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Most air quality studies in agricultural environments use thermal desorption analysis for quantifying semivolatile organic compounds (SVOCs) associated with odor. The objective of this study was to develop a robust sampling technique for measuring SVOCs in humid environments. Test atmospheres were generated at ambient temperatures (23 ± 1.5 °C) and 25, 50, and 80% relative humidity (RH). Sorbent material used included Tenax, graphitized carbon, and carbon molecular sieve (CMS). Sorbent tubes were challenged with 2, 4, 8, 12, and 24 L of air at various RHs. Sorbent tubes with CMS material performed poorly at both 50 and 80% RH due to excessive sorption of water. Heating of CMS tubes during sampling or dry-purging of CMS tubes post sampling effectively reduced water sorption with heating of tubes being preferred due to the higher recovery and reproducibility. Tenax tubes had breakthrough of the more volatile compounds and tended to form artifacts with increasing volumes of air sampled. Graphitized carbon sorbent tubes containing Carbopack X and Carbopack C performed best with quantitative recovery of all compounds at all RHs and sampling volumes tested. The graphitized carbon tubes were taken to the field for further testing. Field samples taken from inside swine feeding operations showed that butanoic acid, 4-methylphenol, 4-ethylphenol, indole, and 3-methylindole were the compounds detected most often above their odor threshold values. Field samples taken from a poultry facility demonstrated that butanoic acid, 3-methylbutanoic acid, and 4-methylphenol were the compounds above their odor threshold values detected most often. relative humidity, CAFO, VOC, SVOC, thermal desorption, swine, poultry, air quality, odor

Introduction

The report by the National Research Council (NRC) highlighted the need for more research in the area of air emissions from animal agriculture (*1*). In fact, this report was a major basis for the EPA's animal feeding operations (AFO) consent agreement (*2*). The NRC report highlighted the need for standardized protocols for sampling and analysis of both volatile organic compounds (VOC, includes both volatile and semivolatile compounds) and odor (*1*). Field methods the NRC report referenced were generally validated with stable, nonpolar hydrophobic compounds associated with industrial pollutants, whereas VOCs measured in agricultural environments are often polar, reactive, and highly sorptive to surfaces (*3–8*). The report acknowledges there is little agreement as to what constitutes odor and points to several different techniques that need to be developed (*1*). The EPA's consent agreement acknowledged the ambiguity associated with odor quantification and proposed no regulation be developed (*2*). However, odors draw significant attention at the local levels of government and community involvement, and the NRC report identified odors as the most significant animal emission at the local level (*1*). Odor intensity has been correlated to VOC emissions (*3, 5*), and it has been linked to a lowering of the quality of life (*9, 10*) and declining property values (*11*). Schiffman and Williams (*12*) speculate that odors may have potential environmental and health effects associated with them; however, data linking odors to any type of respiratory impairment is weak (*13*). Self-reporting of symptoms (i.e., headaches, runny nose, etc.) is currently the only evidence of health-related effects associated with odor in both laboratory (*13*) and rural community surveys (*9, 10*). Developing methods to measure the composition of odor will enable scientists to determine potential health risks associated with animal agriculture.

Field methods used to measure and characterize VOC and SVOC in air include both whole air sampling approach (canisters) and a preconcentration approach (sorbent tubes or solid phase microextraction (SPME)). The use of canisters in quantifying odorants has been shown to be of limited value due to low recoveries of polar compounds (*14*). The use of SPME fibers is limited due to complexity of calibrating fibers to match environmental conditions, reverse diffusion of compounds, and competitive sorption (*15–17*). While sorbent tubes are effective at sampling polar SVOC (*3, 6*), typical sorbents used in agricultural air quality studies are hindered by water sorption in humid environments (*18–21*) and artifact formation during sampling (*22, 23*).

The purpose of this study was to identify commercial adsorbents (i.e., commercially available and custom-made) and water management techniques for sampling in humid environments. The sorbent materials tested included Tenax, graphitized carbon, and carbon molecular sieve (CMS). Sorbent tubes tested contained Tenax TA and a multibed sorbent tube containing Tenax TA and Carboxen 569 (CMS material) both of which have been commonly used in agricultural air quality studies (*3, 4, 6, 8*) along with a commercially available multibed sorbent tube, Carbotrap 300 (Supelco, Inc., Bellafonte, PA), containing CMS material. In addition, a custom multibed sorbent tube containing hydrophobic sorbents Carbopack X (medium strength sorbent) and Carbopack C (weak sorbent) was tested. Carbopack X was used since it has been shown to capture compounds as small as $C_3 - C_5$, and is routinely used as a passive sampling material for VOCs (*24, 25*). Specific objectives of this study were to (i) evaluate commercial sorbent material for sampling and analysis of SVOC; (ii) determine the effect humidity has on sampling and analysis; (iii) assess the effectiveness of water management techniques for minimizing humidity effects; and (iv) test the method at various AFOs.

