 1. Graph illustrating idealized absorption and desorption profiles from an equilibrium sampling device: (A) kinetic uptake by sampler, (B) intermediate phase of uptake, and (C) near-equilibrium phase of compound uptake.

brated with the environment. If little or none of the compounds preloaded onto the sampler prior to its deployment are detected after its retrieval, then it may be assumed that the sampler reached or was near equilibrium, since the environment effectively serves as an infinite sink for the spiked compounds.

Equilibrium sampling implies relatively long sampling times with an increased risk of sampler fouling and degradation as well as the potential for vandalism (Mayer et al., 2003; Vrana et al., 2001). However, if the capacity of the sampler for analytes is relatively low (i.e., low partition coefficients) and the surface area of the sampler is high, equilibrium may be reached relatively quickly (Pawliszyn, 2003).

Recently, Vrana et al. (2001) described a passive sampler for the monitoring of persistent hydrophobic pollutants in the environment. The sampler consisted of a stir bar covered with PDMS tubing that was enclosed within dialysis tubing. The stir bars (marketed under the trade name Twisters®), were developed by Baltussen et al. (1999) as a means for the concentration of organic compounds from aqueous matrices in which compounds adsorbed by the PDMS are subsequently thermally desorbed onto a gas chromatograph. This technique is known as stir bar sorptive extraction (SBSE).

Vrana et al. (2001) deployed their samplers for periods of up to one week, during which time uptake of the hydrophobic pollutants was essentially linear. However, conditions in a waste lagoon or pit are harsh, with potential for degraded sampler performance due to biofilm formation as well as bacterial decomposition of the sampler and/or dialysis tubing. As mentioned, however, sampler equilibration with the environment may occur relatively quickly if the capacity of the sampler for targeted analytes is relatively low (Pawliszyn, 2003).

The PDMS phase in Twisters is non-polar. The compounds responsible for malodors in waste lagoons and anaerobic pits, on the other hand, are relatively hydrophilic. In particular, some of the key components of fecal malodor are stable metabolites of aromatic amino acids (Elsden et al., 1976; Spoelstra, 1980; Williams, 1984). These compounds (phenol, *p*-cresol, *p*-ethylphenol, indole, and skatole) have

log octanol-water partition coefficients (k_{ow}) ranging from 1.5 to 2.6 (National Library of Medicine, 2006). PDMS has relatively low capacity for these compounds (Loughrin, 2006), so equilibration times may be relatively short. This indicates that equilibrium samplers for these compounds might be deployed *in situ* without undue concern for bacterial decomposition of the samplers or biofilm formation.

This article presents data on the use of SBSE as means for sampling malodorous compounds in agricultural wastewater with the use of a simple stirring apparatus to reduce equilibration time. In addition, a simple technique for determining probable sampler equilibration time is described.

MATERIAL AND METHODS

CHEMICALS AND SUPPLIES

All chemicals were purchased from Sigma-Aldrich (St. Louis, Mo.) and were 98% purity or higher. Dialysis tubing (regenerated snakeskin cellulose) with a nominal molecular weight cutoff of 3600 Daltons was purchased from Fisher Scientific (Hampton, N.H.). All preparations involving wastewater as well as phenol and *p*-cresol (toxic and stench), *p*-ethylphenol, indole, and skatole (irritant and stench) were performed in a ventilated fume hood. Selected physical properties of standards and target analytes studied in these experiments are given in table 1.

