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Effect of Ozonation on Odor and Selected Odorants in a Swine Housing Facility

H. Kim-Yang¹, S.H. Davies¹, J. D. Hill² and R. D. von Bernuth³

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Abstract. *The efficacy of a commercial ozonation system for reduction of odors was studied. In this system ozone was distributed throughout the animal housing facility using a manifold. In this study the VOCs in the air and the odor of the air were monitored. The VOCs were measured using thermal desorption tubes and SPME fibers with PDMS/CAR coatings. Ozone was effective in reducing odor detection threshold, but did not significantly reduce the odor intensity or odor offensiveness in the building. Sensory testing indicated that the characteristics of the air in the ozonated rooms were different from those in control room. Monitoring of the VOCs present in the air showed that ozonation reduced the levels of phenolic and indolic compounds in the swine building air, however, it did not reduce the level of volatile fatty acids in the air.*

Keywords. Odor, ozonation, livestock, VOCs, thermal desorption, SPME

¹ Michigan State University, Biosystems Engineering, East Lansing MI. 48824

² Michigan State University, Department of Animal Science, East Lansing MI. 48824; Member ASAE

³ Michigan State University, Biosystems Engineering, East Lansing MI. 48824; Member ASAE

INTRODUCTION

Ozone is a powerful oxidizer. It has been widely used for disinfection and the oxidation of contaminants in water, and municipal and industrial wastewaters, (e.g., Kruithof and Masschelein, 1999; Lezcano et al., 1999; Carini et al., 2001; Finch et al., 2001; Turan-Ertas, 2001). Ozone is able to oxidize odorous volatile compounds such as; phenol, p-cresol, p-ethylphenol, indole and skatole, in swine slurry and reduce malodors in stored swine slurry (Wu, 1999).

In a recent paper, “Century 21 – Pregnant with Ozone”, Rice (2002) summarized the previous research on the use of ozone for odor control. According to this paper, “Many odors can be destroyed by ozone – e.g., hydrogen sulfide, odors caused by cigars and cigarettes, and volatile organic compounds (VOCs), perspiration odors, odors in animal rearing facilities, etc.”

Ozone has been used for the indoor air quality control in recreational areas such as casinos, offices and hotels. A study by Kilham and Dodd (1999) showed that ozone could be used to remove offensive odors and to destroy volatile organic compounds in buildings. Ozone was introduced into the air conditioning system of the building. The ozonation of volatile organic compounds (VOCs) found in tobacco smoke has been examined (Shaughnessy et al. 2001). Shaughnessy et al. showed that ozonation was not effective at reducing the concentrations of the compounds with unsaturated carbon bonds. The effect of ozonation on sub-micron particles in an office building has been studied (Wescheler and Shields, 1999). Terpenes (limonene, alpha-terpene, or a terpene-based cleaner whose major constituent is alpha-pinene) were introduced into the office and the subsequent particle formation and redistribution were monitored. This study showed that ozone/terpene reactions were the significant source of sub-micron particles in the office building.

Ozone in combination of an activated carbon has been used to remove hydrogen sulfide in the presence of concurrent substances, such as toluene, ethanol, and n-butanol (Masuda et al., 2001). This study showed that the ozone increased the removal efficiency for hydrogen sulfide.

Ozonation in livestock production units has been studied in several commercial and University research farms (Edie, 2001; Vansickle, 1999; Ozone Solutions Inc., 2002). It was found that ozone decreased the number of E. coli by 75%, reduced by 50% the number of pigs laid on, and increased pigs weaning weight by 15% (Ozone Solutions Inc., 2002). According to this report, the sows consumed up to 20% more feed because of better air quality. A recent study showed that ozone reduced the concentration of low molecular weight volatile fatty acids on the dust samples taken in a swine house (Oehrl et al., 2000).

Objectives

This research was conducted to observe the air quality changes that resulted during the ozonation of air in a swine housing facility. The most widely reported malodorous volatile organic compounds associated with livestock operations (i.e., VFAs and phenolics) were monitored. The experiment was conducted in rooms where the air was ozonated and in a control room where the air was not ozonated.