Experimental Section

Laboratory and Field Sampling. All samples were collected on glass sorbent tubes (178 × 6 mm diameter) packed with the following: (1) Tenax TA (Supelco, Inc.); (2) Carbotrap 300

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TABLE 1. Properties of Target Compounds and Summary of Analytical Method

compound	MW[d]	boiling point (C)	vapor Pressure (kPa)[e]	odor threshold µg m[-3g]	QI (m/z)[i,h]	LOQ ng[j]	RF (area/ng)[k]	RSE (%)[l]	dynamic range ng	precision (%)[m]
acetic acid	60	118	2.33	356.3	60	0.7	$2.36 \times 10^{+04}$	4.1	30–3002	10.8
propanoic acid	74	140	1.75	108.3	57	0.8	$1.92 \times 10^{+04}$	5.0	37–3704	12.2
2-MPro acid[a]	88	155	1.68	70.8	74	16.6	$1.94 \times 10^{+04}$	6.7	44–4400	9.4
butanoic acid	88	164	0.15	14.1	60	0.2	$3.67 \times 10^{+04}$	7.6	44–4400	7.0
3-MBut acid[b]	102	177	0.07	10.3	60	2.1	$2.70 \times 10^{+04}$	10.3	51–5100	6.7
pentatonic acid	102	186	0.04	20.2	60	1.1	$2.74 \times 10^{+04}$	8.4	51–5100	5.2
4-MPen acid[c]	116	199	0.0008	22.9	57	5.9	$1.60 \times 10^{+04}$	7.5	58–5800	6.1
hexanonic acid	116	205	0.006	60.3	60	0.9	$6.73 \times 10^{+03}$	7.5	58–5800	8.6
heptaonic acid	130	222	0.0004	147.4	60	2.7	$1.80 \times 10^{+04}$	7.2	65–6500	8.9
phenol	94	182	0.065	424.9	94	0.02	$1.12 \times 10^{+05}$	8.1	0.44–144	3.5
4-methylphenol	108	202	0.017	8.3	107	0.42	$6.79 \times 10^{+05}$	5.4	1.1–1143	3.7
4-ethylphenol	122	218	0.029	6.3	122	0.09	$2.15 \times 10^{+05}$	11.9	1.44–144	5.8
4-propylphenol	136	232	0.012		122	0.05	$2.47 \times 10^{+05}$	14.2	0.983–100	6.7
indole	117	254	0.002	0.15	117	0.44	$1.19 \times 10^{+05}$	7.1	0.44–436	6.9
3-methylindole	130	266	0.002[f]	3.0	130	0.08	$1.32 \times 10^{+05}$	5.5	0.43–446	6.9

[a] 2-Mpro acid, 2-methylpropanoic acid. [b] 3-MBut acid, 3-methylbutanoic acid. [c] 4-MPen acid, 4-methylbutanoic acid. [d] MW, molecular weight. [e] Vapor Pressure values determined at 27 °C. [f] vapor pressure value based at 20 °C. [g] Odor Threshold values based on reference 40. [h] QI quantitation ion. [i] m/z mass to charge. [j] LOQ, limit of quantitation. [k] RF, response factor. [l] RSE, relative standard error (residue analysis of linearity). [m] Precision measured as relative standard deviation.

(Carbotrap C:Carbotrap B:Carbosieve S-III); (2) Tenax TA: Carboxen 569 (1:1 packing ratio); and (3) CP-X (Carbopack C:Carbopack X in 1:2 packing ratio). All air samples were collected at 100 mL min^{-1} using field gas samplers (GS1, Gerstel Inc., Baltimore, MD). All materials in contact with sampled air stream were constructed of Teflon or polycarbonate material. All sorbent tubes were stored at <−20 °C until analyzed, and all samples were analyzed within 30 days. Target compounds have been shown to be stable up to 2 months when stored at −20 °C (26).

The safe sampling volume (SSV) for the sorbent tubes was tested by loading sorbent tubes with reference standards and challenged sorbent tubes with 2, 4, 6, and 12 L of air (nitrogen) using gas samplers. The SSV was confirmed by challenging sorbent tubes with 2 and 12 L of air at ambient temperatures (24 °C) and 50% relative humidity (RH) (see description of experiment in water sorption section).

Samples were collected at both swine and poultry production facilities. Sampling locations included the following:

(1) Swine building: The swine building samples were taken inside the Iowa State University Swine Nutrition and Management Research Farm in the swine finishing confinement building. The building is tunnel ventilated; animal waste was collected in shallow pits with a pull-plug flushing system that removes waste through underground piping into a steel storage container. Samples were taken inside the building at approximately a 1.0 m height from the floor with air temperature and RH at 15 °C and 60%, respectively.

(2) Swine pit simulation tanks: Air samples were collected in both the room air and headspace of stainless steel manure storage containers (900 L total volume). Feces and urine from animals were collected twice daily and added to the manure storage containers. Air flow through each storage tank was set at 8 L min^{-1}, tank temperatures averaged 24 °C with average RH of 100%. Air samples were taken from the headspace of the storage tanks and the room the pigs were housed at the end of a three month trial.

(3) Poultry house: Air samples from a commercial broiler production house located in the southeastern United States were collected between flocks during wintertime conditions. Samples were taken from side wall fan, tunnel portion of the building and throughout the building along water and feed lines (see Supporting Information for more detail). Air

temperature and RH conditions during sampling were 0 °C and 76%, respectively.

