

Characterizing non-methane volatile organic compounds emissions from a swine concentrated animal feeding operation

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ABSTRACT

Emissions of non-methane volatile organic compounds (NMVOCs) were determined from a swine concentrated animal feeding operation (CAFO) in North Carolina. NMVOCs were measured in air samples collected in SUMMA and fused-silica lined (FSL) canisters and were analyzed using a gas chromatography flame ionization detection (GC–FID) system. Measurements were made from both an anaerobic lagoon and barn in each of the four seasonal sampling periods during the period June 2007 through April 2008. In each sampling period, nine to eleven canister samples were taken from both the anaerobic lagoon and barn over a minimum of four different days during a period of ~1 week. Measurements of meteorological and physiochemical parameters were also made during the sampling period. In lagoon samples, six NMVOCs were identified that had significantly larger emissions in comparison to other NMVOCs. This included three alcohols (ethanol, 2-ethyl-1-hexanol, and methanol), two ketones (acetone and methyl ethyl ketone (MEK)) and an aldehyde (acetaldehyde). The overall average fluxes for these NMVOCs, ranged from 0.18 $\mu\text{g m}^{-2} \text{min}^{-1}$ for 2-ethyl-1-hexanol to 2.11 $\mu\text{g m}^{-2} \text{min}^{-1}$ for acetone, with seasonal fluxes highest in the summer for four (acetone, acetaldehyde, 2-ethyl-1-hexanol and MEK) of the six compounds. In barn samples, there were six NMVOCs that had significantly larger concentrations and emissions in comparison to other NMVOCs. These consisted of two alcohols (methanol and ethanol), an aldehyde (acetaldehyde), two ketones (acetone and 2,3-butanedione), and a phenol (4-methylphenol). Overall average barn concentration ranged from 2.87 ppb for 4-methylphenol to 16.12 ppb for ethanol. Overall average normalized barn emission rates ranged from 0.10 $\text{g day}^{-1} \text{AU}^{-1}$ (1 AU (animal unit) = 500 kg of live animal weight) for acetaldehyde to 0.45 $\text{g day}^{-1} \text{AU}^{-1}$ for ethanol. The NMVOCs, 4-methylphenol and 2,3-butanedione, which have low odor thresholds (odor thresholds = 1.86 ppb and 0.068–0.264 ppb for 4-methylphenol, and = 4.37 ppb and 1.42–7.39 ppb for 2,3-butanedione) and an offensive odor were identified in canister samples. Both 4-methylphenol and 2,3-butanedione barn concentrations exceeded their odor thresholds frequently. HAPs were identified in lagoon samples (methanol, acetaldehyde and MEK) and barn samples (methanol, acetaldehyde and 4-methylphenol) that were also classified as NMVOCs with significantly larger lagoon and barn emissions in comparison with other NMVOCs. The overall average lagoon fluxes and overall average normalized barn emissions for NMVOCs reported in this paper were used to estimate their North Carolina swine CAFO emissions. Of the NMVOCs, ethanol was estimated to have the largest North Carolina swine CAFO emission at 206,367 kg yr^{-1} . The barns were found to have higher emissions than the lagoons for all NMVOCs, contributing between 68.6 to ~100% of individual compounds estimated North Carolina swine CAFO emissions.

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1. Introduction

Concentrated animal feeding operations (CAFOs) emit a number of trace gases including non-methane volatile organic compounds (NMVOCs). In North Carolina, the primary CAFO is swine, with a swine population of ~10 million, which is mostly concentrated in the southeastern coastal plain. The emission of NMVOCs from swine CAFOs in North Carolina is of concern due to their potential

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environmental impacts. Certain NMVOCs are odorous, therefore emissions of these odorous compounds are important locally, as they can potentially effect human's health (Schiffman and Williams, 2005) and their quality of life (Wing and Wolf, 2000; Thu et al., 1997). Additionally, of the U.S. Environmental Protection Agency (U.S. EPA) listed 188 hazardous air pollutants (HAPs) (U.S. EPA, 2009a), 162 are classified as NMVOCs. HAPs are defined by the U.S. EPA as pollutants that are known to cause cancer or other serious health effects such as damage to the immune system, reproductive, developmental, neurological, and respiratory effects (U.S. EPA, 2009b).

In comparison to other trace gases (i.e. ammonia and methane), measurement studies of NMVOC concentrations and emissions from swine CAFOs have been limited. Additionally, these measurement studies (Blunden et al., 2005; Trabue et al., 2008; Zahn et al., 1997; Schiffman et al., 2001; Feilberg et al., 2010) do not report NMVOC emissions from swine CAFOs with respect to seasonal variations.

This paper presents the measurement of NMVOC concentrations and emissions over four seasonal sampling periods from an anaerobic lagoon and barn at a swine CAFO in North Carolina. NMVOC emissions are reported in three different sub-categories: NMVOCs with large emissions, odorous NMVOC emissions, and HAP emissions. These NMVOC emissions are evaluated with respect to seasonal variations and environmental factors. The potential local environmental impact of the odorous NMVOC emissions is evaluated by comparing NMVOC barn concentrations to their odor threshold. Furthermore, the emissions for NMVOCs reported in this paper are used to estimate their swine CAFO emissions for North Carolina.

2. Methods and materials

2.1. Sampling site

The sampling site was a swine CAFO located in eastern North Carolina. The swine CAFO has eight barns, which are mechanically ventilated. The waste at the swine CAFO is dealt with, using a waste management method known as 'lagoon & spray technology'. In this method, swine waste accumulates in a shallow pit under a slatted floored barn. This waste is then flushed on a weekly basis into an anaerobic lagoon. The average lagoon area over the sampling period was 18,145 m². The waste from the lagoon can then be sprayed on crops as a source of nutrients. Additionally, the lagoon waste is used to flush the shallow pit. This waste management method is used by most swine CAFOs in North Carolina. It should be noted that during sampling, the shallow pit was not flushed.

2.2. Sampling scheme

Measurements of NMVOC emissions were made from both the anaerobic lagoon and barn. Lagoon measurements were made using a dynamic-flow through chamber system over an approximate one week period. Barn measurements were similarly made over a one-week period. Barn concentration measurements were made by placing a sample line directly in front of a ventilation fan. To calculate the emissions, the fan ventilation rate was simultaneously measured. Measurements were made over the four seasonal periods of the year: summer, June 8th–June 28th; fall, October 20th–November 12th, 2007; winter, February 8th–February 29th, 2008; spring, April 11th–April 28th, 2008.

2.3. Field sampling technique and instrumentation

2.3.1. Field sampling

Field samples were collected using both 6-liter (L) SUMMA and fused-silica lined (FSL) canisters, similar to those used in other field sampling programs. The suitability of these canisters for the collection and storage of a wide range of NMVOCs has been reported by Brymer et al. (1996) and Ochiai et al. (2002).