Swine Housing Facility

Four environmental rooms, located at Michigan State University Dairy Teaching and Research Farms, were used for this research. The layout of the facilities is shown in Figure 1. Each room contained one 12' by 16' pen. Each pen contained 24 pigs. A manure handling and storage pan was located directly beneath the flooring of each pen. The air samples were taken 1 meter above

the flooring. Two heating/ventilation/air conditioning (HVAC) systems were installed in the one system controlled rooms 1 and 2 and the other system controlled rooms 3 and 4. Temperature was measured using a digital thermometer (copper constant thermocouple) and a data-logger (CSI 23-X). Ventilation airflow rates were determined based on air velocity traverses across exhaust fan outlet cones. The air velocity measurements were made using a vane anemometer. The air ventilation rate was calculated using the cross sectional area and the air velocity.

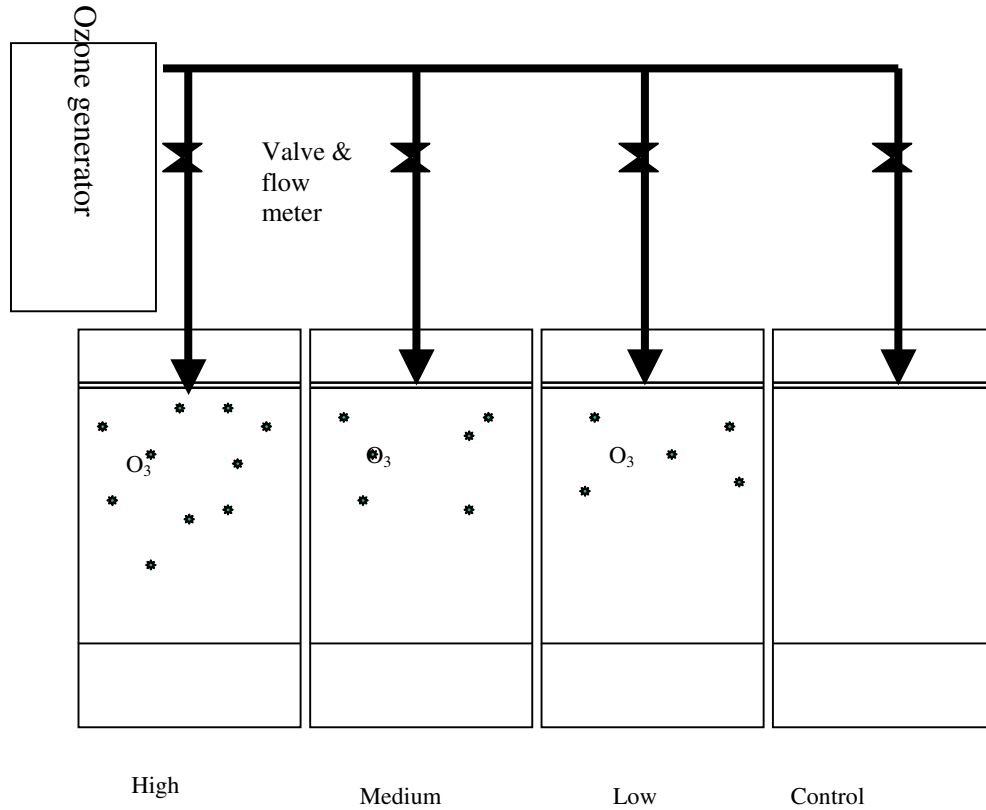


Figure 1. Environmental chambers at Michigan State University.

Ozone Distribution

Figure 2 shows the ozone distribution system in the rooms. Ozone was injected at the rates of 0, 1.36, 2.72, and 4.10 m³/day to produce a target ozone dose of approximately 0 (control), 0.01 (low), 0.05 (medium), and 0.1 (high) ppm, respectively. Ozone was distributed to the rooms through PVC tubing. Every group of 24 pigs was subjected to a fixed level of ozonation, each group of pigs was moved every two weeks to another randomly selected pen.

