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Bias of Tedlar Bags in the Measurement of Agricultural Odorants

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ABSTRACT

Odor regulations typically specify the use of dynamic dilution olfactometery (DDO) as a method to quantify odor emissions, and Tedlar bags are the preferred holding container for grab samples. This study was conducted to determine if Tedlar bags affect the integrity of sampled air from animal operations. Air samples were collected simultaneously in both Tedlar bags and Tenax thermal desorption tubes. Sample sources originated from either a hydrocarbon-free air tank, dynamic headspace chamber (DHC), or swine-production facility, and were analyzed by gas chromatography–mass spectrometry–olfactometry (GC–MS–O). Several background contaminants were identified from Tedlar bags, which included the odorous compounds *N*, *N*-dimethyl acetamide (DMAC), acetic acid, and phenol. Samples from the DHC demonstrated that recovery of malodor compounds was dependent on residence time in the Tedlar bag with longer residence time leading to lower recovery. After 24 h of storage, recovery of C_3–C_6 volatile fatty acids (VFA) averaged 64%, 4-methylphenol and 4-ethylphenol averaged 10%, and indole and 3-methylindole were below the detection limits of GC–MS–O. The odor activity value (OAV) of grab samples collected in Tedlar bags were 33 to 65% lower following 24 h of storage. These results indicate that significant odorant bias occurs when using Tedlar bags for the sampling of odors from animal production facilities.

The expansion of concentrated animal feeding operations (CAFOs) throughout the USA and encroachment of urban development into rural landscape has catalyzed an increased awareness by the general public and governmental agencies of the potential impacts of these facilities on water and air quality. Recent air-monitoring studies have shown that CAFOs exhibit the potential to negatively impact air quality through the release of odor and odorous compounds, such as hydrogen sulfide, ammonia, and volatile organic compounds (VOC) (Schiffman et al., 2001; Zahn et al., 2001a, 2001b). While federal laws do not regulate nuisance odors, nearly all states have some form of odor regulation (Redwine and Lacey, 2000; Mahin, 2001). States may regulate odor directly by setting emission limits of odors or odorous compounds (i.e., hydrogen sulfide or methanethiol) in ambient air, or they may indirectly regulate odor through various odor control statutes (i.e., setbacks, permitting, etc.). Indirect odor statutes are by far the most common odor regulations (Redwine and Lacey, 2000; Fraser, 2001). However, 13 states have statutes that regulate emissions of odors from their point source (Redwine and Lacey, 2000; Mahin, 2001; Mahin et al., 2000; Sheffield and Thompson, 2004), and an additional seven states regulate odor-causing compounds such as hydrogen sulfide and methyl mercaptan (Mahin et al., 2000). States that have regulations on odor typically quantify odor using dynamic dilution olfactometry (DDO) following either ASTM E679–04 (ASTM, 2004) or EN 13725 (EN13725, 2003) protocol.

Dynamic dilution olfactometry determines minimum concentration levels (threshold) at which an odorous air sample can be distinguished from an odorless sample. The method is based on dilution of a whole air sample to its threshold value as determined by human panelists. The point at which 50% of the panelists can positively detect an odor is set as the dilution threshold. Samples with lowest threshold values (i.e., samples with highest dilution in odorless air) are assumed to have the highest odor content. Samples are typically reported in dilution to threshold (D/T) values. The term odor unit (OU) is defined as the dilution threshold ratio expressed for the odorous air in 1 m^3 of odorless air and can be normalized to an equivalent response to a known odorant, typically n-butanol (EN13725, 2003).

One major disadvantage of DDO is that the odor source is invariably separated from the site of analysis, and therefore, grab sampling using 10 to 30 L FEP (tertafluroethylene hexafluoropropylene copolymer), Tedlar (polyvinylfluoride, PVF), or Nalophan (polyethyeneterephthalate, PET) bags are required for transport of odor samples to the laboratory for odor analysis (EN13725, 2003). Because these laboratories are not able to perform direct comparisons between air at the point source and air present in the grab sample, they must rely on the fundamental assumption that the sampling events (transfer of odor-laden air into sampling bags) does not change the characteristics of the sampled odor. To minimize this potential change, many U.S. olfactometry laboratories recommend the use of Tedlar bags with storage times of <30 h (Air and Waste Management Association EE-6 Subcommittee, 2002). The choice of Tedlar bags with holding times of up to 30 h is in need of experimental validation.

Previous research that established the use of olfactory scaling models for measurement of swine odor reported that significant losses of odorant compounds occurred on glass, Tedlar, and other plastic surfaces during gas sampling (Zahn et al., 2001a). Losses were minimized by

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Abbreviations: CAFO, concentrated animal feeding operations; DDO, dynamic dilution olfactometry; DHC, dynamic headspace chamber; OAV, odor activity value; TDS, thermal desorption; VFA, volatile fatty acid.

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limiting total surface area in the sampling flow path, or through pre-equilibration of surface areas. However, equilibrium conditions could not be established for samples collected in 10-L Tedlar bags, which were intended for simultaneous measurements by DDO (Zahn et al., 2001a).

The purpose of this study was to validate odor sampling methods in an attempt to improve correlations between human olfactory measurements and analytical measurements of odorants. There is a need to further characterize the efficiency of grab sampling methods by improving the integrity of odorant compounds present in odor samples (McGarvey and Shorten, 2000; Pet'ka et al., 2000; Zahn et al., 2001a; van Harreveld, 2003). The specific objective of this study was to optimize Tedlar bag grab sampling methods by measuring sorption behavior for the major odorants associated with swine odor in response to (i) flush volume required for sample equilibration between the Tedlar bag surface and air contained in the bag, (ii) sample storage time, and (iii) sample storage temperature.