DETERMINATION OF EQUILIBRATION TIME

Determination that a sampler was near equilibrium for a given compound was based on the criterion that over 95% of a preloaded standard was lost from the sampler after a specific deployment time. Twister stir bars (10 mm long × 0.5 mm phase thickness; Gerstel USA, Baltimore, Md.) were thermally conditioned under a stream of high-purity N₂ at 250°C for 60 min prior to use. Two hundred ng each of *p*-anisaldehyde, benzyl acetate, methyl salicylate, borneol, and L-fenchone in 2 μL CH₂Cl₂ were added to 1 mL deionized water in 2 mL vials along with the stir bars and stirred at 500 rpm for 60 min. The Twisters were then placed in 1 qt (0.95 L) Mason jars along with 800 mL deionized water. Compounds were desorbed from the Twisters for 0, 15,

Table 1. Selected physical properties of compounds used for determination of sampler equilibrium and of analytes.^[a]

Compound	k_{ow} (log ₁₀ k_{ow})	BP (°C)
Preloaded Standards		
<i>p</i> -Anisaldehyde	57.5 (1.76)	248
Benzyl acetate	89.1 (1.95)	213
Methyl salicylate	355 (2.55)	223
Borneol	490 (2.69)	-- ^[b]
Fenchone	1,096 (3.04) ^[c]	--
Target Analytes		
Phenol	28.8 (1.46)	181.8
<i>p</i> -Cresol	87.1 (1.94)	201.9
Indole	138 (2.14)	254
<i>p</i> -Ethylphenol	380 (2.58)	217.9
Skatole	398 (2.60)	266

^[a] Data obtained from National Library of Medicine (<http://chem.sis.nlm.nih.gov/chemidplus/>).

^[b] Decomposes.

^[c] Estimated.

30, 60, 120, 240, and 360 min without stirring and with stirring at 500 rpm. In an additional experiment, conditioned Twisters were placed in 2 cm lengths of dialysis tubing filled with deionized water and desorbed in 800 mL of deionized water. Results from these experiments were expressed relative to the level of compounds retained by the non-desorbed Twisters ($t = 0$) equal to 100. Both experiments were repeated three times.

DETERMINATION OF MINIMUM CALIBRATION VOLUME

Phenol, *p*-anisaldehyde, benzyl acetate, *p*-cresol, methyl salicylate, *p*-ethylphenol, *p*-propylphenol, indole, borneol, skatole, fenchone, and limonene were dissolved in CH_2Cl_2 and added to 1, 2, 5, 10, 20, or 40 mL deionized water in screw-cap vials at a final concentration of 500 ng mL^{-1} each and extracted with preconditioned Twisters for 2 h while stirring at 500 rpm. The Twisters were then removed from the vials and a second Twister added. The sample was re-extracted, and compounds adsorbed by both stir bars were analyzed as described below. Compound amounts obtained from the second extraction were expressed as a percentage of that obtained from the first extraction. These experiments were replicated three times for each sample volume. For a given compound, a calibration volume was considered adequate if the amount found upon re-extraction was 95% or more of that of the initial extraction.

ENVIRONMENTAL SAMPLING

A submersible stirrer was constructed from a 12 V computer fan connected to a rechargeable 9 V battery (fig. 2). A 1.0 cm wide \times 0.5 cm tall cylindrical ceramic magnet was glued to the rear of the fan motor housing so that it was free to rotate, and the fan was enclosed within a 10 cm \times 10 cm \times 5 cm tall enclosure constructed of welded aluminum. The stirrer was enclosed in a heat-sealed polyethylene food-grade bag (Rival Seal-a-Meal, The Holmes Group, Milford, Mass.) and placed between two aluminum plates connected with three 9 cm bolts. Between the top plate and the stirring apparatus, a 56 mm diameter \times 17 mm high glass Petri dish was placed. The top plate had a number of holes drilled in it to allow water movement into the Petri dish and aluminum woven wire cloth was placed between it and the Petri dish in order to ensure retention of the Twister stir bar. For collection of passive samples (unstirred), a Petri dish was simply enclosed within two aluminum plates and woven wire cloth.

Prior to deployment of samplers, standards of *p*-anisaldehyde, benzyl acetate, methyl salicylate, borneol, and fenchone were added to Twisters by spiking 1 mL of deionized

water with 200 ng of each compound and stirring the samples at 500 rpm for 60 min.