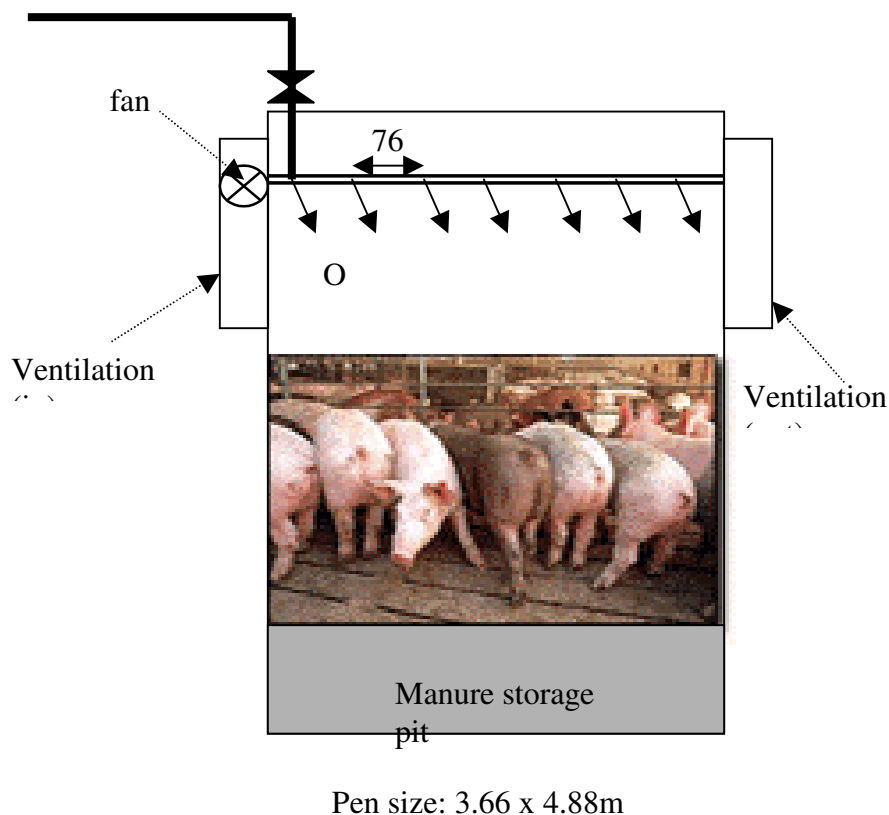


Figure 2. Diagram of one pen in the environmental chamber at MSU.

Air sampling

The experiment began on July 15th, 2001 and was terminated on September 30th, 2001. Air samples were taken bi-weekly. Sampling was started at noon and was conducted every four hours until noon of the next day. Samples were collected on thermal desorption tubes and Solid Phase Microextraction (SPME) fibers.

The thermal desorption tubes were purchased from Supleco Co. (Bellefonte, PA). The tubes contained Tenax TA and Carboxen or Tenax TA and Carbosieve SIII. The tubes were conditioned at 280°C for 30 minutes to remove any contaminants on the sorbent material. Three liters (3L) of high purity helium was passed through the tube during conditioning. The conditioned tube was sealed with a Teflon plug and wrapped with aluminum foil and placed in an opaque clean container and stored in a refrigerator at 4°C until it was analyzed. The sampling

flow rate was regulated between 150 to 200 mL/min and the total sample volume did not exceed 5 liters.

Supelco field SPME field samplers (504831) were used to collect the SPME samples. PDMS/CAR fiber coatings were used. New fibers were conditioned at 280°C for 30 minutes prior to use according to the manufacturers. The conditioned samplers were wrapped in aluminum foil and stored in the refrigerator until they were used. After sampling, SPME fibers were carried in an ice-box to the laboratory and the samples was stored in the refrigerator until they were analyzed.

Desorption methods

An Aerotrap 6000 (Tekmar) was used for the thermal desorption of the sorbent tubes. A cryo-trap in the Aerotrap concentrates the volatiles in -165°C . The instrument contains a moisture trap to remove water from the sample. The conditions used for the thermal desorber are as follows; trap cool at -165°C , sample desorption at 250°C for 20 minutes, trap desorb preheat at 200°C , the traps were desorbed for 5 minutes. High purity helium was used for the carrier gas and a carrier gas flow rate of 20 mL/min was used.

A DB-5MS (60m, 0.25mm ID, 0.25 μm film thickness) capillary column was used for the separation of the analytes.

Results

Air ventilation and temperature

Figure 3 shows the temperature in the four rooms. Temperature was measured at two locations in each room and the data reported in this figure is the average temperature in each room.

Temperature readings were recorded every 5 minutes. In this figure, one hour average temperature values were used.

Figure 4 shows the temperature changes and ventilation rates in room 1 and 2 from July 31st to September 28th. The graph shows that the ventilation rates increased as the room temperature increased.