MATERIALS AND METHODS

Laboratory Experiment

The generation of gaseous emissions of odorants in the dynamic headspace chamber (DHC) was described previously in Zahn et al. (2001a). The chamber consisted of a glass impinger, containing a synthetic odor solution and a stir bar, connected to an air inlet (Fig. 1). Hydrocarbon-free compressed air was purchased from Scott Specialty Gases (Plumsteadville, PA) and introduced into the chamber at a height of 10 cm above the odorant solution. Olfactory and chemical controls performed on chambers containing ultra-pure water showed that the emission chamber, flow path, and air source had no detectable odor or VOCs in the absence of an odorant solution (Zahn et al., 2001a). The flow of the clean air was maintained at 1.5 L min^{-1} using a thermal mass flow controller (Series 810, Sierra Instruments, Monterey, CA).

The odor solution (50 mL) was added to the glass impinger along with a 1.5-cm stir bar, stirred, and kept at ambient temperature. Teflon tubing, 50.4 cm in length, was equilibrated for 35 min with the odorant gas generated from the DHC. After the equilibration time had elapsed, a Tedlar bag was placed into a 10-L grab sampler box (Model 1062, Supelco, Bellefonte, PA) and loaded at a flow rate of 1 L min^{-1}. A Teflon tee was placed in the line before the tubing entering the box to enable simultaneous loading of thermal desorption tubes and Tedlar bags. The thermal mass flow controller was set to 250 mL min^{-1} for the loading of the Tenax GR (Supelco, Inc.) thermal desorption tubes.

Three Tedlar bags (A, B, and C) were filled randomly with the generated odorant gas (average volume 9.06 L). After filling, bags were allowed to sit at either ambient temperature (Bags A and B) or at −20°C (Bag C) for 30 min to equilibrate. After equilibration, two thermal desorption tubes per bag were loaded directly from the bag (8 min at 0.25 L min^{-1}). After 24 h, two more thermal desorption tubes were loaded from each bag (8 min at 0.25 L min^{-1}). At this point, any remaining gas in the bag was expelled using a vacuum pump and the process was repeated two additional times using the same bags (total of three).

Tedlar bags (10 L) were purchased from SKC (Eighty Four, PA) and listed as TST20SG4-grade material. The synthetic odor solution was made using 14 compounds in nano-pure water (Barnstead, Dubuque, IA) adjusted to pH 3.31 (phosphoric acid). The solution consists of the following compounds: acetic acid (8 m*M*), propanoic acid (3.5 m*M*), 2-methylpropanoic acid (0.5 m*M*), butanoic acid (1.4 m*M*), 3-methylbutanoic acid (0.2 m*M*), pentanoic acid (0.5 m*M*), 4-methylpentanoic acid (0.2 m*M*), hexanoic acid (0.2 m*M*), heptanoic acid (0.25 m*M*),

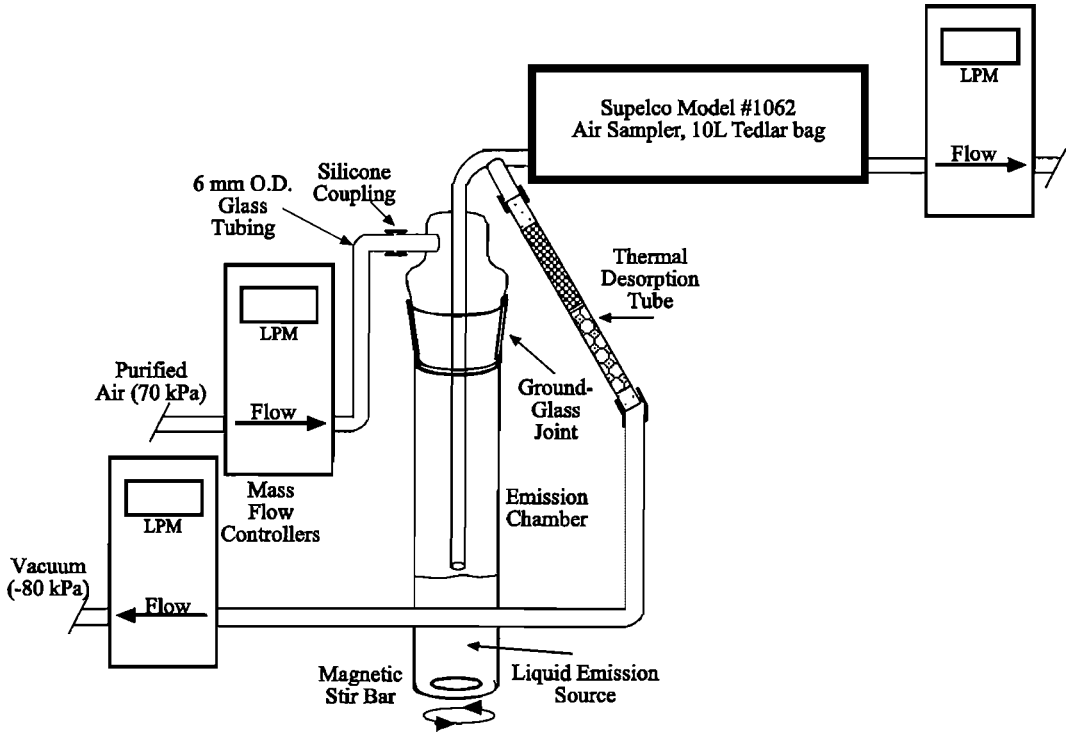

Fig. 1. Design of the dynamic headspace chamber.

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phenol (0.1 m*M*), 4-methylphenol (0.07 m*M*), 4-ethylphenol (0.043 m*M*), indole (0.023 m*M*), and 3-methylindole (0.04 m*M*). Volatile fatty acid (VFA) standards were obtained as a mix (10 m*M*) from Supelco (Bellefonte, PA), whereas aromatic standards were made in the lab, using nano-pure water and chemicals purchased from Aldrich (Sigma-Aldrich, St. Louis, MO): phenol (99.99%), 4-methylphenol (99%), 4-ethylphenol (99%), indole (99%), and 3-methylindole (98%), at a concentration of 5 m*M*.