Water Sorption. Sorbent tubes were connected to a Teflon cylindrical manifold (i.d., 4.1 cm, Savillex, Co., Minnetonka, MN) maintained at ambient temperatures (23 °C ± 2) and pressures. Controlled humidified air was introduced into the manifold using zero grade air after passing through an Alpha-MOS 720 (Hanover, MD) sampling chamber at 5 L min^{-1}. The RH and temperature of the diluting zero grade air was verified at the end of the manifold using a traceable hydrometer temperature recorder (Fisher Scientific, New Castle, DE). Sorbent tubes were connected to the manifold via GS1 gas sampler and samples collected at predetermined sampling volumes 2, 4, 6, 12, and 24 L). Each sorbent tube was weighed (Sartorious, Inc.) before and after passing humidified air through, with total water sorbed determined by difference. The sorption study was repeated for Carbotrap 300 sorbent tubes with tube heaters (set at 41 °C, approximately 15 °C above ambient) and without heaters. Tubes that did not use heaters were dry purged with 2 L of dry nitrogen.

Thermal Desorption GC/MS Analysis. Three chemical stock solutions were prepared for standards. The first stock solution was volatile fatty acid (VFA) standards prepared in HPLC grade water (Burdican and Jackson, Mustegon, MI) pH adjusted to approximately 2.5 (1% formic acid solution). The second and third stock solutions were phenol and indole compounds prepared in HPLC grade methanol (Burdican and Jackson). All chemicals were 98% or higher (GC grade) and purchased from Aldrich (Sigma-Aldrich, St. Louis, MO) or Supelco, Inc. (Bellafonte, PA). Table 1 shows target compounds with molecular weight, odor threshold, and vapor pressure.

Sorbent tubes were analyzed by thermal desorption-gas chromatography–mass spectrometry (TDS-GC-MS). The TDS (Gerstel TDSA, Gerstel, Inc., Baltimore, MD) GC (6890, Agilent Technologies, Wilmington, DE), and MS (5973N Inert MSD, Agilent Technologies) instrument was equipped with cooled inlet (CIS 4, Gerstel, Inc.), and FFAP column (30 m × 0.25 mm × 0.25 µm, J&W Scientific, Inc., Wilmington, DE) using helium gas.

The TDS parameters were the following: splitless mode; initial temperature, 60 °C; final temperature, 300 °C (hold 3 min); ramp, 60 °C min°[-1]; and heated transfer line set at 320

TABLE 2. Recovery (%) and RSD[a] of Odorants from Sorbent Tubes after Challenging Tubes with Either 2 or 12 L of Air

compound	Tenax		Carbotrap 300		CP-X		water management[d]	
	2 L	12 L	2 L	12 L	2 L	12 L	heating tubes	dry purge
acetic acid	27(26)[b]	13(56)	107(14)	93(7)	98(24)	94(8)	68(36)	52(29)
propanoic acid	96(3)	76(24)	115(8)	108(11)	93(11)	93(8)	111(26)	45(58)
2-methylpropanoic acid	94(4)	100(18)	110(4)	99(20)	87(5)	85(11)	98(20)	86(25)
butanoic acid	95(3)	103(2)	107(4)	102(6)	90(2)	91(7)	101(8)	95(14)
3-methylbutanoic acid	95(2)	110(9)	106(3)	91(17)	90(3)	101(5)	102(5)	97(6)
pentatonic acid	92(4)	112(10)	105(3)	91(8)	93(3)	103(6)	100(4)	84(22)
4-methylpentatonic acid	ND[c]	104(7)	ND	92(1)	ND	91(18)	ND	ND
hexanonic	ND	101(8)	ND	94(2)	ND	95(15)	100(7)	107(22)
heptaonic acid	ND	91(15)	ND	93(4)	ND	100(18)	100(7)	99(19)
phenol	ND	121(10)	ND	85(9)	ND	104(7)	104(9)	72(39)
4-methylphenol	ND	83(31)	ND	91(8)	ND	105(7)	97(6)	107(38)
4-ethylphenol	ND	115(8)	ND	95(7)	ND	101(10)	101(6)	83(24)
4-propylphenol	ND	110(13)	ND	84(18)	ND	95(10)	ND	ND
indole	ND	106(14)	ND	61(57)	ND	103(6)	101(17)	91(12)
3-methylindole	ND	107(13)	ND	87(18)	ND	102(11)	100(8)	117(18)

[a] RSD, relative standard deviation. [b] Numbers in parentheses represent RSD for recovery. [c] ND, not determined. [d] Water management, Carbotrap 300 tubes challenged with 12 L of 80% RH air.

°C. The cooled inlet was glass bead packed and operated in solvent vent mode with the following parameters: initial temperature, −20 °C, final temperature, 320 °C, initial time, 0.2 min, final time, vent flow 20 mL min⁻¹, and purge split flow 20 mL min⁻¹. This method is essentially a 20:1 split injection from TDS to analytical column. The GC oven temperature program was (1) initial temp, 80 °C hold 0.05 min; (2) ramp 10 to 220 °C; and (3) ramp 50−240 °C and hold 5 min. The MS was operated under SIM (selective ion monitoring) mode using the following ions and time windows: (1) VFA compounds 43, 57, 60, 73, 74, and 87, 94, 101 m/z from 3 to 14.1 min; and (2) phenolic/indolic compounds 43, 57, 60, 73, 74, and 87, 94, 101 m/z from 14.1 to 20.0 min).