During each sampling period, 9–11 canister samples were taken from each the lagoon and barn. Before sampling, the canisters were cleaned using a XonTech Model 960 canister cleaning system. With this system, canisters maintained at 120 °C are evacuated, filled with humidified air, and then re-evacuated. For this study, two cleaning cycles were used. On the final cycle, the canisters are evacuated by the system to < 0.05 mm Hg. Both 6-L SUMMA and FSL canisters were used for sampling, of which approximately a quarter were FSL canisters. Canister samples were taken over ~5 min collection periods at different times of the day (from 8:00–18:00 EST). Canister samples from the lagoon and barn were collected for a minimum of four different days over each sampling period.

2.3.2. Analytical system

Samples were analyzed using a Gas Chromatography–Flame Ionization Detection (GC–FID) system at the National Exposure and Research Laboratory of the U.S. Environmental Protection Agency (EPA) in Research Triangle Park, NC. A 60 m × 0.32 mm ID fused-silica column containing a one micron DB-1 coating was used for this activity. A cryogenic pre-concentration procedure was used to prepare the samples for detailed NMVOC analysis. The study samples collected in 6-L canisters at the swine CAFO were returned to the laboratory for GC analysis. Compounds were identified based on column retention time using a CALTABLE that contains more than 300 compounds identified by retention times. The GC/FID system was calibrated using a propane in air NIST/SRM standard. A uniform carbon response factor determined from the calibration standard was used to report observed compounds in parts-per-billion-carbon (ppbc). The utilization of a uniform response factor is valid for all hydrocarbon type NMVOCs. The majority of the NMVOCs reported here are oxygenated hydrocarbons that do not respond uniformly in the FID. To correct for the reduced FID response, individual values of effective carbon number (ECN) are used for each reported compound. These ECN values are available from past literature (Scalon and Willis, 1985; Kallai and Balla, 2002; Jorgensen et al., 1990) and are valid for GC–FID systems operated according to manufacturer specification. Dividing the measured compound concentration by the ECN value corrects ppbc to ppbV concentration. The ECN values used for the compounds reported here are provided in Table 1. To confirm compound identification and to identify unknown compounds, a gas chromatography–mass spectrometry system (GC–MS) was used. For more details on the GC materials and procedures, the reader is referred to Blunden et al. (2005).

Table 1
ECN values for reported NMVOCs.

Compound	Number of carbons	ECN value
Acetaldehyde	2	1.12
Acetone	3	2.00
2,3-butanedione	4	2.00
Ethanol	2	1.5
2-ethyl-1-hexanol	8	7.5
Hexane	6	6
Methanol	1	0.50
Methyl ethyl ketone	4	3
4-methylphenol	7	6.5

2.4. Lagoon, barn and environmental parameter measurements

2.4.1. Lagoon measurements

Anaerobic lagoon flux measurements were made using a dynamic flow-through chamber system (Blunden and Aneja, 2008; Aneja et al., 2008, 2000). A summary of the lagoon measurements are presented in this paper. For more information on the dynamic flow-through chamber system, the reader is referred to Blunden and Aneja (2008), which includes a detailed description of the chamber system used in this study.

The dynamic chamber (0.46 m internal height, 0.25 m internal diameter) is an open bottom cylinder, inserted into a floatable platform. The chamber penetrates the lagoon surface by ~7 cm, forming a seal between the lagoon surface and the air within the chamber. Compressed cylinder zero air flows into the chamber through Teflon tubing at a flow rate of 4–6 L min⁻¹. It should be noted that approximately half of the cylinders used in this experiment were sampled and analyzed by the GC–FID to confirm that the cylinders contained zero air. A Teflon impeller rotates inside the chamber, ensuring that the air is well mixed similarly to ambient air. The air then leaves the chamber and flows through more Teflon tubing into the canisters. The steady state flux is thus determined by the following equation:

$$J = [C] \left[\frac{q}{V} \right] h \quad (1)$$

where J , the compound flux is a function of C , the compound concentration in the chamber air, q , the flow rate of the zero air, and v and h , which are the volume and height of the chamber, respectively.

2.4.2. Barn measurements

Barn emissions were measured from one of the eight barns at the swine CAFO. The barn used five fans for ventilation (Maxi-Brute™ fans; AAA Associates Inc, Niles, MI), which were located on the west side of the barn facing towards the anaerobic lagoon. As temperature increases inside the barn, the fans turn on in a set sequence.

Barn emissions rates were calculated using the following equation:

$$J = C^* \sum f \quad (2)$$

where J is the compound emission, C is the compound gas concentration at the fan, $\sum f$ is the sum of the flow rates of each individual fan.

The concentration was measured by placing a Teflon sampling line directly in front of the first fan to turn on. The concentration distribution was assumed uniform across the fan. Additionally, the concentration was assumed to be the same for all the fans that were on during the sampling. While collecting barn samples, background barn samples were simultaneously collected, upwind of the swine barns. Net sample concentrations were calculated for each compound.

The individual fan flow rates were calculated using the following equation:

$$\text{Calculated fan flow rate} = \text{Manufactures fan flow rate} \times \left(\frac{\text{Measured RPM}}{\text{Specified RPM}} \right) \quad (3)$$

where RPM represents the revolutions per minute of the fan. The RPM of the fans were measured by attaching motors to the fans that produced a voltage, when the fans were turning. To determine the relationship between voltage and RPM, the motors were calibrated

prior to the sampling campaign using a controlled DC motor (2M168C, Dayton), a contact tachometer (DT-207B, Shimpo Direct Contact Digital Tachometer; Itasca, IL) a stroboscopic tachometer (DT-725, Shimpo Stroboscopic Digital Tachometer) and a multi-meter (22–185, Micronta Digital Multimeter). Also, during each sampling season the stroboscopic tachometer was used to check and evaluate each fan's performance. Additionally, the manufactures flow rate was adjusted for static pressure difference between the inside and outside of the barn. Measurements of the static pressure difference were made between the inside and outside of the barn using a hand held pressure sensor (Dwyer Series 475 Mark III hand held pressure sensor; Michigan City, IN). Pressure readings were taken daily during all the sampling seasons. When taking readings, it was noted how many fans were on. These measurements were used to determine the average static pressure difference, when a certain number of fans were on. The manufacturers fan flow rate was adjusted accordingly for the average static pressure difference. More information on the fans and the methodology used to determine the fan flow rate is available in Blunden and Aneja (2008).

2.4.3. Environmental parameter measurements

During lagoon measurements, lagoon temperature (CS107; Campbell Scientific Inc., Logan, UT) and pH (CSIM11; Campbell Scientific Inc.) were recorded at a depth of ~7 cm below the lagoon surface. For barn sampling, barn temperature was measured at the fan outlet. During both lagoon and barn sampling, meteorological measurements of wind speed and wind direction (034-B Windset, Met One Instruments; Campbell Scientific Inc.) at a height of 10 m were made. Additionally, measurements of air temperature and relative humidity (RH) were made using a temperature and RH probe (CS500-L Vaisala 50Y; Campbell Scientific Inc.) at a height of 2 m. The temperature/RH probe was housed in a 6-plate gill solar radiation shield (41303 RM Young; Campbell Scientific Inc.). Solar radiation (LI200X; Campbell Scientific Inc.) was also measured at a height of 2 m. To record and collect data, a CR23X data logger and a CR10X data logger (Campbell Scientific, Inc) were used. The data loggers were housed inside a temperature controlled mobile laboratory (Ford Aerostar Mini-Van.).