Field Experiment

For field comparison of odor samples, air samples were collected from the swine-finishing confinement building at the Iowa State University Swine Nutrition and Management Research Farm in Ames, IA. The tunnel-ventilated facility contained 118 finisher pigs that had an average weight of 92.9 kg at the time of sampling. At the research farm, samples were either loaded directly onto thermal desorption tubes, placed on dry ice, and then transported back to the lab, or a Tedlar bag was filled with air from the finishing house and then transported back to the lab for later adsorption onto thermal desorption tubes and then GC–MS–O analysis. Controls were also taken by filling a Tedlar bag with compressed hydrocarbon-free air (Scott Specialty Gases, Plumsteadsville, PA). The compressed-air tank was checked by thermal desorption-GC–MS–O to assure purity and absence of odorant compounds. Thermal desorption tubes were then loaded with the air from the Tedlar bag in the same intervals as the laboratory study.

Sorbent Tube Analysis

Thermal desorption tubes were analyzed by GC–MS–O (gas chromatography–mass spectrometry–olfactometry) (Agilent 6890 GC with 5973N MS [Agilent Technologies, Wilmington, DE] and olfactometry sniffing port, [Gerstel, Baltimore, MD]) using a thermal desorption system (Gerstel, Baltimore, MD) equipped with a 30 m by 0.25 mm by 0.25 μm FFAP column (J&W Scientific, Wilmington, DE). The compounds were separated using the following temperature program: initial temperature 20°C (0.5-min hold) to 240°C (5-min hold) at 11°C min^{-1} in constant flow mode (1.3 mL min^{-1}). The sample was split 20:1. Analytical GC effluent was split 1:1 between sniffing port and mass spectrometer, respectively. Thermal desorption (TDS) parameters were the following: splitless mode; temperature program 25°C (0.5 min) to 250°C (3 min) at 60°C min^{-1}; and transfer line temperature, 275°C. The TDS effluent was focused onto the analytical column using a Tenax TA-packed inlet used in an PTV (programmed temperature vaporizer) inlet with the following parameters: split mode; temperature program −50°C (0.2 min) to 280°C (3 min) at 12°C s^{-1}, vent flow 26 mL min^{-1}.

The transfer line of the GC–O sniffing port was held at 250°C, and humidified air was added in the sniffing port at 100 mL min^{-1}. Eluting odor-active compounds were recorded on an olfactory intensity device (ODP2, Gerstel). Mass spectra (m/z 40–350) were collected at 4.58 scans per second with a MS transfer line and source temperatures set at 240 and 150°C, respectively. Compounds were identified using mass spectra and retention times of reference standards and/or mass spectra of NIST98 library (NIST, Gaithersburg, MD) matches of > 70%.

Compounds were quantified using external standards spiked on to blank TDS tubes. The calibration curve for VFA used loading rates of 1.25 to 10 n*M* per tube and loading rates of 0.5 to 5 n*M* per tube for phenolic and indolic compounds. Compounds not part of the original standard set were quantified using estimates based on molecular weight and chemical class.

Statistical Analysis

Comparisons of variance and mean separation (LSD) techniques were used to test for significant differences ($p < 0.05$) of the concentration individual compounds. There were three observations per treatment. All statistical analyses were performed using JMP version 5.1 (SAS Institute, 2003) statistical software.

RESULTS

Background Contaminants in Tedlar Sample Bags

Analysis of Tedlar bags 30 min after filling with hydrocarbon-free air showed elevated levels of phenol (200.1 ng L^{-1}), acetic acid (43.6 ng L^{-1}), and *N*, *N*-dimethylacetamide (DMAC, 226.2 ng L^{-1}) (Fig. 2). However, the air stream tested directly from the compressed air cylinder showed no contaminants (data not shown). Olfactory analysis by GC–MS–O revealed six odorous compounds including acetic acid and phenol (Table 1). Direct olfactory analysis of the bulk air sample contained in the Tedlar bag was described as having a weak petroleum solvent or phenolic odor. The compounds acetic acid, 2-furancarboxaldehyde, and phenol could all be described as having these characteristics. The compound, DMAC, though significant in terms of off-gassing concentration, has a high odor threshold value (Devos et al., 1990). Consequently, it was not expected to contribute to the background odor of Tedlar bags as evidenced by our olfactometry analysis (Table 1). The DMAC peak is seen as a very large artifact peak for samples removed from Tedlar bags (Fig. 2) and makes the quantification of acetic acid difficult due to the potential co-elution of these analytes.

Analysis of Tedlar bags 24 h after filling with hydrocarbon-free air showed even higher levels of phenol (312.8 ng L^{-1}), acetic acid (305.6 ng L^{-1}), and DMAC (791.5 ng L^{-1}), along with some early eluting hydrocarbon compounds (Fig. 2). Olfactory analysis of the bags detected an additional odorous compound, 2-methylpentane (estimated at 153 ng L^{-1}). This compound was described as having a hydrocarbon odor. The whole air sample for the Tedlar bag was described as having a mild petroleum solvent odor after 24 h of storage. It should be noted that the majority (15 out of 23) of the compounds identified as off-gassed are petroleum hydrocarbons (Table 1).

Analysis of Tedlar bags 72 h after filling with hydrocarbon-free air showed little to no increase in phenol (290.7 ng L^{-1}), acetic acid (368.2 ng L^{-1}), and DMAC (748.6 ng L^{-1}), with more volatile compounds actually having lower concentrations (Table 1). The reduction in lighter-weight compounds is evidence of the permeable nature of Tedlar bags (Polasek and Bullin, 1978). Olfactory analysis of the 72-h bag detected only one additional odorous compound, benzoic acid. Its odor was described as pleasant and is likely an artifact of the Tenax-trapping material (Dettmer and Engerwald, 2002).