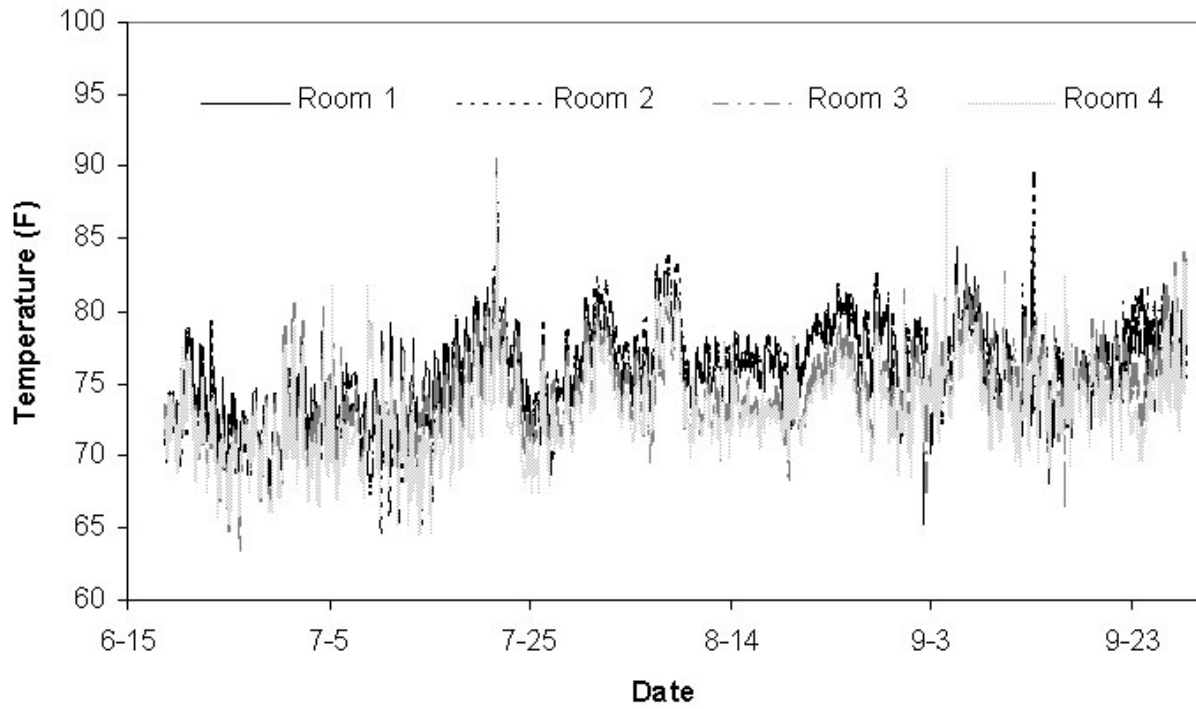


Figure 3. Temperature changes in the environmental chambers.