3. Results and discussion

3.1. NMVOCs with largest emissions

3.1.1. Lagoon fluxes

Observational analysis suggests that there are over 100 NMVOCs in lagoon canister samples. Of these NMVOCs, there were six compounds that had significantly larger emissions in comparison to other NMVOCs. These six compounds were identified in almost every sample and included three alcohols, (ethanol, 2-ethyl-1-hexanol, and methanol), two ketones, (acetone and methyl ethyl ketone (MEK)), and an aldehyde, (acetaldehyde). All six compounds were identified by retention time, and confirmed by GC–MS. These compounds' seasonal fluxes and their overall average flux are shown in Table 2. It should be noted that canister sampling was conducted during the daytime. Therefore the lagoon fluxes presented for the NMVOCs are not representative of a full day as they do not take into account diurnal variations in flux. Of these six compounds, it can be seen that the highest seasonal fluxes for each compound range from 4.41 $\mu\text{g m}^{-2} \text{min}^{-1}$ for acetone in summer to 0.54 $\mu\text{g m}^{-2} \text{min}^{-1}$ for 2-ethyl-1-hexanol in summer. The highest seasonal flux for acetone is at least an order of magnitude higher than seasonal fluxes for other NMVOCs (i.e. compounds that were not included in the group of six compounds). For 2-ethyl-1-

Table 2
Seasonal and overall seasonal fluxes of NMVOC with largest lagoon emissions.

	Flux ($\mu\text{g m}^{-2} \text{min}^{-1}$)				
	Summer	Fall	Winter	Spring	Overall average
Acetaldehyde	1.67 ^a (1.20) ^b , $n = 10^c$	0.40 (0.14), $n = 10$	0.34 (0.19), $n = 11$	0.24 (0.10), $n = 10$	0.66
Acetone	4.41 (1.26), $n = 10$	1.00 (0.31), $n = 10$	1.19 (0.20), $n = 11$	1.82 (0.84), $n = 10$	2.11
Ethanol	0.55 (0.37), $n = 10$	0.26 (0.16), $n = 10$	1.54 (3.78), $n = 11$	0.02 (0.01), $n = 10$	0.59
2-ethyl-1-hexanol	0.54 (0.66), $n = 10$	0.06 (0.02), $n = 10$	0.06 (0.07), $n = 11$	0.06 (0.02), $n = 10$	0.18
Methanol	1.39 (1.15), $n = 10$	1.53 (0.41), $n = 6$	0.67 (0.23), $n = 11$	1.16 (0.84), $n = 10$	1.19
MEK	0.97 (0.22), $n = 10$	0.42 (0.14), $n = 10$	0.41 (0.16), $n = 11$	0.42 (0.06), $n = 10$	0.56

^a Mean value.

^b ± 1 standard deviation.

^c Number of samples.

hexanol, the highest seasonal flux was at a minimum approximately two times larger than seasonal fluxes for other VOCs.

Of the six NMVOCs with largest lagoon emissions, acetone has the largest overall average lagoon flux with a flux of $2.11 \mu\text{g m}^{-2} \text{min}^{-1}$. The lowest was 2-ethyl-1-hexanol with an overall average flux of $0.18 \mu\text{g m}^{-2} \text{min}^{-1}$.

From Table 2, it can be observed that there are large seasonal variations in NMVOCs fluxes. With the exceptions of methanol and ethanol, the other four NMVOCs had their highest seasonal fluxes are in the summer. For these four compounds, the fluxes are significantly higher in summer than any of the other seasons. The lowest seasonal fluxes occurred in spring for three (acetaldehyde, 2-ethyl-1-hexanol, and ethanol) of the six NMVOCs. These spring fluxes are however, well within the winter flux values minus 1 standard deviation.

In comparison to previous anaerobic lagoon studies at swine CAFOs, Schiffman et al. (2001) identified four of these six compounds in three lagoon samples from three different North Carolina swine CAFOs. The two compounds they did not identify were methanol and ethanol. However, it should be noted that Schiffman et al. (2001) used Tenax to capture the compounds, which can be poor at trapping and quantifying alcohols.

3.1.2. Barn concentrations and emissions

Observational analysis of barn samples showed a similar number of compounds to lagoon samples (i.e. over 100). In barn samples, six NMVOCs had significantly larger concentrations and emissions in comparison to other NMVOCs. These six compounds were also identified in almost every sample and consisted of two alcohols (methanol and ethanol), an aldehyde (acetaldehyde), two ketones (acetone and 2,3-butanedione) and a phenol (4-methylphenol). With the exception of 2,3-butanedione, these compounds were identified by retention time and confirmed by GC–MS. 2,3-butanedione was not in the retention time database, however, it was identified by GC–MS.

Seasonal and overall average concentrations of the six NMVOCs with the largest barn emissions are presented in Table 3. It should be noted that canister sampling was conducted during the daytime. Therefore the barn concentrations and emissions values presented

for the NMVOCs are not representative of a full day as they do not take into account diurnal variations in flux. Of these six compounds, it can be seen that the highest seasonal concentrations for each compound range from 28.80 ppb for ethanol in spring to 5.25 ppb for 4-methylphenol in spring. The highest seasonal concentration for ethanol is at least an order of magnitude higher than seasonal concentrations for other NMVOCs (i.e. compounds that were not included in the group of six compounds). For 4-methylphenol, the highest seasonal flux was at a minimum approximately three times larger than the seasonal fluxes for other NMVOCs. Overall average concentrations ranged from 2.87 ppb for 4-methylphenol to 16.12 ppb for ethanol.

Of these six NMVOCs with large barn emissions, four of them also had large lagoon emissions in comparison to other VOCs. The exceptions were 2,3-butanedione and 4-methylphenol. In lagoon samples, 2,3-butanedione was identified, however its fluxes were $<0.01 \mu\text{g m}^{-2} \text{min}^{-1}$ for all seasons, and were therefore considered negligible. The compound, 4-methylphenol was also identified in lagoon samples and had a highest seasonal lagoon flux of $0.17 \mu\text{g m}^{-2} \text{min}^{-1}$ in summer and an overall average lagoon flux of $0.07 \mu\text{g m}^{-2} \text{min}^{-1}$. Conversely, the compounds MEK and 2-ethyl-1-hexanol, which had large lagoon emissions, were not included in the set of compounds that have the largest barn emissions. In barn samples, MEK had a largest seasonal concentration of 1.71 ppb in the fall and an overall average concentration of 1.10 ppb. 2-ethyl-1-hexanol had a largest seasonal barn concentration of 0.33 ppb in spring and an overall average barn concentration of 0.23 ppb.