Dynamic Headspace Chamber

A second set of experiments was designed to determine if there is a bias in removing odorous compounds

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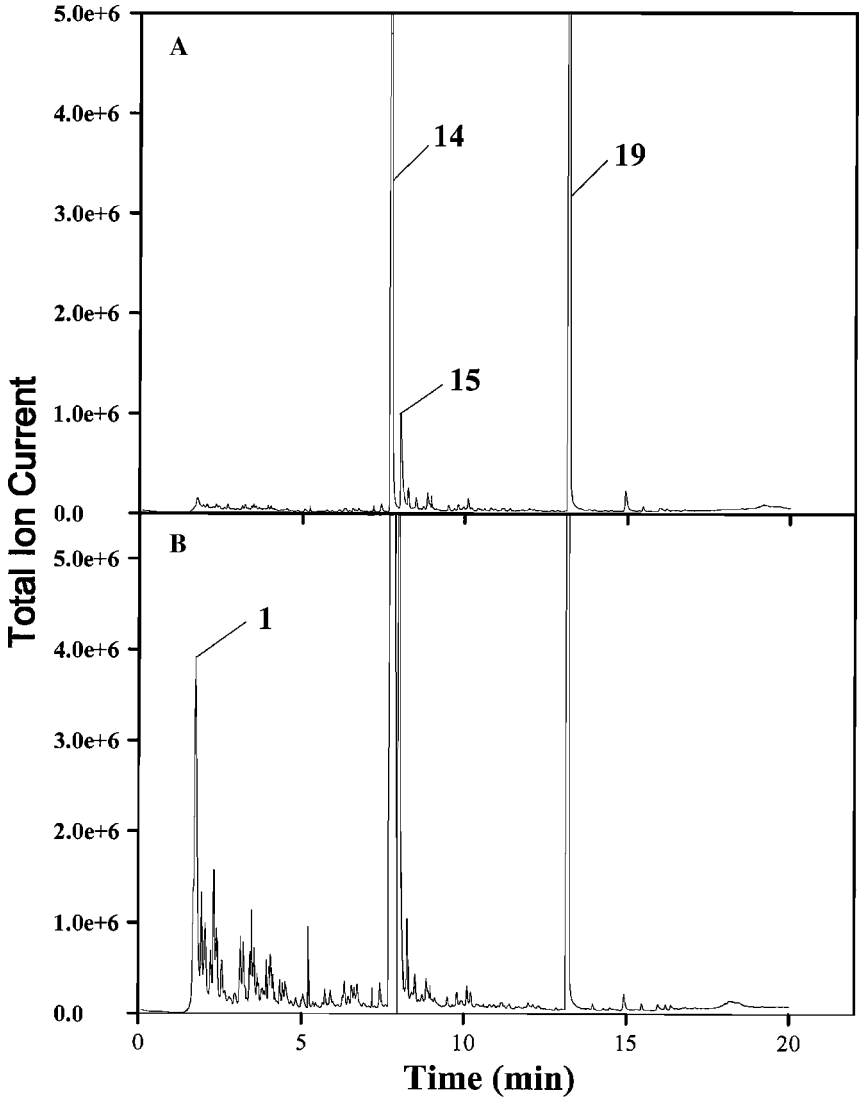

Fig. 2. Chromatograms of gas samples collected from a Tedlar bag filled with hydrocarbon-free air following storage times of (A) 0.5 and (B) 24 h. Compounds identified are as follows: 1) 4-methylpentane; 14) DMAC; 15) acetic acid; and 19) phenol.

from Tedlar bags. The experiment used a dynamic headspace chamber to generate a constant emission from a synthetic swine-odor solution. The compounds in the solution have been reported in Zahn et al. (2001a) as the dominant odors associated with swine manure. Composition of this solution is similar to what others have reported concerning synthetic swine odor solutions (Schaefer et al., 1974; Yasuhara, 1980; Qu and Feddes, 2004; Willig et al., 2004). The chamber was designed to simultaneously sample the emission gas stream with both TDS tubes and Tedlar bags (Fig. 1).

Acetic acid and phenol concentration levels greatly increased with bag residence time. For acetic acid, concentrations increased by 47 and 86%, following an equilibration period of 30 min and 24 h, respectively (Table 2). Phenol emissions increased 20-fold after 30 min and an additional 37% following 24 h of equilibration in Tedlar bags (Table 2). Each successive bag-fill showed a decline in both acetic acid and phenol emission levels (Fig. 3). Acetic acid emission declined by 31% following three successive bag-fills, while phenol emission declined by 18% (Fig. 3). Despite declining emissions for both acetic acid and phenol following three successive bag-fills, levels of these compounds were still elevated compared with initial loading of these bags. These results are consistent with our previous findings showing elevated levels of acetic acid and phenol off-gassed in Tedlar bags.

Analysis of the TDS tubes taken directly from the DHC compared with TDS tubes loaded from Tedlar bags shows that residence time in Tedlar bags had a major impact on the recovery of the other odorous compounds (Table 2). After 24 h, indole and 3-methylindole could not be recovered from the Tedlar bags. Phenolic compound (4-methylphenol and 4-ethylphenol) recovery was approximately 30% for samples held 30 min, but <10% after 24 h of storage. Short-chain fatty acids (propanoic and butanoic acids) and branched-chain fatty acids (2-methylpropanoic acid, 3-methylbutanoic acid, and 4-methylpentanoic acid) both followed similar trends

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Table 1. Volatile organic compounds emitted from a Tedlar bag, filled with hydrocarbon-free air, after equilibrating for 0.5, 25, and 72 h.