The samplers were deployed in an approximately 10 m wide lagoon that served as the primary receiver of waste from a farrowing operation of about 950 sows. Stirred and passive (unstirred) samplers were suspended at a depth of 14 cm from a wooden frame float by means of galvanized steel bolts. Samplers were deployed for 3 h, at the end of which the Twisters were removed from the Petri dishes and stored in 2 mL autosampler vials at 4°C until analyzed. The Twisters were analyzed within 24 h of sample collection. Amounts of compounds from the lagoon were expressed as ng of compound per mL of water based on external standard calibration using 40 mL water samples as described below. Amounts of the pre-applied standards were normalized to those from passive samplers set equal to 100%. These experiments were replicated seven times to obtain mean values for both treatments.

GAS CHROMATOGRAPHY-MASS SPECTROSCOPY

Twisters were desorbed in a Gerstel model TDSA thermal desorption unit interfaced to a Varian model 3800 gas chromatograph (GC) and Varian Star 2200 mass spectrometer (Varian Associates, Palo Alto, Cal.). After an initial time of 0.25 min, desorption of the stir bars was performed with an initial temperature of 100°C , programmed at $60^\circ\text{C min}^{-1}$ to 260°C , and then held for 30 min. Compounds were transferred in splitless mode to a glass wool packed injection liner maintained at -50°C with liquid CO_2 . Compounds were then transferred to the GC column with a 20:1 split ratio by ramping the injector at $12^\circ\text{C sec}^{-1}$ to 300°C . Compound separation was performed on a 30 m \times 0.25 mm VF-23MS column (50% cyanopropylmethylpolysiloxane) with a film thickness of $0.25 \mu\text{m}$ (Varian, Inc.). GC operating conditions were: He carrier constant flow rate of 1 mL min^{-1} and column oven at 60°C for 1 min, programmed at 7°C min^{-1} to 115°C , at $1.5^\circ\text{C min}^{-1}$ to 140°C , and then at $15^\circ\text{C min}^{-1}$ to 195°C . The mass spectrometer was operated in electron ionization mode with an emission current of $10 \mu\text{A}$, a scan time of 0.35 s per scan, and a scan range of 45 to 225 amu. Odor compounds were quantified by a 6-point external standard calibration using standards dissolved in 40 mL of water at the same pH as the wastewater samples. For each odor compound measured in the wastewater, quantitation was based on its most prominent ion, while identification was based on computer matching of spectra. R^2 values for each compound were above 0.99.

RESULTS AND DISCUSSION

DETERMINATION OF EQUILIBRATION TIME

Results of loss of preloaded standards from stirred and unstirred Twisters are presented in figure 3. For unstirred Twisters, the amount of analyte retained after 6 h ranged from about 32% for *p*-anisaldehyde to 108% for fenchone. It is interesting to note that for the unstirred samples, levels of fenchone seemed to rise after the Twisters were removed from the spike solution and placed in clean water. This could perhaps be due to a layer of weakly sorbed analyte present after the initial spiking procedure ($t = 0$) that was lost during the thermal desorber's water purge time of 0.25 min. Then, after the Twisters were placed in the Mason jars and stirred

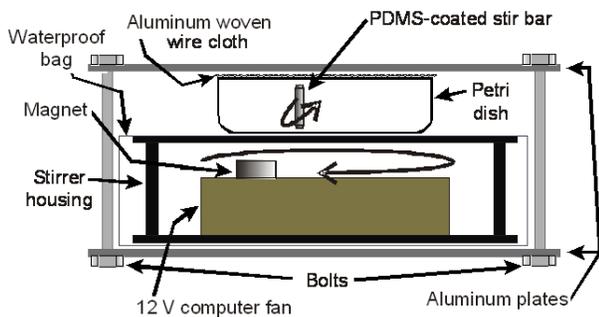


Figure 2. Side view diagram of apparatus used to stir sampler in waste lagoons.