Variations can be observed in the NMVOCs seasonal concentrations (Table 3). For example, methanol has its highest seasonal concentration in the fall season with a concentration of 20.33 ppb and its lowest concentration in the summer with a concentration of 6.84 ppb. Overall, it can be observed that the highest seasonal concentrations for all six compounds occur in the spring or fall, and all the lowest seasonal concentrations in the summer or winter.

Table 4 presents concentrations of these six NMVOCs from previous swine CAFO barn studies as well as the seasonal concentrations from this study. Compound concentrations observed in this study were similar to the concentrations measured in previous swine CAFO barn studies. Seasonal acetaldehyde concentrations in

Table 3
Seasonal and overall concentrations of NMVOCs with largest emissions from barns.

	Concentration (ppb)					
	Acetaldehyde	Acetone	2,3-butanedione	Ethanol	Methanol	4-methylphenol
Summer	1.44 ^a (2.21) ^b , $n = 10^c$	2.03 (2.72), $n = 10$	2.33 (3.04), $n = 10$	12.85 (15.28), $n = 10$	6.84 (6.29), $n = 10$	0.95 (1.11), $n = 10$
Fall	7.20 (6.59), $n = 10$	10.29 (4.30), $n = 10$	6.23 (6.22), $n = 10$	14.15 (7.81), $n = 10$	20.33 (11.35), $n = 9$	2.37 (2.50), $n = 10$
Winter	2.39 (4.86), $n = 9$	7.31 (4.49), $n = 9$	1.36 (2.08), $n = 9$	8.67 (15.89), $n = 9$	14.17 (12.32), $n = 9$	2.91 (4.31), $n = 9$
Spring	6.54 (2.32), $n = 9$	12.85 (4.89), $n = 9$	4.33 (2.30), $n = 9$	28.80 (7.33), $n = 9$	19.18 (5.89), $n = 9$	5.25 (1.73), $n = 9$
Overall average concentration	4.17	8.12	3.56	16.12	15.13	2.87

^a Mean value.

^b ± 1 standard deviation.

^c Number of samples.

this study ranged from 1.4 to 7.2 ppb, compared to 1.2–4.0 ppb in previous studies (Schiffman et al., 2001; Blunden et al., 2005). For acetone, previous studies measured concentrations ranged from 0.1 to 13.7 ppb (Feilberg et al., 2010; Schiffman et al., 2001; Blunden et al., 2005) in comparison to measured seasonal concentrations of 2.0–12.9 ppb in this study. Seasonal 2,3-butanedione concentrations in this study ranged from 1.4 to 6.2 ppb. Feilberg et al. (2010) is the only other known swine CAFO barn study that has reported 2,3-butanedione concentrations. This study reported a concentration of 1.3 ppb. In addition, Schiffman et al. (2001) identified the compound as being present in barn air samples, however, no concentration was reported. Measured ethanol and methanol concentrations in this study ranged from 8.7 to 28.8 ppb and 6.8–20.3 ppb, respectively. Blunden et al. (2005) is the only other study that has reported concentrations of these compounds, with concentrations ranging from 0.5 to 45.1 ppb for ethanol and 1.2–21.6 ppb for methanol. The Schiffman et al. (2001) study also identified the compounds in barn air samples, but no concentration was reported. Seasonal 4-methylphenol concentrations in this study ranged from 1.0 to 5.2 ppb, compared to 1.6–9.0 ppb in previous studies (Schiffman et al., 2001; Blunden et al., 2005; Trabue et al., 2008; Feilberg et al., 2010).

Seasonal emissions were calculated using the ventilation rate at the time of sampling. The barn ventilation rates and the seasonal and overall average emissions for the six NMVOCs in units of g day^{-1} are presented in Table 5. The NMVOC with the highest overall average emission is ethanol with a value of 37.95 g day^{-1} . The lowest was acetaldehyde with an overall emission rate of 7.97 g day^{-1} .

Four of the six compounds (acetone, methanol, 4-methylphenol, and ethanol) have their highest emission rate in the spring. The two other compounds, acetaldehyde and 2,3-butanedione had their highest emissions in the fall. With the exception of ethanol, all the other compounds have their 1st and 2nd highest seasonal emission rates in the spring and fall seasons. For all six compounds, the winter season had the lowest emission rate. The emission rates in this study (Table 5) are at least an order of magnitude higher than those reported by Feilberg et al. (2010). Their study, in addition to making concentration measurements, also determined emission rates. They reported emissions for acetone, 2,3-butanedione and 4-methylphenol with emission rates of 0.58 g day^{-1} for acetone, 0.21 g day^{-1} for 2,3-butanedione and 0.86 g day^{-1} for 4-methylphenol.

Animal weight is considered to be a factor that influences barn emissions, therefore seasonal emissions were normalized for 500 kg of live animal weight, also referred to as 1 animal unit (AU).

The live animal weight was calculated, based on pig production information at the barn during the sampling periods. The live animal weight, the corresponding pig production numbers, the number of weeks in rotation, and the normalized NMVOC seasonal emissions are presented in Table 5. Normalizing the emissions for live animal weight only affected the seasonal trend of one of the six compounds, which was methanol. In units of g day^{-1} the highest seasonal methanol emission rate was in the spring (28.46 g day^{-1}), followed by the fall with an emission rate of 26.92 g day^{-1} . However, the larger live animal weight in the spring compared to the fall, resulted in higher normalized emissions for methanol in the fall than the spring, 0.39 compared to $0.32 \text{ g day}^{-1} \text{ AU}^{-1}$, respectively. The overall average normalized emission rates ranged from acetaldehyde with an emission of $0.10 \text{ g day}^{-1} \text{ AU}^{-1}$ to ethanol with an emission of $0.45 \text{ g day}^{-1} \text{ AU}^{-1}$. The Feilberg et al. (2010) study did not report emissions normalized for the live animal weight during the sampling. However, an approximate comparison between this study and the Feilberg et al. (2010) study can be achieved by normalizing both studies' emissions for the number of pigs. In this study, the seasonal emissions for acetone, 2,3-butanedione and 4-methylphenol were normalized by the number of pigs in the barn in each sampling season. Similarly for the Feilberg et al. (2010) study, the emissions were normalized by the reported number of pigs during sampling, which was 16. As previously mentioned, the emission rates between the studies in units of g day^{-1} were an order of magnitude different. However, after normalizing the emissions for the number of pigs, the emissions rates were much similar. Seasonal emissions rates in this study ranged from 0.010 to $0.040 \text{ g day}^{-1} \text{ pig}^{-1}$ for acetone, 0.004 – $0.023 \text{ g day}^{-1} \text{ pig}^{-1}$ for 2,3-butanedione and 0.010 – $0.032 \text{ g day}^{-1} \text{ pig}^{-1}$ for 4-methylphenol. In comparison, emission rates from the Feilberg et al. (2010) study were $0.036 \text{ g day}^{-1} \text{ pig}^{-1}$ for acetone, $0.013 \text{ g day}^{-1} \text{ pig}^{-1}$ for 2,3-butanedione and $0.054 \text{ g day}^{-1} \text{ pig}^{-1}$ for 4-methylphenol.