Compound	Peak no. and retention time	Concentration† 0.5 h	24 h	72 h	ODP‡
	min	(ng L^{-1})			
4-methylpentane	(1) 1.75	<LOD	153.0	40.5	+
4-methylheptane	(2) 1.94	<LOD	21.2	10.6	−
2,4-dimethylheptane	(3) 2.05	<LOD	16.8	7.2	−
4-methyloctane	(4) 2.22	<LOD	7.1	3.3	−
2,4-dimethylheptene	(5) 2.32	<LOD	6.8	4.2	−
2-propanol	(6) 2.57	<LOD	17.8	23.4	−
benzene	(7) 2.65	<LOD	5.6	2.7	−
toluene	(8) 3.49	<LOD	7.2	9.4	−
p-xylene	(9) 4.52	<LOD	6.2	5.8	−
undecane	(10) 5.44	<LOD	2.8	2.8	−
nonadecane	(11) 5.65	<LOD	2.6	6.0	+
alpha-methylstyrene	(12) 6.72	<LOD	1.5	1.5	−
tetradecane	(13) 7.42	<LOD	1.0	1.3	−
N,N-dimethylacetamide	(14) 7.72	226.2	791.5	748.6	−
acetic acid	(15) 7.97	86.6	611.2	736.4	+
2-furancarboxaldehyde	(16) 8.26	2.6	9.1	9.8	−
benzaldehyde	(17) 8.85	1.6	2.8	3.8	+
acetophenone	(18) 10.10	0.8	1.1	1.4	+
phenol	(19) 13.17	200.1	312.8	290.7	+
cyclotetradecane	(20) 15.98	<LOD	3.0	4.6	−
benzoic acid	(21) 16.37	<LOD	2.8	3.5	+

† <LOD, below detection limits.
‡ ODP, olfactometry detection port, +, odor detected, −, no odor.

with excellent recovery after 30 min (90–100%), but poorer recovery (approximately 70%) with increasing residence time in the bags (Table 2). Longer-chain fatty acids (i.e., pentanoic, hexanoic, and heptanoic acids) had poorer recovery than either the short-chain or branched-chain fatty acids with recoveries of less than 80 and 35% following bag residence time of 30 min and 24 h, respectively (Table 2).

Temperature of storage also had a significant effect ($p < 0.05$) on integrity of the air samples held in Tedlar bags. Storage of Tedlar bags at reduced temperatures (−20°C) had the tendency to reduce off-gassing of acetic acid and phenol while also reducing the sorption of phenolic compounds (Table 3). Storage of Tedlar bags at −20°C reduced off-gassing of acetic acid and phenol by 45 and 32%, respectively, and reduced the sorption of 4-methylphenol and 4-ethylphenol by 3.5- and 1.0-fold, respectively. Sorption of short-chain VFA was similar at both ambient and −20°C, but branched and long-chain VFA sorption decreased by 18 and 51%, respectively. It should be noted that even at reduced temperatures, indole and 3-methylindole were still nonrecoverable from Tedlar bags.

Field Samples

Field samples collected from a swine-finishing barn gave similar trends in terms of sorption and off-gassing of malodor compounds. However, the levels of sorption or off-gassing were different compared with blank samples and samples taken from DHC (Table 4). The field samples did not have as many hydrocarbon compounds detected as our laboratory blank sample, and the levels of DMAC in field samples were one-third the levels measured in the blank air samples. This discrepancy is most likely a result of our source of air, with the blank samples having a dry hydrocarbon-free air source (H_2O = 5 mg L^{-1}) and our field samples having an estimated relative humidity of > 75 to 90% (Schiffman et al., 2001; Zahn et al., 1997, 2001b). There was no evidence of off-gassing of acetic acid in field samples because acetic acid levels of field samples were fourfold higher than background levels measured in either blank or DHC samples (Table 4). Sorption of VFA and 4-methylphenol in field samples was greatly reduced with average recoveries of 81 and 77%, respectively, (Table 4) compared with DHC recoveries of 65 and 6%, respectively. Sorption of the compounds 4-ethylphenol, indole, and 3-methylindole were still strong and similar to laboratory samples because these compounds could not be detected in our field samples collected in Tedlar bags (Table 4). The compounds hexanal and trimethylamine were both detected in the field samples that were collected directly in thermal desorption tubes, but not in field samples stored in Tedlar bags (Table 4). In both this study and Wright et al. (2005), trimethylamine was identified as odorous (Table 4), and potentially a key odorant associated with CAFOs.

Table 2. Concentrations for 14 malodor compounds removed from Tedlar bags, filled and incubated at ambient lab temperature.

Compound	Inlet sample Concentration	SD	Tedlar bags 0.5 h Concentration	SD	24 h Concentration	SD
	ng L^{-1}†		ng L^{-1}		ng L^{-1}	
N,N-dimethylacetamide	<LOD	–	813.8	226.2	2073.4	289.3
acetic acid	130.4	12.3	191.8	27.7	356.0	29.8
propanoic acid	59.3	12.0	62.2	11.8	42.7	6.3
2-methylpropanoic acid	20.4	3.7	20.0	3.6	17.3	2.9
butanoic acid	32.1	6.8	31.6	5.8	22.0	3.1
3-methylbutanoic acid	8.3	2.2	6.6	2.1	5.2	1.7
pentanoic acid	15.7	3.4	14.7	2.5	7.9	1.2
4-methylpentanoic acid	12.8	2.4	11.6	1.8	7.6	1.1
hexanoic acid	10.0	1.9	8.6	1.2	4.8	0.6
heptanoic acid	7.0	3.6	3.9	1.8	<LOD	–
phenol	4.1	0.5	83.9	12.8	114.5	10.3
4-methylphenol	11.2	1.9	3.1	0.6	0.6	0.2
4-ethylphenol	2.3	0.4	0.7	0.1	0.3	0.1
indole	0.9	0.1	<LOD	–	<LOD	–
3-methylindole	4.4	1.6	<LOD	–	<LOD	–

† <LOD, below limit of detection.