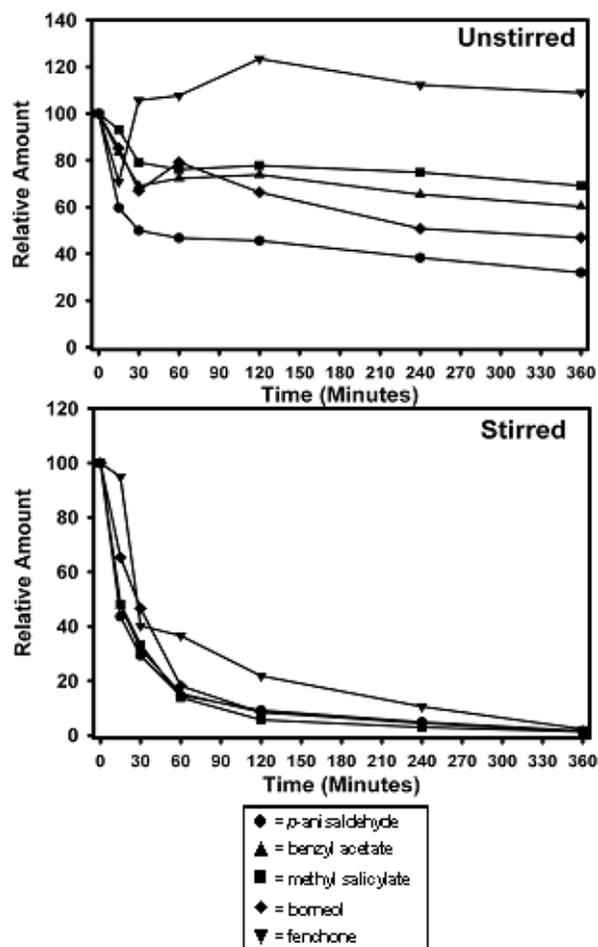


Figure 3. Loss of standard compounds from stirred and unstirred PDMS-coated stir bars.

for up to 6 h, the fenchone present in this layer had time to become more strongly absorbed to the PDMS and thus was not easily lost during the instrument's water purge cycle. This may serve as an indication that equilibrium had not quite been reached for fenchone during the standards preloading procedure. Regardless, results indicate that for non-stirred samples, equilibration between the Twisters and the 800 mL water samples had not been reached for any of the five spiked compounds.

As expected, Twisters lost the initial spike more quickly when stirred. Again, the most hydrophobic compound, fenchone, was lost at a slower rate than were the other compounds. Still, after 6 h of stirring, less than 3% of the original amount of fenchone was retained by the Twisters, and less than 2% of the initial amounts of any of the other analytes were present. Since, for the purpose of this experiment, 800 mL of water was considered infinite in size compared to the volume of the PDMS phase (approx. 24 μ L, manufacturer's data), this indicated that 6 h was adequate for stirred Twisters to obtain equilibrium for compounds with $\log k_{ow}$ values of 3 and below regardless of sample volume. For compounds more hydrophilic than fenchone, 3 h appeared to be an adequate equilibration time.

When placed in dialysis tubing, compounds were lost at a slower rate than from bare Twisters (fig. 4). Still, for the most polar analyte, *p*-anisaldehyde, only about 1% of the

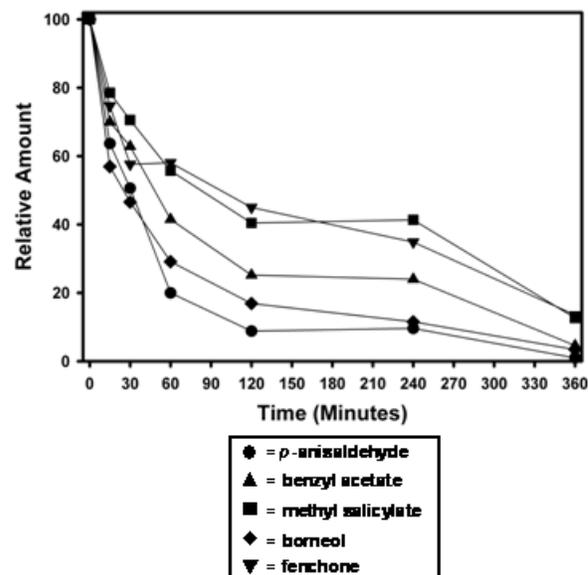


Figure 4. Loss of standard compounds from stirred PDMS-coated stir bars enclosed in dialysis tubing.