A 3 min solvent delay time was incorporated into standards analysis due to the use of methanol as a diluting agent in the phenol and indole standards. Identification and quantitation of each compound was based on retention time and ion ratio match of the target compounds. External standard curves were used for quantitation of samples. Standard curves for each compound were based on at least a five point calibration curve for the MS using a linear regression with inverse concentration weighing of calibration points. All calibrating reference standard points were run in duplicate as a minimum. The limit of quantitation (LOQ) was calculated as 10 times the standard deviation of the mean blank value as measured by peak height, and precision was determined by four replicates of standards at four different concentration levels and calculated as relative standard deviation (RSD).

Results and Discussion

Table 1 is a list of the method's parameters for all target compounds and includes the LOQ, linearity, dynamic range, and precision. The GC method resulted in complete resolution of all target compounds and show this method is adaptable to GC-FID (see Supporting Information). The method is extremely sensitive with LOQ at the sub ng to single digit ng levels for most compounds (Table 1). On average, VFAs had about an order of magnitude lower response than did either phenol or indole compounds (Table 1). It should be noted that due to the pK_a of the VFAs (approximately 4.7), a 0.1 M formic acid solution was used to dilute VFA standards, which added approximately 3 ng of acetic acid to each sorbent tube since it contains 0.5% acetic acid (see Supporting Information). While acetic acid can be detected in the sub ng levels, analytical quantitation was limited to 30 ng. The method's linear dynamic range for each compound was a little over 2 orders of magnitude as

measured by relative standard error (RSE) of each regression being less than 15% (Table 1), criteria set by FDA (27). The linear dynamic range for VFAs was between 30 and 6500 ng or 2.5 and 3250 μg m⁻³ assuming sampling volume of 12 and 2 L of air, respectively, whereas the linear dynamic range for phenol and indole compounds ranged from 0.43 to 1143 ng or 0.036 to 571 μg m⁻³, respectively. Precision of the method was acceptable since no single RSD was greater than 15%, a criteria set by FDA for acceptance (27).

The SSV were monitored based on compound recovery, and not on the basis of the 10% recovered in back-up tubes as is typical for SSV determination. Measuring SSV using percent recovered in both main and back-up tubes is only valid when sorbent tubes contain a single sorbent material (see Supporting Information). Sorbent tubes containing CP-X and CMS material had the highest recovery for odorants following 12 L of air with recoveries averaging 98 and 91%, respectively (Table 2). The CP-X tubes had recoveries greater than 85% for all compounds, while CMS tubes had low recoveries for both 4-ethylphenol, 84%, and indole, 61%. Tenax tubes had significant loss of both acetic acid and propanoic acid following 12 L of air with recoveries averaging 13 and 76%, respectively, but gave excellent recovery of all other compounds, averaging 105%. It should be pointed out that levels of both benzaldehyde and 1-phenylethanone, known artifacts associated with Tenax material (23), increased with increasing sample volumes. Lowering the sampling volume to 2 L still resulted in a significant decline in acetic acid recoveries from Tenax tubes with an average recovery of only 47%. In all, odorants were quantifiable down to their odor threshold values. The high recoveries in the CP-X and CMS containing sorbent tubes demonstrate these sorbent tubes are excellent choices for monitoring of emissions of SVOC since there was little to no breakthrough of target compounds; however, the poor recovery of the most volatile SVOC demonstrate Tenax sorbent tubes is a poor choice for monitoring purposes due to the potential breakthrough of these compounds after only 2 L of air. In addition, artifact formation of compounds associated with AFOs on Tenax limits its use for monitoring purposes.

Sampling in Humid Environments. The type of sorbent material used had a significant effect on the amount of water sorbed during sampling as did the RH and total volume of air sampled (Figure 1). Tubes containing CMS material sorbed significantly ($p > 0.0001$) more water than tubes containing either Tenax or CP-X material. There was no significant difference in water sorption between Tenax or CP-X tubes.
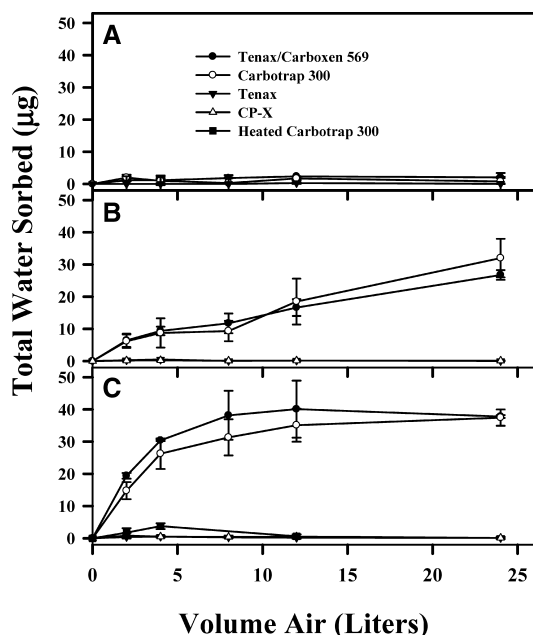
FIGURE 1. Sorption of water on sorbent tubes as a function of volume and relative humidity (RH): Closed circles custom Tenax TA/Carboxen 569 sorbent tubes; Open circles Carbotrap 300 sorbent tubes; Closed triangle Tenax TA sorbent tubes; Open triangles custom Carbopack X/Carbopack C sorbent tubes; Closed squared Carbotrap 300 sorbent tubes heated to 41 °C; and Error bars are standard deviation. (A) 25% RH; (B) 50% RH; and (C) 80% RH.