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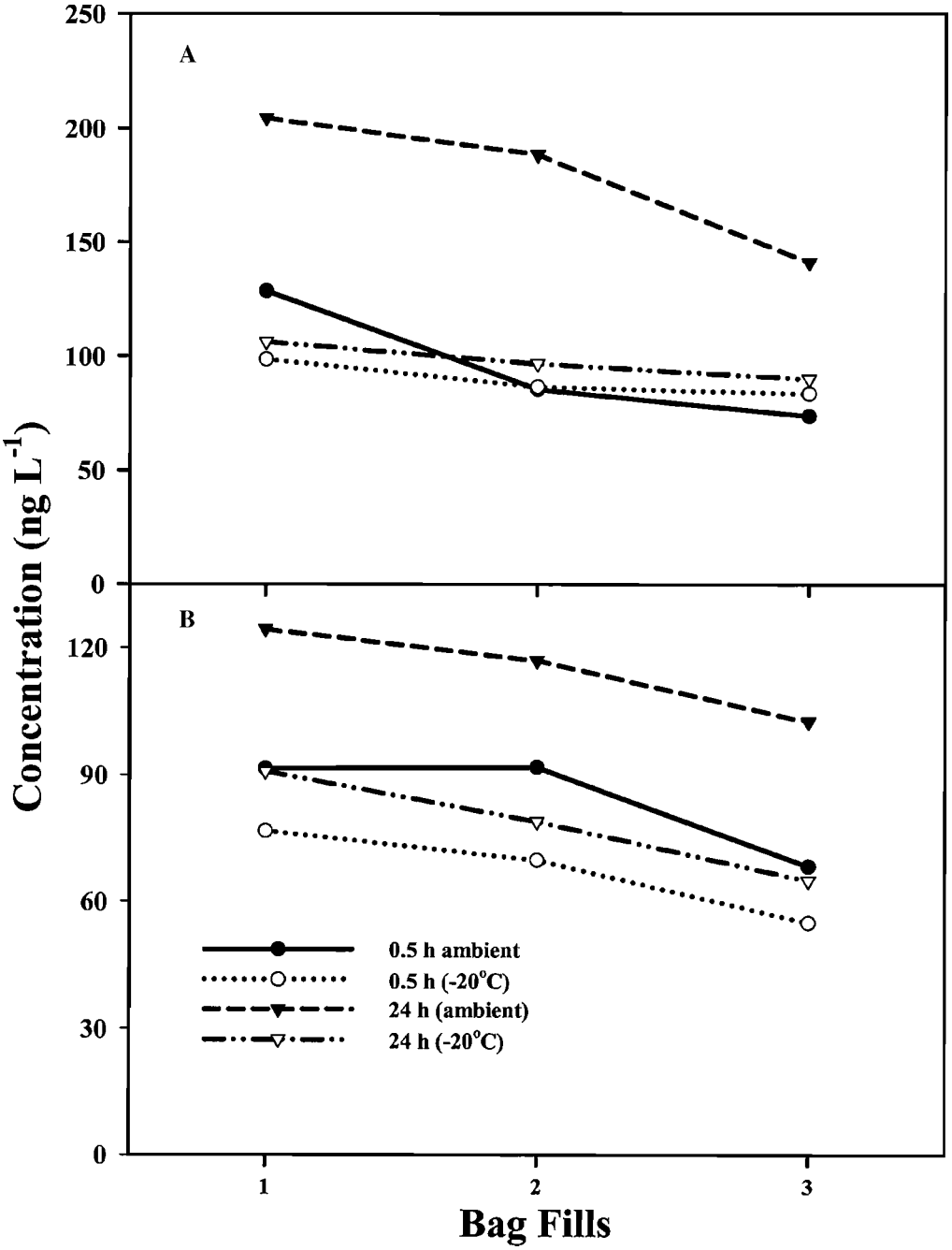

Fig. 3. Declines in the levels of (A) acetic acid and (B) phenol in Tedlar bags following successive bag-fills at ambient and −20°C storage temperatures.

Odor Activity Value

Both off-gassing and sorption of compounds on Tedlar bags have the potential to significantly affect sensory data. Calculating changes in the odor activity values (OAV) for individual compounds is one way of determining overall affect Tedlar bags have on odor measurements. The OAV is used to quantify the potential contribution of individual compounds to the overall aroma (Guadagni et al., 1966; Acree et al., 1984). The OAV is calculated by dividing the concentration of a compound in the sample (ambient air) by the odor threshold value for that compound from the literature. Compounds with an OAV below one are not considered part of the odor.

Calculated OAV clearly demonstrate that there was a reduction in the total amount of odorous compounds detected from Tedlar bags compared with samples collected directly from the DHC. Samples held in Tedlar bags for 30 min or more had reductions in the OAV of 75 to 80% (Table 5). The compounds indole, 3-methylindole, and 4-methylphenol accounted for most of this reduction in OAV. These compounds initially contributed 78% of the total OAV, but after 30 min in a Tedlar bag, indole and 3-methylindole made no contribution to the total OAV. Based on OAV, the dominant odors asso-

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Table 3. Concentrations for 14 VOCs† removed from a Tedlar bag filled with the VOCs and then incubated at −20°C to simulate winter shipment conditions.

	Inlet sample		Tedlar bags			
			0.5 h		24 h	
Compound	Concentration	SD	Concentration	SD	Concentration	SD
	ng L^{-1}		ng L^{-1}		ng L^{-1}	
N,N-dimethylacetamide	<LOD‡	–	718.9	143.3	892.4	133.8
acetic acid	130.4	12.3	179.2	8.0	195.4	8.1
propanoic acid	59.3	12.0	58.8	6.0	38.0	8.8
2-methylpropanoic acid	20.4	3.7	19.9	2.2	16.9	2.3
butanoic acid	32.1	6.8	30.8	3.9	24.7	3.6
3-methylbutanoic acid	8.3	2.2	7.2	1.2	6.4	1.1
pentanoic acid	15.7	3.4	14.2	2.3	11.8	1.9
4-methylpentanoic acid	12.8	2.4	11.3	1.5	10.1	1.6
hexanoic acid	10.0	1.9	8.5	1.4	7.3	1.3
heptanoic acid	7.0	3.6	3.2	2.1	1.2	1.7
phenol	4.1	0.5	67.1	11.1	78.2	13.0
4-methylphenol	11.2	1.9	4.4	0.8	2.7	0.7
4-ethylphenol	2.3	0.4	0.9	0.2	0.6	0.1
indole	0.9	0.1	<LOD	–	<LOD	–
3-methylindole	4.4	1.6	<LOD	–	<LOD	–

† VOC, volatile organic compound.
‡ <LOD, below limit of detection.

ciated with the DHC were indole, butanoic acid, 3-methylindole, and 4-methylphenol.