3.2. Odorous NMVOC emissions

The emission of odorous NMVOCs are important locally, as odorous compounds can potentially effect human's health (Schiffman and Williams, 2005). In this study, two compounds with offensive odors, 4-methylphenol and 2,3-butanedione, were identified as having concentrations that exceeded their odor threshold. 4-methylphenol has reported odor thresholds of 0.06793 – 0.264 ppb (Rychlik et al., 1998) and 1.86 ppb (Devos et al., 1990), and has odor characteristics described as medicinal, phenolic and barnyard (Cai et al., 2006; Schiffman et al., 2001).

Table 4
NMVOCs concentrations from previous swine CAFO barn studies (ACE = Acetaldehyde, ACT = Acetone, 2,3 B = 2,3-butanedione, ETH = Ethanol, MET = Methanol, 4-MP = 4-methylphenol).

Reference	Location	Vent system	Manure collection system/description of sample location	Production type	Month	Concentration (ppb)					
						ACE	ACT	2,3 B	ETH	MET	4-MP
Schiffman et al. (2001)	NC	NS	NS/inside barn	NS	NS	4.0	1	– ^a	– ^a	– ^a	9
Blunden et al. (2005)	NC	N	Shallow pit/outside of barn near fan	Finish	Sep	2.1 ^b	13.7	–	45.1	21.6	5.0
Blunden et al. (2005)	NC	N	Shallow pit/outside of barn near fan	Finish	Jan	1.2	0.1	–	0.5	1.2	0
Blunden et al. (2005)	NC	M	Shallow pit/outside of barn near fan	Finish	Oct	3.6	1.5	–	1.0	3.0	0
Blunden et al. (2005)	NC	M	Shallow pit/outside of barn near fan	Finish	Feb	1.8	1.7	–	12.5	9.0	1.6
Trabue et al. (2008)	IA	M	Shallow pit/inside barn	Finish	NS ^c	–	–	–	–	–	2.4
Feilberg et al. (2010)	Denmark	M	Shallow pit/~ 1 m above exhaust duct entrance	Finish	May–June	–	5.1	1.3	–	–	3.9
This study	NC	M	Shallow pit/barn fan	Finish	June	1.4	2.0	2.3	12.8	6.8	1.0
This study	NC	M	Shallow pit/barn fan	Finish	Oct–Nov	7.2	10.3	6.2	14.1	20.3	2.4
This study	NC	M	Shallow pit/barn fan	Finish	Feb	2.4	7.3	1.4	8.7	14.2	2.9
This study	NC	M	Shallow pit/barn fan	Finish	Apr	6.5	12.9	4.3	28.8	19.2	5.2

NS = not specified, N = naturally ventilated, M = mechanically ventilated.

^a Compound identified, but concentration not reported.

^b Original concentrations reported by Blunden et al. (2005) in ppbC, therefore concentrations have been converted to ppb.

^c Barn temperature was reported as 15 °C.

Table 5

Seasonal ventilation rates, pig production information, NMVOC emissions, and normalized NMVOCs emissions (ACE = Acetaldehyde, ACT = Acetone, 2,3 B = 2,3-butanedione, ETH = Ethanol, MET = Methanol, 4-MP = 4-methylphenol).

Sampling Season	Ventilation rate ($\text{m}^3 \text{min}^{-1}$)	Number of pigs	Number of weeks in rotation	Average weight (kg)	Total live animal weight (kg)	Emissions ($\text{g day}^{-1}/\text{g day}^{-1} \text{AU}^{-1}$)					
						ACE	ACT	2,3 B	ETH	Met	4-MP
Summer	2040 ^a (589) ^b	884.5	7–8	48.7	43,049	5.07 ^c (6.79) 0.06 ^d (0.08)	9.58 (11.12) 0.11 (0.13)	16.60 (17.62) 0.19 (0.20)	55.33 (44.98) 0.64 (0.52)	22.25 (16.36) 0.26 (0.19)	9.05 (8.25) 0.11 (0.10)
Fall	725 (289)	994.5	4–5	34.6	34,428	13.92 (11.91) 0.20 (0.17)	24.96 (11.92) 0.36 (0.17)	22.93 (21.57) 0.33 (0.31)	28.40 (19.73) 0.41 (0.29)	26.92 (21.62) 0.39 (0.31)	10.90 (14.77) 0.16 (0.21)
Winter	435 (296)	476	20–21	116.6	55,513	1.78 (3.62) 0.02 (0.03)	9.10 (7.41) 0.08 (0.07)	2.04 (2.99) 0.02 (0.03)	6.71 (12.25) 0.06 (0.11)	11.32 (14.87) 0.10 (0.13)	5.43 (7.75) 0.05 (0.07)
Spring	850 (366)	874.5	8–9	50.6	44,262	11.12 (4.08) 0.13 (0.05)	34.85 (12.63) 0.39 (0.14)	18.00 (13.17) 0.20 (0.15)	61.34 (17.98) 0.69 (0.20)	28.46 (9.23) 0.32 (0.10)	28.22 (14.67) 0.32 (0.17)
Overall average emissions						0.10	0.24	0.19	0.45	0.27	0.16

^a Mean value.

^b ± 1 standard deviation.

^c Emissions in units of g day^{-1} .

^d Normalized emissions in units of $\text{g day}^{-1} \text{AU}^{-1}$ (1 AU (animal unit) = 500 kg of live animal weight).

2,3-butanedione has reported odor thresholds of 1.42–7.39 ppb (Rychlik et al., 1998) and 4.37 ppb (Devos et al., 1990), and an odor characteristic described as chlorine like, and buttery (Schiffman et al., 2001; Cai et al., 2006).

Of the thirty eight 4-methylphenol sample concentrations, 34 (~89%) were found to exceed the lowest odor threshold of 0.068 ppb and over two-thirds (26) of the sample concentrations also exceeded the 2nd highest odor threshold of 0.264 ppb. Furthermore, exactly half of the sample concentrations (19) exceeded the highest odor threshold of 1.86 ppb. Sample concentrations were generally highest in the spring sampling season, with all nine-sample concentrations exceeding the highest odor threshold. However, the highest individual sample concentration was 11.67 ppb, which occurred in the winter season. 23 of the 38 (~61%) 2,3-butanedione sample concentrations exceeded the lowest odor threshold of 1.42 ppb. There were 14 (37%) sample concentrations that exceeded the 2nd highest odor threshold of 4.37 ppb and 4 (11%) sample concentrations that exceeded the highest odor threshold of 7.39 ppb. Sample concentrations were highest in the fall and spring, with the highest sample concentration occurring in the fall with a concentration of 22.28 ppb.