original analyte was retained after 6 h, while approximately 13% of the original methyl salicylate and fenchone were still present. The relatively slow rate at which the membrane-enclosed Twisters lost compounds as compared to unenclosed Twisters is probably due to a combination of the dialysis tubing serving as an impediment to diffusion as well as its hindering free movement of the stir bars. For this reason, when environmental sampling was conducted, the dialysis tubing was dispensed with, and the Twisters were simply placed in small Petri dishes. Given the relatively short equilibration times involved, we felt that any protective role against bacterial growth on or decomposition of the Twisters by the dialysis tubing was unnecessary.

MINIMUM CALIBRATION VOLUME

Determination of the minimal volume of water necessary for calibration of environmental samples was based on the criterion that the standard solution should not be significantly depleted when extracted, that is, that upon re-extraction of the same sample, levels of standards would decline by less than 5% (Mayer et al., 2003; Zeng and Noblet, 2002). Based on this requirement, we found that a volume of 40 mL was adequate for calibration for all compounds but fenchone and limonene (table 2). Since these compounds have $\log k_{ow}$ values higher than our target analytes in animal wastewater, we considered this volume adequate for calibration of the environmental samples.

While calibrations were performed with pure water instead of a more complex mixture that might have more closely mimicked the environmental samples, we felt that this was adequate for determining that pool of free volatile compounds that contribute to malodor. However, a sampling device placed in a complex sample obtains equilibrium not only with solutes in the water phase but also with compounds sorbed with dissolved organic matter. Nevertheless, matrix effects appear to be less important as the volume of the sampler increases, and hydrophobic compounds are more strongly absorbed to dissolved organic matter (DOM) than are relatively polar compounds (Zeng and Noblet, 2002). The

Table 2. Relative amounts (%) of analytes found upon re-extraction of a solution with PDMS-coated stir bars.^[a]

Compound	log ₁₀ <i>k</i> _{ow}	Volume (mL)					
		1	2	5	10	20	40
Phenol	1.46	75.6	84.0	89.9	95.2	93.0	104.9
<i>p</i> -Anisaldehyde	1.76	80.4	90.0	93.6	94.1	93.9	95.7
<i>p</i> -Cresol	1.94	82.8	98.4	98.1	103.7	99.3	98.8
Benzyl acetate	1.96	50.7	68.0	85.7	87.6	94.3	98.7
Indole	2.14	74.0	80.3	92.2	94.9	96.0	97.4
Methyl salicylate	2.55	30.1	47.0	71.5	80.2	86.2	97.7
<i>p</i> -Ethylphenol	2.58	87.2	88.8	96.7	97.7	95.7	98.9
Skatole	2.60	51.9	70.1	84.3	88.3	97.1	95.6
Borneol	2.69	70.6	84.5	94.8	98.8	98.6	98.5
Fenchone	3.04	28.8	46.8	70.6	75.3	88.0	91.1
<i>p</i> -Propylphenol	3.20	74.8	80.3	91.1	94.6	95.7	97.8
Limonene	4.57	1.3	1.3	4.7	6.6	18.3	25.9

^[a] Data normalized to first extraction of standards solution equal 100%. Data represent the average of three determinations.

receiving phase volume of Twisters is almost 50-fold higher than that of 85 μm SPME fibers that are commonly used for sampling of dissolved volatile compounds, and the target analytes of the present study all have log *k*_{ow} values below 3.0. For these reasons, DOM may have negligible effects on the Twister calibrations. Still, research will need to be done to address this issue.