Relative humidity had a significant effect ($p > 0.0001$) on total water sorbed for CMS material, but no effect on either Tenax or CP-X tubes. Total volume of air sampled had a significant effect on water sorbed for CMS material ($p < 0.001$). At 25% RH, there was no significant difference in amount of water sorbed on any sorbent materials, but at 50 and 80% RH, CMS material sorbed greater amounts of water than either Tenax or CP-X tubes. Total water sorbed following 12 L of air at 50% RH based on mass of CMS material was approximately 55 and 124 mg g^{-1} for Carboxen 569 and Carbosieve III, respectively, and 132 and 236 mg g^{-1}, respectively, at 80% RH. The higher sorption of water and slower saturation of the Carbosieve III compared to Carboxen 569 sorbent material is consistent with others (19, 20).

On CMS material, water sorption is initially low at low RH with sorption mainly associated with polar surface functional groups of the CMS material, but as the partial pressure of water increases (i.e., higher RH) sorption of water increases due to water cluster formation on previously sorbed water which eventually leads to filling of pores that plateau when all pores are filled (28). Sorbed water on CMS material not only affects trapping efficiency during sampling, but also significantly degrades laboratory analysis (29–31). In this study, 15 μL of water on sorbent tube typically resulted in complete loss of data from either shutdown of the instrument due to over pressurization (ice blockage), or chromatograms that were impossible to interpret due to shifting retention times, poor peak shape, and loss of resolution of compounds (see Supporting Information). Consequently, recovery studies of SVOCs on CMS tubes sampled at 80% RH were not attempted. Chromatograms were affected by as little as 5 μL of water with declining signal intensity and poorer reproducibility after 10 μL of water (Figure 2). There were also lower recoveries and poorer reproducibility for SVOCs on CMS tubes with only 6.2 μL of sorbed water (2 L of 50% RH air) (see Supporting Information).

Water management techniques were developed for CMS tubes to mitigate effect of excess water sorption. These
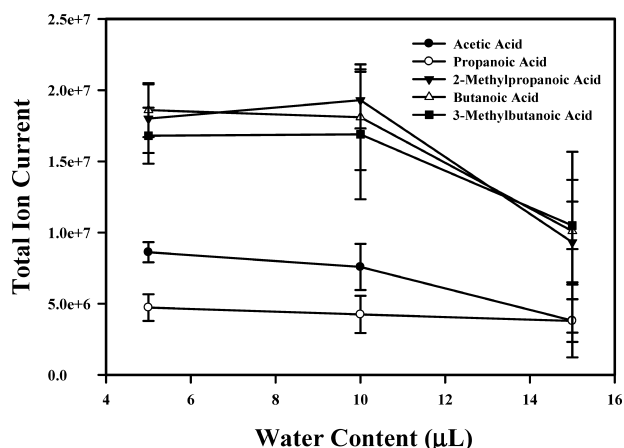

FIGURE 2. Signal intensity for volatile fatty acids as a function of water on tube. Error bars are standard deviation.

techniques were tested on Carbotrap 300 tubes using 80% RH air. The first technique involved heating of tubes to 41 °C (i.e., 15 °C above ambient temperatures) as suggested by others (18, 32) during sampling. Heating of tubes changed the RH condition from 80 to 34% which is just below the critical level for significant sorption of water to begin (20). Lowering of the effective RH resulted in a significant decline ($p < 0.001$) in total water sorbed during sampling (Figure 1C). Water reduction of more than 90% was recorded for sampling of 12 L of air at 80% RH, which is close to 98% estimate of Helmig and Vierling (18) for lowering the RH from 80 to 27%. The second technique involved dry purging of tubes with 2 L dry nitrogen. Total water sorbed was reduced from 38 μg water/tube to less than 0.5 μg water (98% reduction). Clearly both techniques are effective at reducing sorption of water; however, heating of tubes during sampling was considered superior due to improved recoveries of odorants and reproducibility of the method compared to dry-purging of tubes post sampling (Table 2).

Field Sampling. Based on the laboratory studies the CP-X tubes were chosen to measure SVOCs in the field. Table 3 shows concentrations levels for the various odorants measured at both swine and poultry facilities. Distinct differences in the pattern of odorants can be seen across animal production facilities and sampling locations within the facility (i.e., room air vs manure storage).

Inside the swine facility, acetic acid and butanoic acid were often the most abundant compounds on a mass basis, but based on their odor activity value (OAV, mean concentration in air divided by odor threshold value) key odorants were butanoic acid, 3-methylbutanoic acid, and 4-methylphenol since they were all on average above their odor thresholds values. Compounds such as 4-ethylphenol, indole, and 3-methylindole were above their odor threshold during at least one sampling event. Room air in the swine pit simulation study demonstrated that indole and butanoic acid were both detected on average above their odor threshold values, while 3-methylbutanoic and 4-methylphenol were detected several times above their odor threshold values (Table 3). The room blank (no animals in room) showed that volatile fatty acids were not present indicating that VFAs originated from the animals themselves or fresh manure (data not shown). Monitoring of the manure tanks revealed that key odorants in the aged manure were indole and 3-methylindole based on OAV with 4-methylphenol and 4-ethylphenol also being detected above their odor thresholds. The VFAs were low in the headspace of the aged manure vessels. This is not surprising given that the pH of manure was close to 8.4 indicating that the majority of the VFAs were in their less volatile ionized forms. Indole typically had the highest OAV of the compounds. This agrees with Zahn et al.