Field-sampled OAV declined by 45% following storage in Tedlar bags (Table 6). The lower decline in the field samples compared with DHC samples was partially attributed to the higher level of VFAs in field samples and the higher recovery of VFA and 4-methylphenol from field samples compared to DHC samples. It should be noted that indole and 3-methylindole contributed 67% of the OAV in DHC samples, but <5% in field samples. Based on OAV, the dominant odors associated with field samples were butanoic acid, trimethylamine, 4-methylphenol, and 3-methylbutanoic acid. These same odorants have been found to be priority odorants near the source of large CAFOs (Wright et al., 2005). Minor odorants in field samples included acetic acid, propanoic acid, indole, and pentanoic acid.

DISCUSSION

Background Odor

Our results are consistent with others who have demonstrated significant off-gassing of VOCs from Tedlar bags with storage (Polasek and Bullin, 1978; Pet'ka et al., 2000; Keener et al., 2002; Parker et al., 2003). Increased levels of the specific compounds acetic acid, phenol, and DMAC have been reported previously (Keener et al., 2002; Parker et al., 2003; Koziel et al., 2005). The elevated levels of DMAC and phenol in Tedlar bags can be attributed to the manufacturing pro-

Table 4. Concentrations of 22 VOCs† found in a direct-inlet sample and a Tedlar bag sample taken from a swine-production facility.

		Inlet Sample		Tedlar Bag sample	
Compound‡	Peak no. and retention time	Concentration	ODP¶	Concentration	ODP
		ng L^{-1}§		ng L^{-1}#	
hexane	(1) 1.71	40.5	+	84.4	+
trimethylamine	(2) 2.43	40.4	+	<LOD	−
Hexanal	(3) 3.54	3.2	−	<LOD	−
n-butanol	(4) 4.30	16.2	−	10.0	−
n-pentanol	(5) 5.40	3.6	−	<LOD	−
3-hydroxy-2-butanone	(6) 5.94	25.0	+	21.3	+
tetradecane	(7) 6.95	ND	−	0.3	−
DMAC	(8) 7.48	ND	−	283.9	−
acetic acid	(9) 7.74	802.3	+	594.3	+
benzaldehyde	(10) 8.77	1.1	−	0.6	−
propanoic acid	(11) 8.83	282.1	+	220.8	+
2-methylpropanoic acid	(12) 9.22	36.7	+	30.6	+
butanoic acid	(13) 9.90	205.6	+	173.8	+
3-methylbutanoic acid	(14) 10.42	51.3	+	42.9	+
pentanoic acid	(15) 11.18	52.4	+	39.3	+
hexanoic acid	(16) 12.34	4.8	+	4.07	+
phenol	(17) 14.03	8.7	+	132.1	+
4-methylphenol	(18) 14.76	55.6	+	12.78	+
4-ethylphenol	(19) 15.63	1.0	+	<LOD	−
indole	(20) 18.04	0.3	−	<LOD	−
3-methylindole	(21) 18.42	0.2	+	<LOD	−

† VOC, volatile organic compound.
‡ DMAC, *N,N*-dimethylacetamide.
§ ND, not detected.
¶ ODP, olfactometry detection port, +, odor detected, −, no odor.
# <LOD, below detection limits.

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Table 5. Comparison of OAV† for 13 malodor compounds from a dynamic headspace chamber identified and collected either directly from the in-let or stored in a Tedlar bag.

Compound	Olfactory threshold	Inlet air		Tedlar bag 0.5 h		Tedlar bag 24 h	
	nL L^{-1}‡	nL L^{-1}	OAV	nL L^{-1}	OAV	nL L^{-1}	OAV
acetic acid	144.0	52.70	0.37	77.51	0.54	143.87	1.00
propanoic acid	35.5	19.41	0.55	20.36	0.57	13.98	0.39
2-methylpropanoic acid	19.5	5.61	0.29	5.51	0.28	4.77	0.24
butanoic acid	3.89	8.84	2.27	8.69	2.23	6.06	1.56
3-methylbutanoic acid	2.45	1.98	0.81	1.56	0.64	1.23	0.50
pentanoic Acid	4.79	3.73	0.78	3.49	0.73	1.88	0.39
4-methylpentanoic acid	n/a	2.68	–	4.71	–	3.07	–
hexanoic acid	12.6	2.09	0.17	3.50	0.28	1.93	0.15
heptanoic acid	27.5	1.30	0.05	0.82	0.03	0.00	0.00
phenol	109.6	1.06	0.01	33.90	0.31	46.27	0.42
4-methylphenol	1.86	2.51	1.35	1.26	0.68	0.24	0.13
4-ethylphenol	n/a	0.46	–	0.29	–	0.13	0.10
indole	0.032	0.18	5.55	0.01	0.27	0.00	0.00
3-methylindole	0.56	0.81	1.45	0.00	0.00	0.00	0.00
Total OAV	–	–	10.61	–	2.23	–	2.56

† OAV, odor activity value.
‡ n/a, not available.

cess of the Tedlar bags (Chase, 2001; R. Dyl, personal communication, 2002), whereas elevated levels of acetic acid found in Tedlar bags are likely a result of the hydrolysis of DMAC into its original carboxylic acid (acetic acid) and primary amine (dimethylamine). There was no detection of dimethylamine in the Tedlar bags, but this is not surprising given the volatility of this compound.