ENVIRONMENTAL SAMPLING

We deployed the samplers in the lagoon for 3 h since, based on loss of preloaded analytes from the Twisters (fig. 2), this seemed an adequate time for compounds with log *k*_{ow} values below 3.0 to reach equilibration. The results of this sampling are presented in table 3.

As we anticipated, the amount of preloaded standards was much higher from the passive samplers than from the stirred ones. Contrary to our expectations, however, not only did stirred Twisters retain detectable amounts of some standards, but those that were quantifiable, methyl salicylate and borneol, had intermediate log *k*_{ow} values. Fenchone, a much more hydrophobic compound than either of these two, disappeared almost completely from the stirred Twisters.

Table 3. Concentration of compounds found by stir bar sorptive extraction after 3 h sampling in a swine waste lagoon.

Compound	Treatment ^[a]	
	Unstirred Samples	Stirred Samples
Preloaded Standards	Relative Concentration	
<i>p</i> -Anisaldehyde	100 ±45.3	trace ^[b]
Benzyl acetate	100 ±10.2	trace
Methyl salicylate	100 ±15.0*	23.5 ±0.7
Borneol	100 ±5.8*	4.4 ±1.0
Fenchone	100 ±22.1	trace
Retained Analytes	Concentration (ng mL ⁻¹ water)	
Phenol	76.1 ±30.7	75.8 ±32.5
<i>p</i> -Cresol	1,140 ±491	4,680 ±1,810*
<i>m</i> -Cresol	52.2 ±21.7	81.6 ±22.2
<i>p</i> -Ethylphenol	971 ±296	886 ±242
Indole	115 ±31.4	135 ±43.5
3-Octanone	1.6 ±0.5	10.5 ±1.0*
Skatole	456 ±91.1	977 ±241*
3-Octanol	2.7 ±1.0	6.9 ±1.8*

^[a] Data represent the mean of seven determinations ±standard error of the mean. Within a row, means followed by an asterisk are significantly higher by analysis of variance (*P* < 0.05).

^[b] Compound detected but below limit of quantitation.

Similarly, differences in the amount of targeted malodorous analytes retained on the stirred and passive Twisters did not follow a simple pattern based on *k*_{ow} values. Of the major contributors to lagoon malodor, significantly higher concentrations for stirred samples were obtained only for *p*-cresol and skatole, with log *k*_{ow} values of 1.94 and 2.60, respectively. Otherwise, for the remainder of the five major target analytes, the levels of compounds retained on stirred and passive Twisters were quite similar.

Three additional, quantitatively minor, compounds were identified from the swine waste lagoon. These were *m*-cresol, 3-octanone, and 3-octanol, compounds with log *k*_{ow} values of 1.96, 2.22, and 2.73, respectively (National Library of Medicine, 2006). The stirred samplers retained higher amounts of all three compounds, but the difference was significant only for 3-octanone and 3-octanol. It is unlikely to be coincidental that the three most hydrophobic compounds identified, 3-octanone, skatole, and 3-octanol, were all found in higher amounts in stirred rather than unstirred Twisters.

Still, these results indicate that, in addition to polarity effects on the retention of compounds by the Twisters, other factors may affect the speed at which compounds reach equilibration. Perhaps steric aspects also affect diffusion through the PDMS phase and therefore equilibration times. Nevertheless, our results indicate that preloading samplers with compounds that possess similar physical attributes to those of target analytes can serve as a guide for determining sampling time. After this time is determined, either the preloaded standards could be omitted from the samplers or they could be used to judge sampler performance (i.e., to determine if samples were actually stirred). Since performance of the sampler would be expected to vary based on the nature of the liquid environment and target analytes, initial deployment of the sampler with preloaded standards should be done.