TABLE 3. Mean value and odor activity value (OAV) of compounds in air from swine and poultry production.

| | swine finisher room | | swine pit simulation | | | | poultry broiler facility | | | | | |
| | | | animal and fresh manure | | aged manure | | side wall fan | | tunnel | | feed and water Line | |
compound	μg m^{-3}	OAV[a]	μg m^{-3}	OAV	μg m^{-3}	OAV	μg m^{-3}	OAV[a]	μg m^{-3}	OAV	μg m^{-3}	OAV
acetic acid	51.3	0.14	63.4	0.18	17.1	0.05	332.7	0.93	62.4	0.18	174.3	0.49
propanoic acid	24.5	0.23	36.8	0.34	5.6	0.05	34.4	0.32	5.1	0.05	27.2	0.25
2-methylpropanoic acid	6.4	0.09	6.1	0.09	0.9	0.01	19.0	0.27	2.9	0.04	17.3	0.24
butanoic acid	28.8	2.04	24.2	1.71	3.2	0.23	129.9	9.19	10.3	0.73	66.4	4.70
3-methylbutanoic acid	4.0	0.39	9.0	0.87	1.3	0.13	22.4	2.17	3.5	0.34	17.5	1.70
pentatonic acid	4.1	0.20	0.9	0.05	0.2	0.01	3.8	0.19	0.8	0.04	1.9	0.10
hexanonic	ND[b]	NA[c]	ND	NA	ND	NA	3.0	0.13	0.5	0.02	2.2	0.09
heptaonic acid	ND	NA	ND	NA	ND	NA	1.0	0.02	0.6	0.01	1.3	0.02
phenol	2.3	0.01	3.9	0.01	6.6	0.02	0.4	0.00	0.3	0.00	0.6	0.00
4-methylphenol	10.7	1.29	70.0	8.43	56.0	6.75	7.1	0.86	3.7	0.45	15.8	1.90
4-ethylphenol	0.3	0.05	6.0	0.95	27.0	4.28	24.0	3.81	9.9	1.57	31.1	4.94
indole	0.2	1.33	4.0	26.67	15.0	100.0	ND	NA	ND	NA	ND	NA
3-methylindole	0.1	0.03	11.0	3.67	96.0	32.0	ND	NA	ND	NA	ND	NA

[a] OAV odor activity value, mean concentration in air/odor threshold. [b] ND not determined. [c] NA not applicable.

(36) who created a mixture of compounds said to resemble swine manure odor; based on the OAV of individual compounds in his system, indole was also the key odorant associated with swine manure.

In the poultry facility, samples were taken repeatedly in two areas of the building, the tunnel portion and near one of the side wall fans. In addition, samples were taken along the feed and water lines throughout the building. The results show that acetic acid is the most abundant compound detected on a mass basis (Table 3), but OAVs indicate key odorants are butanonic acid, 3-methylbutanoic acid, and 4-methylphenol. In fact, 4-methylphenol is the only compound detected above its odor threshold value in all areas monitored, with the volatile fatty acids being the most abundant compounds in the wettest areas of the facility. It was interesting to note that there was little to no indole or 3-methylindole detected. The key odorants associated with a broiler facility included butanoic acid, 3-methylbutanoic acid, and 4-methylphenol similar to what has been reported by Cai et al. (35). Absence of indole and 3-methylindole may reflect the age of the litter (fresh vs aged) and temperature during sampling (25 vs 0 °C).

This study calls into question much of the previous work on agricultural air quality using CMS material. The use of CMS tubes requires the RH to be below 35% (20, 21, 32) to prevent sorption of water, but this level is often surpassed in field sampling (3, 4, 8). This would indicate that in previous studies sorbent tubes would have sorbed large amounts of water since water management techniques were never discussed (3, 5, 6, 8). Water sorbed on CMS material would have limited its usefulness in trapping volatile compounds due to water blockage of sorption sites (30). In this study, water sorption also resulted in a significant loss in signal intensity from either detector response or ice blockage in the inlet. All these issues relating to excess water sorption have implications on the quantitation levels reported in previous work. In addition, we have shown that Tenax sorbent tubes also have analytical issues, with breakthrough of the more volatile odorants occurring with sampling volumes as low as 2 L, a volume commonly surpassed in many air quality studies (4, 37). This again has implication on quantitation levels from previous studies.

This method was developed in recognition of the need to quantify VOCs including SVOCs in air from animal agriculture (1). This method along with canister based sampling mandated by EPA air consent agreement should complement each other in speciating VOCs associated with AFOs (2). This study is the first to use Carbopack X in a multibed tube for the purpose of sampling in humid environments. While Ribes et al. (34) used Carbopack X in multibed tube, they also included CMS material, a sorbent shown in this study to sorb large amounts of water. Future research is in progress to determine the full range of compounds this method can accurately quantify from AFOs since Carbopack X has been shown to chemically transform small alcohols during analysis (38).