Parker et al. (2003) measured background odors from Tedlar bags at 20 to 60 D/T after 24 h of holding and van Harreveld et al. (1999) reported the background odor from Tedlar bags at 80 OU_E or more (based on *n*-butanol standard). These levels of background odor are unacceptable given that most states that regulate odor have set DDO levels between 2 and 50 D/T (Redwine and Lacey, 2000; Mahin, 2001). Heating of bags to 100°C for 24 h followed by purging with N_2 gas has been shown to reduce background odor levels to between 6 and 12 D/T (Parker et al., 2003), and in this study we also show that repeated filling of Tedlar bags reduces off-gassing of phenol and acetic acid. The 6 to 12 D/T level is acceptable for use in odor analysis of CAFO (Parker et al., 2003) because odor units as high as 25 to 424 D/T have been recorded for swine facilities (Chen et al., 1999).

Table 6. Comparison of OAV† for 13 malodor compounds identified in air samples from a swine-production facility and collected either directly from the in-let or stored for 24 h in a Tedlar bag.

Compounds	Olfactory threshold	In-let air		Tedlar bag	
	nL L^{-1}‡	nL L^{-1}	OAV	nL L^{-1}	OAV
trimethylamine	2.40	16.58	6.91	0.00	0.00
acetic acid	144.0	324.22	2.25	240.17	1.67
propanoic acid	35.5	92.30	2.60	72.24	2.04
2-methylpropanoic acid	19.5	10.12	0.52	8.42	0.43
butanoic acid	3.89	56.57	14.54	47.84	12.30
3-methylbutanoic acid	2.45	12.18	4.97	10.18	4.16
pentanoic acid	4.79	12.46	2.60	9.34	1.95
hexanoic acid	12.6	1.00	0.08	0.85	0.07
phenol	109.6	2.25	0.02	34.02	0.31
4-methylphenol	1.86	12.46	6.70	2.87	1.54
4-ethylphenol	n/a	0.19	–	0.00	–
indole	0.032	0.07	2.09	0.00	0.00
3-methylindole	0.56	0.04	0.07	0.00	0.00
Total OAV	–	–	42.66	–	23.65

† OAV, odor activity value.
‡ n/a, not available.

Recovery of Malodor Compounds

Our results are consistent with others who have shown that recovery of certain VFAs, phenolic compounds, and indolic compounds from Tedlar bags are lower with increased residence time in the bag (Keener et al., 2002; Koziel et al., 2005). In fact, Posner and Woodfin (1986) recommend storage of air in Tedlar bags to be <4 h. The results of this study show that hold times as short as 0.5 h result in significant changes in odorant concentration for samples stored in Tedlar bags. While low storage temperatures (−20°C) clearly reduced the losses for certain odorants, severe and complete losses of other key livestock odorants, such as indole and 3-methyl indole, indicate that this method is unacceptable as a sample preservation strategy. Future studies should evaluate the recovery of odorants from alternative sampling containers.

The data sets for field and laboratory samples showed a trend toward improved recovery of odorants that were sampled from Tedlar bags that originated from the field. One of the most significant differences between these samples was the amount of water vapor that was present in the sampling streams. The relative humidity of the DHC stream was estimated at 62% (Zahn et al., 2001a), whereas the relative humidity of the swine confinement during sampling ranged between 74 and 82%. Increasing levels of relative humidity inside the Tedlar bag is expected to lower the recovery of polar compounds due to increased sorption (i.e., partitioning) into condensed water (Andino and Butler, 1991; Groves and Zellers, 1996; Cariou and Guillot, 2006). Permeation of water into and out of Tedlar bags during storage has been shown to occur (Groves and Zellers, 1996; Nielsen and Jonsson, 2002; Cariou and Guillot, 2006) with an estimated 8 h needed before contents in the bag reflect ambient relative humidity levels (Nielsen and Jonsson, 2002). Recovery of polar compounds such as methanol

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from Tedlar bags has been shown to be reduced with the increasing water content in the Tedlar bag (Andino and Butler, 1991; Groves and Zellers, 1996). In general, recoveries of polar compounds are lower than expected when using dry N as the matrix gas in Tedlar bags (Posner and Woodfin, 1986; McGarvey and Shorten, 2000; Keener et al., 2002; Parker et al., 2003; Koziel et al., 2005). In fact, Koziel et al. (2005) noted that using dry N as source air reported average recoveries of only 25% for various VFAs, phenols, and indole compounds after being stored for 24 h in commercial Tedlar bags; however, in this study, recovery of those same compounds averaged 50% in the DHC (relative humidity levels measure 62%, Zahn et al., 2001a) and 74 to 82% for samples taken from the field (typical levels are between 75 and 90%, Schiffman et al., 2001; Zahn et al., 1997, 2001b). The effect that relative humidity had on sorption of polar compounds in our study may also explain why lower temperatures (−20°C) during storage resulted in improved recovery of certain odorous compounds (i.e., low water content in the freezer air). Consequently, it appears that laboratory samples generated with dry N_2 gas may overestimate the extent sorption occurs in Tedlar bags. Further studies will need to be conducted to increase understanding of the role water (relative humidity) has on sorption of polar compounds in Tedlar bags and what, if any, impact it has on the storage of compounds in Tedlar bags.

Several of the compounds with the lowest odor-threshold values in our study were strongly sorbed to Tedlar surfaces; this included both laboratory-generated and field-collected samples. In fact, indole and 3-methylindole were never recovered from Tedlar bags. In addition, trimethylamine was not recovered from field-collected samples. These compounds have been identified as compounds having a significant impact on odor at both swine and cattle facilities, along with 4-methylphenol (Wright et al., 2005). Sorption of malodor compounds to Tedlar bags may explain why quantification of odor measured in the field is substantially higher than quantified in the laboratory (Schiffman et al., 2001), or may explain why correlating odor with malodor compounds has been unsuccessful (Obrock-Hegel, 1997; Schiffman et al., 2001; Gralapp et al., 2001). Further research into the extent these and other compounds sorb to Tedlar surfaces is essential before the appropriateness of this material for DDO analysis can be evaluated for use at animal facilities. This study clearly demonstrates that knowledge of the compounds associated with an odor is crucial before choosing a proper storage container for use in DDO. We recommend caution when interpreting results from Tedlar bags knowing that odors from the field are not well-preserved by the time they arrive in the laboratory for DDO analysis.

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