4-methylphenol and 2,3-butanedione were classified as having large emissions from barns in comparison to other compounds, therefore the seasonal barn concentrations, emissions, and normalized emissions of these odorous compounds are presented in Table 4 and Table 5.

Lagoon emissions are also a potential source of odorous compounds. As mentioned, 4-methylphenol had a highest seasonal lagoon flux of $0.17 \mu\text{g m}^{-2} \text{min}^{-1}$ in summer and an overall average lagoon flux of $0.07 \mu\text{g m}^{-2} \text{min}^{-1}$. All seasonal lagoon fluxes for 4-methylphenol are presented in Table S1 (see Supplementary information). However, for 2,3-butanedione, seasonal lagoon fluxes were all $<0.01 \mu\text{g m}^{-2} \text{min}^{-1}$ and are therefore considered negligible.

It should be noted that the barn samples are taken at the barn exhaust and the lagoon samples just above the lagoon surface, therefore the odorous NMVOC concentrations presented are likely not representative of fence-line/property boundary concentrations.

3.3. Hazardous air pollutants emissions

Hazardous air pollutants (HAPs) are defined by the U.S. EPA as pollutants that are known to cause cancer or other serious health effects such as damage to the immune system, reproductive, developmental, neurological, and respiratory effects (U.S. EPA, 2009b). The U.S. EPA listed 188 HAPs (U.S. EPA, 2009a), of which

162 are NMVOCs. In this study, three HAPs were identified, that were also classified as having the largest emissions from the lagoon in comparison to other compounds. These were acetaldehyde, methanol, and MEK. Acetaldehyde and methanol were also NMVOCs that were classified as having the largest emissions from barns in comparison to other compounds. A further HAP identified with the large emissions from barns in comparison to other compounds was 4-methylphenol. The HAP, hexane was also identified in lagoon and barn emissions. Lagoon emissions for acetaldehyde, methanol, and MEK are presented in Table 2, as these compounds were identified as having large lagoon emissions. As 4-methylphenol was also identified as an odorous compound, its lagoon emissions are presented in Table S1 (see Supplementary information). Seasonal lagoon fluxes for hexane were $<0.01 \mu\text{g m}^{-2} \text{min}^{-1}$ and were therefore considered negligible. Barn emissions for acetaldehyde, methanol, and 4-methylphenol are presented in Tables 3 and 5, as these compounds were identified as having large barn emissions. Barn emissions for MEK and hexane are presented in Table S2 (see Supplementary information). In summary, MEK had an overall average concentration of 1.10 ppb and an overall average normalized emission of $0.04 \text{g day}^{-1} \text{AU}^{-1}$. For hexane, the overall average concentration was 0.63 ppb and the overall average normalized emission was $0.02 \text{g day}^{-1} \text{AU}^{-1}$. For the HAP compounds that have been previously identified as a NMVOC with large emissions or as an odorous compound, further analysis of the emissions can be found in the relevant sections.

Additionally, nine other HAPs were identified by retention time in lagoon and barn samples. These were benzene, ethylbenzene, methyl chloride, styrene, toluene, o-xylene, m-xylene, p-xylene and 2,2,4-trimethylpentane. All of these compounds had lagoon fluxes less than $0.01 \mu\text{g m}^{-2} \text{min}^{-1}$ and barn concentrations less than 0.1 ppb.

3.4. Influence of environmental parameters on NMVOC emissions

3.4.1. NMVOC lagoon fluxes

Seasonal environmental parameters for the canister samples are presented in Table 6. Seasonal average lagoon temperature and air temperature for the canisters samples varied from 12.34 to 27.00 °C and 8.59–26.74 °C, respectively. Seasonal average pH for the canister samples varied from 7.33 to 8.08. The influence of environmental parameters on lagoon fluxes was investigated using the coefficient of correlation (r^2) and their respective p -values. This statistical analysis was performed on the six NMVOCs with large lagoon emissions and on any odorous or HAP compound that has seasonal lagoon fluxes greater than $0.01 \mu\text{g m}^{-2} \text{min}^{-1}$, which

Table 6
Seasonal environmental parameters for canister samples.

Season	Lagoon temperature (°C)	Lagoon pH	Air temperature (°C)	Wind speed (m s ⁻¹)
Summer	27.00 ^a (3.34) ^b , n = 10 ^c	7.33 (0.16), n = 5	26.74 (3.32), n = 10	2.23 (0.87), n = 10
Fall	23.27 (1.67), n = 10	7.63 (0.16), n = 10	25.49 (3.01), n = 10	3.07 (2.03), n = 10
Winter	12.34 (2.50), n = 11	8.08 (0.11), n = 11	8.59 (1.23), n = 11	2.38 (0.77), n = 11
Spring	19.59 (1.77), n = 10	8.03 (0.07), n = 10	18.30 (6.24), n = 10	4.37 (1.80), n = 10

^a Mean value.

^b ±1 standard deviation.

^c n is the number of observations.

applied to 4-methylphenol. The environmental parameters investigated in the analysis were lagoon temperature, lagoon pH and ambient air temperature. Ambient air temperature was included in the analysis, as the effect of the dynamic-flow through chamber system on chamber air temperature is small. Arkinson (2003) using this chamber system for flux measurements determined the difference in air temperature to be 1.55 ± 2.30 °C between the inside and outside of the chamber.

Of the seven compounds, all but ethanol had a highly significant correlation ($p < 0.01$) with an environmental parameter. Furthermore, ethanol also did not have a significant ($p < 0.05$) correlation with an environmental parameter. Five NMVOCs (acetaldehyde, acetone, 2-ethyl-1-hexanol, MEK and 4-methylphenol) had a highly significant relationship ($p < 0.01$) with lagoon pH. Of these, the compound with the highest r^2 value was acetaldehyde (0.324) (Fig. 1), which was only slightly higher than the r^2 value for MEK (0.317). The r^2 values for acetone, 2-ethyl-1-hexanol and 4-methylphenol were 0.20, 0.26 and 0.23, respectively. The relationship between lagoon flux and lagoon pH was negative for all five NMVOCs. Two of these five compounds, acetone and MEK also had highly significant relationships ($p < 0.01$) with lagoon temperature, and had higher r^2 values than for lagoon pH. The r^2 values for these positive correlations were 0.33 for MEK (Fig. 2) and 0.32 for acetone. Methanol was the only compound with a highly significant relationship ($p < 0.01$) with air temperature. The r^2 value for this positive correlation was 0.29. It is not known why methanol lagoon flux had a better correlation with air temperature than lagoon temperature. Some compounds also had secondary significant ($0.01 \leq p < 0.05$) correlations with environmental parameters. A presentation of these results is included in Table S3 (see Supplementary information), which provides all the r^2 values and p -values for each compound against each environmental parameter.