Supporting Information Available
Details on sampling location, and placement of samplers at the poultry facility; Chromatogram of target compounds separated on FFAP column Figure S2; Details on the use of formic acid to dilute VFA standards; Details on measuring SSV with multibed sorbent tubes with Figure S3; Chromatograms of VFA compounds after various sorbent tubes were challenged with various RH conditions, Figures S4–S6; Table S1 showing the high variability in thermal desorption analysis of a sorbent tube with CMS material affected by water. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited
(1) National Research Council. *Air Emission from Animal Feeding Operations Current Knowledge Future Needs*; The National Academies Press: Washington, D.C., 2003.
(2) Animal feeding operations consent agreement and final order. Fed. Regist. 2005 70, 4958–4977.
(3) Zahn, J.; Hatfield, J. Y; Do, A.; DiSpirito; Laird, D.; Pfeiffer, R. Characterization of volatile organic emissions and wastes from a swine production facility. *J. Environ. Qual.* 1997, 26, 1687–1696.
(4) Schiffman, S.; Bennett, J.; Raymer, J. Quantification of odors and odorants from swine operations in North Carolina. *Agric. For. Meteorol.* 2001, 108, 213–240.
(5) Zahn, J.; Hatfield; Laird, D; Hart, T; Do, Y.; DiSpirito, A. Functional classification of swine manure management systems based on effluent and gas emission characteristics. *J. Environ. Qual.* 2001, 30, 635–642.
(6) Rabud, N.; Ebeler, S.; Ashaugh, L.; Flocchini, R. 2003. Characterization and quantification of odorous and non-odorous volatile organic compounds near a commercial dairy in California. *Atmos. Environ.* 2003, 37, 933–940.

(7) Blunden, J.; Aneja, V.; Lonneman, W. Characterization of non-methane volatile organic compounds at swine facilities in eastern North Carolina. *Atmos. Environ.* **2005**, *39*, 6707–6718.

(8) Filipy, J.; Rumburg, B.; Mount, G; Westberg, H.; Lamb, B. Identification and quantification of volatile organic compounds from a dairy. *Atmos. Environ.* **2006**, *40*, 1480–1494, 2006.

(9) Thu, K.; Donham, K; Ziegenhorn, R; Reynolds, S; Thorne, P; Subramanian, P; Whiten, P.; Stookesberry, J. A control study of the physical and mental health of residents living near a large-scale swine operation. *J. Agric. Saf. Health* **1997**, *3*, 13–26.

(10) Wing, S.; Wolf, S. Intensive livestock operations, health, and quality of life among eastern North Carolina residents. *Environ. Health Perspect.* **2000**, *108*, 233–238.

(11) Palmquist, R.; Roka, F.; Vukina, T. Hog operations, environmental effects, and residential property values. *Land Economics* **1997**, *73*, 114–124.

(12) Schiffman, S.; Williams, C. Science of odor as a potential health issue. *J. Environ. Qual.* **2005**, *34*, 129–138.

(13) Schiffman, S.; Studwell, C.; Landerman, L.; Berman, K.; Sundy, J. Symptomatic effects of exposure to diluted air sampled from a swine confinement atmosphere on healthy human subjects. *Environ. Health Perspect.* **2005**, *113*, 567–576.

(14) Koziel, J.; Spinhirne, J; Lloyd, J; Parker, D; Wright, D.; Kuhrt, F. Evaluation of sample recovery of malodorous livestock gases from air sampling bags, solid phase microextraction fibers, Tenax TA sorbent tubes, and sampling canisters. *J. Air Waste Manage. Assoc* **2005**, *55*, 1147–1157.

(15) Namiesnick, J; Gorlo, D.; Walska, L; Zygmunt, B. Analysis of selected gaseous organic micro-pollutants in air by means of solid phase microextraction gas chromatography mass spectrometry, calibration problems. *Analysis* **1998**, *26*, 170–174.

(16) Namiesnick, J.; Jastrzebska, A.]?>; Zygmunt, B. Determination of volatile aliphatic amines in air by solid-phase microextraction coupled with gas chromatography with flame ionization detection. *J. Chromatogr., A.* **2003**, *1016*, 1–9.

(17) Lestremau, F.; Andersson, F. A. T.; Desauziers, V.; Fanlo, J. L. Evaluation of solid-phase microextraction for time-weighted average sampling of volatile sulfur compounds at ppb concentrations. *Anal. Chem.* **2003**, *75*, 2626–2632.

(18) Helmig, D.; Vierling, L. Water adsorption capacity of the solid adsorbents Tenax TA, Tenax GR, Carbotrap, Carbotrap C, Carbosieve SIII, and Carboxen 569 and water management techniques for the atmospheric sampling of volatile organic trace gases. *Anal. Chem.* **1995**, *67*, 4380–4386.

(19) Gawlowski, J.; Gierczak, T; Jezo, A.; Niedzielski., J. Adsorption of water vapour in the solid sorbents used for the sampling of volatile organic compounds. *Analyst* **1999**, *124*, 1553–1558.

(20) Fastyn, P.; Kornacki, W; Kardas, M; Gawlosski, J.; Niedzielski, J. Adsorption of water vapour from humid air in carbon molecular sieves: Carbosieve S-III and Carboxen 569, 1000, and 1001. *Analyst* **2003**, *128*, 198–203.