CONCLUSION

We found that Twister stir bars can be used for environmental sampling of some low molecular weight malodorous compounds from wastewater; using small battery-powered stir plates significantly reduces equilibration time. While similar results might be obtained by collecting samples in the field and laboratory analysis, *in situ* sampling offers a number

of potential benefits. First, labile compounds may be sampled with less chance of degradation. Secondly, samplers may be deployed in locations and water depths that may not be otherwise accessible. In addition, deployment of samplers at a series of depths could make possible flux measurements of compounds moving through a water column. For analysis of hydrophobic water pollutants, stirring the Twisters would significantly reduce equilibration time, and could make such analyses more convenient. If high-capacity batteries are used, sampling times might be extended long enough to make such analyses practical.

ACKNOWLEDGEMENTS

We thank Joe St. Claire for technical assistance. This research was part of USDA-ARS National Program 206: Manure and By-product Utilization. Mention of a trademark or product anywhere in this article is to describe experimental procedures and does not constitute a guarantee or warranty of the product by the USDA and does not imply its approval to the exclusion of other products or vendors that may also be suitable.

REFERENCES

Baltussen, E., P. Sandra, F. David, and C. Cramers. 1999. Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: Theory and principles. *J. Microcolumn Separations* 11(10): 737-747.

Chen, Y., and J. Pawliszyn. 2004. Kinetics and the on-site application of standards in a solid-phase microextraction fiber. *Anal. Chem.* 76(19): 5807-5815.

Elsden, S., M. Hilton, and J. Waller. 1976. The end products of the metabolism of aromatic amino acids by clostridia. *Arch. Microbiol.* 107(3): 283-288.

Lim, T., J. Heber, J.-Q. Ni, D. Kendall, and B. Richert. 2004. Effects of manure removal strategies on odor and gas emissions from swine finishing. *Trans. ASAE* 47(6): 2041-2050.

Loughrin, J. 2006. A comparison of solid-phase microextraction and stir bar sorptive extraction for the quantification of malodors in wastewater. *J. Agric. Food Chem.* 54(9): 3237-3241.

Lu, Y., Z. Wang, and J. Huckins. 2002. Review of the background and application of triolein-containing semipermeable membrane devices in aquatic environmental study. *Aquatic Toxicol.* 60(1-2): 139-153.

Luellen, D., and D. Shea. 2003. Semipermeable membrane devices accumulate conserved ratios of sterane and hopane petroleum biomarkers. *Chemosphere* 53(7): 705-713.

Mayer, P., J. Tolls, and D. MacKay. 2003. Equilibrium sampling devices. *Environ. Sci. Tech.* 37(9): 184A-191A.

National Library of Medicine. 2006. ChemIDplus Advanced. Bethesda, Md.: U.S. National Library of Medicine. Available at: <http://chem.sis.nlm.nih.gov/chemidplus/>. Accessed 17 March 2006.

Pawliszyn, J. 2003. Sample preparation: Quo vadis? *Anal. Chem.* 75(11): 2543-2558.

Spoelstra, S. 1977. Simple phenols and indoles in anaerobically stored piggery wastes. *J. Sci. Food Agric.* 28(3): 415-423.

Spoelstra, S. 1980. Origin of objectionable odorous components in piggery wastes and the possibility of applying indicator components for studying odour development. *Agric. Environ.* 5(3): 241-260.

Vrana, B., P. Popp, A. Paschke, and G. Schullermann. 2001. Membrane-enclosed sorptive coating: An integrative passive sampler for monitoring organic contaminants in water. *Anal. Chem.* 73(21): 5191-5200.

Williams, A. 1984. Indicators of piggery slurry odour offensiveness. *Agric. Wastes* 10(1): 15-36.

Zahn, J., J. Hatfield, Y. Do., A. DiSpirito, D. Laird, and R. Pfeiffer. 1997. Characterization of volatile organic emissions and wastes from a swine production facility. *J. Environ. Qual.* 26(6): 1687-1696.

Zeng, E., and J. Noblet. 2002. Theoretical considerations on the use of solid-phase microextraction with complex environmental samples. *Environ. Sci. Tech.* 36(15): 3385-3392.