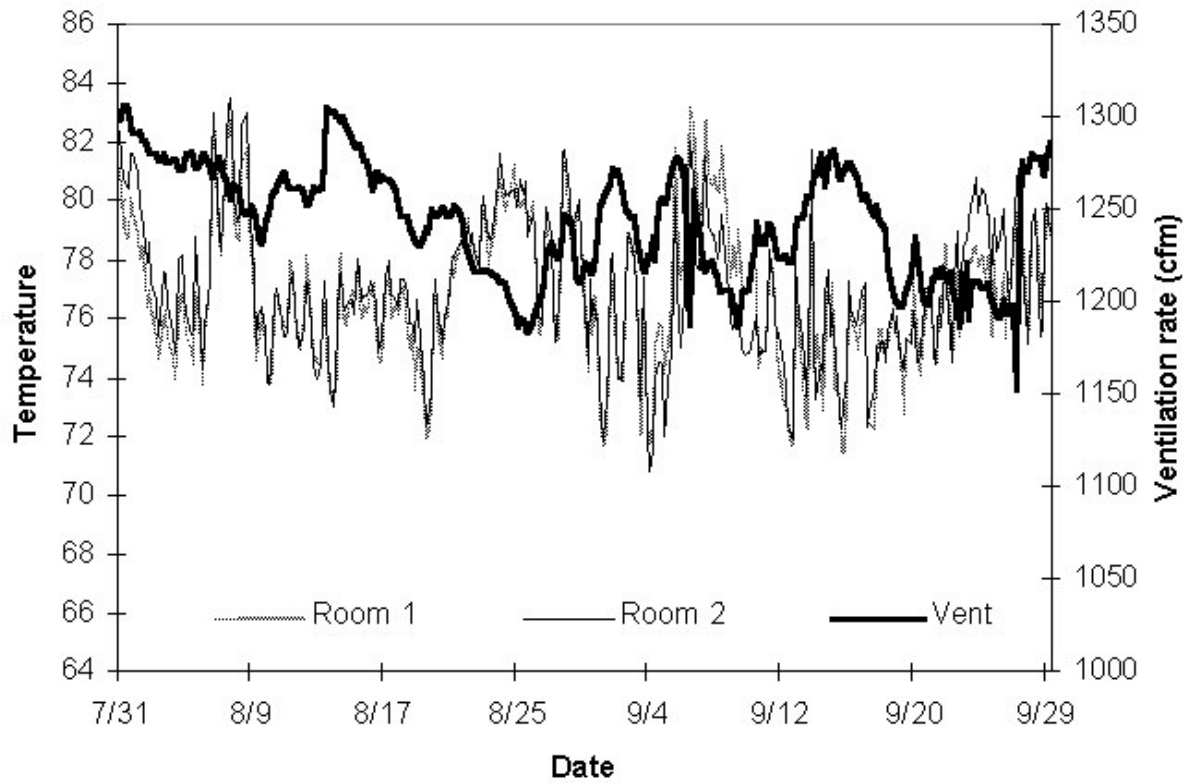


Figure 4. Temperature and ventilation rate in swine building (Room 1&2).

Olfactometry data

Four olfactometric measurements were made: dilution threshold, offensiveness, intensity, and odor characteristics. These measurements were made by the Agricultural Air Quality Laboratory at Purdue University, West Lafayette, IN.

Dilution threshold (DT)

The data in Table 1 show that the detection threshold for odor was higher for the control room and that the DTs decreased as ozone dosage increased. The effect of ozone on the odor dilution threshold was highly significant at $p < 0.01$ for all ozonated rooms. The odor dilution threshold at the high dosage was significantly different from that low ozone dosage, while there were no differences in odor DTs at medium and low ozone dosages, or between the odor DTs in the rooms that were dosed at high and medium levels. These results some benefit is gained by ozonation but that there is no significant additional benefit as to the reduction of odor DTs in highly ozone dosage room as compared to the medium dosage.

Table 1. Detection Threshold for air samples in swine building.

Date	Inlet	High Ozone	Medium Ozone	Low Ozone	Control	NB*
7/6/01	46	327	386	621	1090	1510
8/3/01	48	382	683	683	808	1580
8/31/01	63	676	866	799	1110	1430
9/28/01	39	317	622	734	944	1030

*NB: normal butanol

Odor offensiveness and intensity

Figure 5 shows the odor offensiveness of the air samples. Ozone did not significantly reduce the odor offensiveness in swine building air at $P > 0.5$ for all treatments. The result suggests that the VOCs that affect offensiveness are still present after ozone treatment or the by-products by the ozonation have an offensive odor. Figure 6 shows the odor intensity in the swine building air in the control and ozonated rooms. Again, ozonation had no significant effect on odor intensity.