The positive relationship between lagoon temperature and flux can be explained by the effect of temperature on flux, as increases

in lagoon temperature can increase the mass transfer coefficient of chemical compounds at the air-lagoon surface interface. Increases in lagoon temperature can also increase the Henry's law constant which relates to the equilibrium of a chemical compound at the lagoon-air surface interface. Additionally, an increase in lagoon temperature can increase the rate of decomposition and thus increase the amount of organic carbon available.

As mentioned, the relationship between lagoon flux and pH was negative i.e. as pH increased, the flux of NMVOCs decreased. However, there is no known literature on the effects of pH to support this relationship.

3.4.2. NMVOC barn emissions

The variance in observed NMVOC emissions is the result of the influence of a range of factors. Some of the most important factors are those that influence the amount of organic carbon in the barn, which is determined by the amount of manure in the barn and the organic carbon content of the manure. The amount of barn manure is influenced by the total animal weight, which was taken into account in this study. However, there are other manure management factors such as the amount of time since the barn was cleaned and flushing frequency that will also influence the amount of manure inside the barn. The organic carbon content of the manure is influenced by the carbon content of the feed and the efficiency of the swine in retaining the carbon. NMVOC emissions are also influenced by environmental factors that affect the rate of release of compounds from the manure into the air. Important environmental factors that may influence emissions include temperature, which was measured at the barn fan outlet. Using barn temperatures at the time of canister sampling, the average barn temperature was highest in the summer, with a temperature of 31.15 ± 2.48 °C, followed by spring and fall with average barn temperatures of 27.61 ± 1.62 °C and 23.70 ± 1.18 °C, respectively. The lowest average barn temperature was winter with a value of 19.78 ± 2.78 °C. The

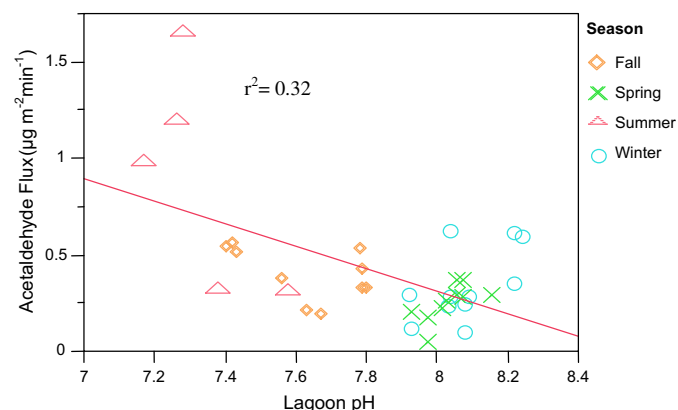


Fig. 1. The relationship between acetaldehyde flux ($\mu\text{g m}^{-2} \text{min}^{-1}$) and lagoon pH.

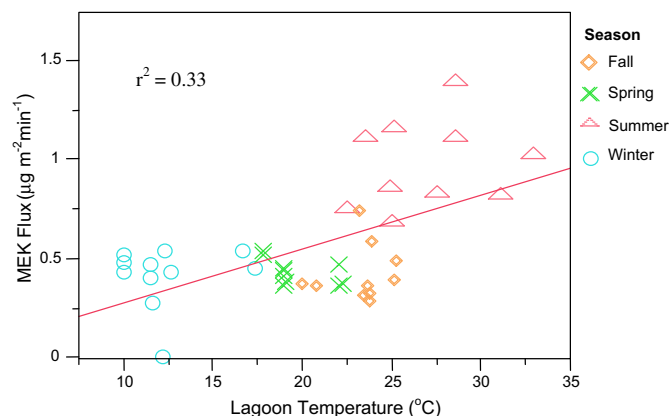


Fig. 2. The relationship between methyl ethyl ketone (MEK) flux ($\mu\text{g m}^{-2} \text{min}^{-1}$) and lagoon temperature (°C).

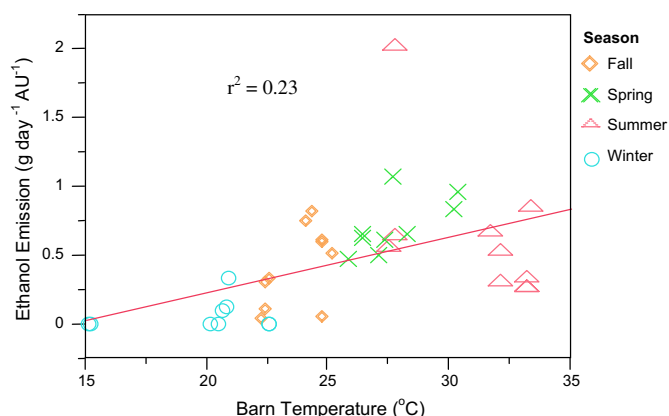


Fig. 3. The relationship between ethanol emissions ($\text{g day}^{-1} \text{AU}^{-1}$) and barn temperature ($^{\circ}\text{C}$).

Table 7

Live animal weight calculations for the state of North Carolina for the December, 2008–February, 2009 period.

	Average weight (lb)	Number	Total weight (lb)
Breeding	433	980,000	4.24×10^8
< 60 lbs	30	3,300,000	9.90×10^7
60–119 lbs	90	1,930,000	1.74×10^8
120–179 lbs	150	1,750,000	2.63×10^8
>180 lbs	220	1,640,000	3.61×10^8
Total live animal weight (lbs)			1.32×10^9
Total live animal weight (kg)			5.99×10^8

influence of barn temperature on normalized barn emissions was determined using r^2 values and their respective p -values. This statistical analysis was performed on the six NMVOCs with large emissions and any odorous or HAP compound that has seasonal barn concentrations greater than 0.1 ppb, which applied to hexane and MEK.

Of the eight NMVOC's, only ethanol had a significant relationship with barn temperature (i.e. p -value < 0.05) with a r^2 value of 0.23 ($p < 0.01$) (Fig. 3). The other seven NMVOCs normalized emissions were found to have little or no relationship with barn temperature, with all the r^2 values for this relationship less than 0.06 and the corresponding p -values greater than 0.05. However, the weak relationships between barn temperature and NMVOCs normalized emissions were expected, due to the dynamic barn environment. A barn has a varying ventilation rate, therefore the amount of gaseous emissions leaving the barn is constantly

Table 8

NMVOC's North Carolina lagoon, barn and swine CAFO (lagoon + barn) emissions.

Compound	NC lagoon emissions (kg yr^{-1})	% lagoon contribution to swine CAFO emissions	NC barn emissions (kg yr^{-1})	% barn contribution to swine CAFO emissions	NC swine CAFO emissions (kg yr^{-1})
Acetaldehyde	9782 ^a (9954) ^b	18.2	44,016 (35,563)	81.8	53,798 (45,517)
Acetone	30,983 (23,158)	23.0	103,781 (71,467)	77.0	134,765 (94,625)
2,3-butanedione	NQ	–	81,704 (56,460)	~100	81,704 (56,460)
Ethanol	8701 (9805)	4.2	197,666 (126,032)	95.8	206,367 (135,837)
2-ethyl-1-hexanol	2616 (3519)	18.9	11,232 (8520)	81.1	13,848 (12,039)
Hexane	NQ	–	9642 (6133)	~100	9642 (6133)
Methanol	17,464 (5546)	13.0	117,268 (53,920)	87.0	134,732 (59,466)
MEK	8208 (4089)	31.4	17,997 (13,231)	68.6	26,238 (17,320)
4-methylphenol	1097 (947)	1.6	68,967 (50,824)	98.4	70,064 (51,771)

NQ = Not quantified.