(21) Fastyn, P.; Kornacki, W; Kardas, M; Gawlosski, J.; Niedzielski., J. Adsorption of water vapour from humid air by selected carbon adsorbents. *J. Chromtogr., A.* **2005**, *1078*, 7–12.

(22) MacLeod, G.; Ames, J. Comparative assessment of the artifact background on thermal desorption of Tenax GC and Tenax TA. *J. Chromatrogr.* **1986**, *393*, 398.

(23) Lee, J. H.; Batterman, S; Jia, C.; Chernyak, S. Ozone artifacts and carbonyl measurements using Tenax GR, Tenax TA, Carbopack B, and Carbopack X adsorbents. *J. Air Waste Manage. Assoc.* **2006**, *56*, 1503–1517.

(24) McClenny, W. H.; Jacumin, K; Oliver, E.; Daughtrey, D.; Whitaker. Comparison of 24 h averaged VOC monitioring results for residential indoor and outdoor air using Carbopack X-filled diffusive samplers and active sampling—A pilot study. *J. Environ. Monitor.* **2006**, *8*, 263–269.

(25) Strandberg, B.; Sunesson, A.; Sundgren, M; Levin, J; Sallsten, G.; Barregard, L. Field evaluation of two diffusive samplers and two adsorbent media to determine 1,2-butadiene and benzene levels in air. *Atmos. Environ.* **2006**, *40*, 7686–7695.

(26) Odam, E. M., Page, J. Townsend M. G., and Wilkins J. Identification of volatile components in heaspace from animal slurries. In *Odour Prevention and Control of Organic Sludge and Livestock Farming*; Nielsen, V. C.,Voorburg, J. H., L'Hermite, P., Eds.; Elsevier Applied Science: New York, 1986.

(27) Guidance for Industry: Bioanlytical Method Validation, U.S. Department of Health and Human Services, Food and Drug Administration, Rockville, MD; May, 2001; http://www.fda.gov/cder/guidance/4252fnl.pdf. (verified February 8, 2008).

(28) Brennan, J.; Bandosz, T; Thomson, K.; Gubbins, K. Review: Water in porous carbons. *Colloids Surf.* **2001**, *187–188*, 539–568.

(29) Ciccioli, P.; Cecinato, A.; Brancaleoni, E.; Frattoni, M. Use of carbon adsorption traps combined with high resolution gas chromatography-mass spectrometry for the analysis of polar and non-polar C_4-C_{14} hydrocarbons involved in photochemical smog formation. *J High Resolut Chromatogr.* **1992**, *15*, 75–84.

(30) Woolfenden, E. Monitoring VOCs in air using sorbent tubes followed by thermal desorption-capillary GC analysis: summary of data and practical guidelines. *J. Air Waste Manage. Assoc.* **1997**, *47*, 20–36.

(31) Rabud, N.; Ebeler, S.; Ashaugh, L.; Flocchini, R. The application of thermal desorption GC/MS with simultaneous olfactory evaluation for the characterization and quantification of odor compounds from a dairy. *J. Agric. Food Chem.* **2002**, *50*, 5139–5145.

(32) Gawrys, M.; Fastyn, P.; Gawloski, J.; Gierczak, T.; Niedzielski, J. Prevention of water vapour adsorption by carbon molecular sieves in sampling humid gases. *J. Chromtogr., A.* **2001**, *933*, 107–116.

(33) Martin, N. A.; Duckworth, P; Henderson, M. H.; Swann, N. R. W.; Granshaw, S. T.; Lipscombe, R. P.; Goody, B. A. Measurements of environmental 1,3-butadiene with pumped and diffusive samplers using the sorbent Carbopack X. *Atmos. Environ.* **2005**, *39*, 1069–1077.

(34) Ribes, A.; Carrera, G; Gallego, E; Roca, X; Berenguer, M.; Guardino, X. Development and validation of a method for air-quality and nuisance odors monitoring of volatile organic compounds using multi-sorbent adsorption and gas chromatography/mass spectrometry thermal desorption system. *J. Chromtogr., A.* **2007**, *1140*, 44–55.

(35) Cai, L.; Koziel, J.; Liang, Y; Nguyen, A.; Xin, H. Evaluation of zeolite for control of odorants emissions from simulated poultry manure storage. *J. Environ. Qual.* **2007**, *36*, 184–193.

(36) Zahn, J.; DiSpirito, A.; Do, Y; Brooks, B; Cooper, E.; Hatfield, J. Correlation of human olfactory responses to airborne concentrations of malodorous volatile organic compounds emitted from swine effluent. *J. Environ. Qual.* **2001**, *30*, 624–634.

(37) Lim, T-T.; Heber, A; Ni, J.-Q; Sutton, A.; Shao, P. Odor and gas release from anaerobic treatment lagoons for swine manure. *J. Environ. Qual.* **2003**, *32*, 406–416.

(38) Kornacki, W.; Fastyn, P.; Gawlowski, J; Gierczak, T.; Niedzielski, J. Chemical transformation of alcohols sampled with the use of adsorptive enrichment on the carbon adsorbent traps followed by thermal desorption. *Analyst* **2005**, *130*, 632–636.

(39) Devos, M; Patte, F.; Rouault, J.; Laffort, P.; Van Gemert, L. Standardized Human Olfactory Thresholds; IRI Press at Oxford University Press: New York, 1990.

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