^a estimated emissions.

^b Uncertainty values associated with emissions. These values were calculated, based on the standard deviation of the overall average lagoon fluxes and overall average normalized barn emissions, respectively.

changing with time. This in turn affects the concentration of a gaseous compound inside the barn. Therefore, it is hard to determine the extent of the influence of environmental parameters, such as barn temperature on gaseous barn emissions.

There are other environmental factors that may influence NMVOC barn emissions such as manure pH and the air velocity above the manure surface. It was though beyond the scope of this study to measure these environmental parameters.

3.5. North Carolina NMVOCs emissions

The overall average lagoon fluxes and the overall average normalized barn emissions for the NMVOCs reported in this paper were used to estimate their swine CAFO emissions for North Carolina. To determine the North Carolina lagoon emissions for the NMVOCs, the total lagoon area for North Carolina was estimated. Aneja et al. (2000) used a SPOT satellite image of North Carolina to determine that the average size of a swine lagoon is approximately 1 ha (10,000 m^2). The number of swine CAFOs in North Carolina was provided by the United States Department of Agriculture (USDA). Their most recent estimate of the number of swine CAFOs was 2800 for the year 2007 (USDA, 2009). Using this information and the NMVOCs overall average lagoon flux, the North Carolina lagoon emissions for these compounds were estimated.

The North Carolina barn emissions for the NMVOCs were calculated based on the most recent estimate of the number and weight of pigs in North Carolina (December, 2008–February, 2009 period), as provided by the USDA (USDA, 2009). The USDA provided information on swine population in five different classes; breeding, under 60 lbs, 60–119 lbs, 120–179 lbs, and over 180 lbs. It was determined that the average weight of a breeding pig was 433 lbs (Williams, 2005). The under 60 lbs category was interpreted as representing feeder pigs, which is estimated to have an average weight of 30 lbs (Williams, 2005). For 60–119 lbs and 120–179 lbs the average of the weight range was used, i.e. 90 and 150 lbs. For the >180 lbs category, 220 lbs was estimated to be the average pig weight. From this the total live animal weight for North Carolina was calculated, which is presented in Table 7. Using this and the NMVOCs overall average normalized barn emission, the North Carolina barn emissions for these compounds were estimated. The North Carolina barn emissions, the North Carolina lagoon emissions, and the North Carolina Swine CAFO (lagoon + barn) emissions for the NMVOCs reported in this paper are presented in Table 8. Of the NMVOCs, ethanol has the largest North Carolina swine CAFO emission at $206,367 \text{ kg yr}^{-1} \pm 135,837$ (\pm represents the uncertainty associated with emissions. Values were calculated, based on the standard deviation of the overall average lagoon fluxes and overall average normalized barn emissions, respectively.). The

second highest is acetone with an emission of $134,765 \text{ kg yr}^{-1} \pm 94,625$, which is closely followed by methanol with an emission of $134,732 \text{ kg yr}^{-1} \pm 59,466$. The 4th and 5th highest are 2,3-butanedione and 4-methylphenol with emissions of $81,704 \text{ kg yr}^{-1} \pm 56,460$ and $70,064 \text{ kg yr}^{-1} \pm 51,771$, respectively. The next highest is acetaldehyde with an emission of $53,798 \text{ kg yr}^{-1} \pm 45,517$. MEK and hexane had smaller emissions, $26,238 \text{ kg yr}^{-1} \pm 17,320$ and $9642 \pm 6133 \text{ kg yr}^{-1}$, respectively. From Table 8, it can be observed that barns contribute 68.6% to ~100% of individual NMVOCs estimated North Carolina swine CAFO emissions.

4. Conclusions

A comprehensive analysis of NMVOC emissions from a swine CAFO was performed by measuring NMVOCs emissions over four seasonal sampling periods from an anaerobic lagoon and barn at a swine CAFO in North Carolina during 2007–2008. In lagoon samples, there were six NMVOCs (acetone, acetaldehyde, ethanol, 2-ethyl-1-hexanol, methanol and methyl ethyl ketone (MEK)) that were classified as having significantly larger emissions in comparison to other NMVOCs. Overall average lagoon fluxes of these NMVOCs ranged from $0.18 \mu\text{g m}^{-2} \text{ min}^{-1}$ for 2-ethyl-1-hexanol to $2.11 \mu\text{g m}^{-2} \text{ min}^{-1}$ for acetone. In barn samples there were also six NMVOCs (acetaldehyde, acetone, 2,3-butanedione, ethanol, methanol and 4-methylphenol) that were classified as having significantly larger emissions in comparison to other compounds. Overall average concentrations for these six compounds ranged from 2.87 ppb for 4-methylphenol to 16.12 ppb for ethanol. The overall average normalized emissions ranged from $0.10 \text{ g day}^{-1} \text{ AU}^{-1}$ for acetaldehyde to $0.45 \text{ g day}^{-1} \text{ AU}^{-1}$ for ethanol.

To investigate the potential local environmental impact of NMVOCs emissions, compounds with offensive odors were identified in lagoon and barn samples. Two compounds (2,3-butanedione and 4-methylphenol) were identified as such in lagoon and barn samples. Both compounds were found to exceed their odor thresholds frequently.

Hazardous air pollutants (HAPs) were identified in lagoon and barn samples. Three HAPs (methanol, acetaldehyde and MEK) were identified in lagoon samples that were classified as having large lagoon emissions in comparison to other NMVOCs. There were also three HAPs (methanol, acetaldehyde and 4-methylphenol) identified in barn samples that were classified as having large barn emissions in comparison to other NMVOCs.

The overall average lagoon fluxes and overall average normalized barn emissions for the NMVOCs reported in this paper were used to estimate their swine CAFO emissions for North Carolina. There were three NMVOCs that had considerably larger North Carolina swine CAFO emissions than other compounds. These were ethanol, acetone and methanol, with emissions of $206,367 \text{ kg yr}^{-1} \pm 135,837$, $134,765 \text{ kg yr}^{-1} \pm 94,625$ and $134,732 \text{ kg yr}^{-1} \pm 59,466$, respectively. Barns were found to compose the majority of individual compounds North Carolina swine CAFO emissions, with contributions ranging from 68.6% to ~100%.

This body of research will add to the current limited information on NMVOCs emissions from swine CAFOs and help to assess the impacts of the intensification of agriculture on air quality.

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Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2011.10.055.

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