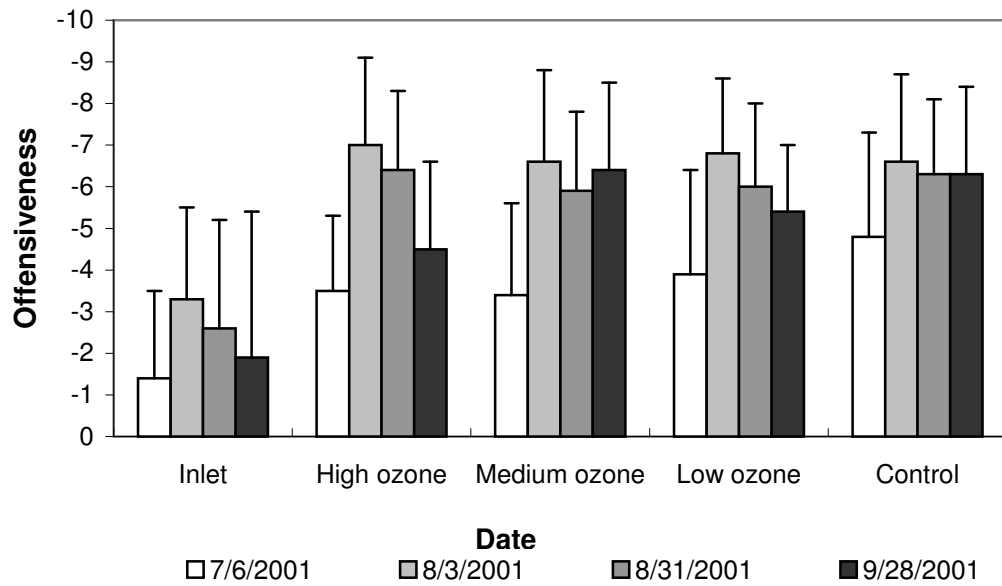


Figure 5. Effect of ozonation on odor offensiveness in swine building air. Samples were taken at noon.

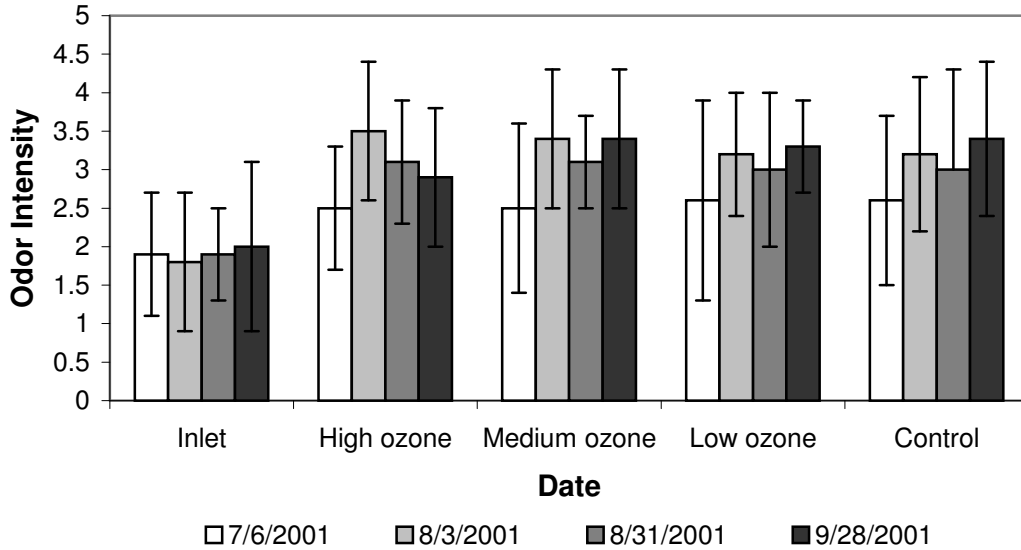


Figure 6. Effect of ozonation on odor intensity in swine building air. Samples were taken at noon.

Odor characteristics

Table 2 shows the odor characteristics of the air samples from the control and ozonated rooms. Both ozonated and control room had odor characteristics of manure and urine. The highlighted data indicates the unique smells in the ozonated rooms which are different from the odor

characteristics in control room. The data indicate that the air in the ozonated rooms had slightly different odor characteristics from that in the control room. Air in the ozonated room was reported to have a greasy, soapy, sour, mossy or musky odor, whereas the control room did not show such odor characteristics. Soapy smell was reported in all ozonated rooms. Smells, such as sour, sauerkraut, vomit smells were reported in low, medium, and high ozone level room, respectively. As ozone level increased the intensity of the these smells increased. This finding suggests that ozone may produce the smells commonly associated with fatty acids.

Olfactometry Summary

Olfactometry data showed that the ozone was effective in the reducing odor dilution threshold, however ozone did not significantly reduce the odor offensiveness and intensity. The odor characteristics of the ozonated air were different from those of the air in the control room. These results suggest that some odorous compounds were destroyed by ozone but the residual compounds still exhibited a strong and offensive odor. Another possibility is that the by-products formed during ozonation had an offensive odor. A previous study of the effect of ozonation on odor and taste in drinking water also showed that ozone altered odor characteristics in drinking water, but it did not reduce odor intensity (Hargesheimer and Watson, 1996). A study by Esswein and Boeniger (1994) showed that ozone was not effective in reducing formaldehyde where formaldehyde is the main odor producer. A publication from US EPA also showed that the ozone was not effective in reducing odor causing chemicals at concentrations below the public health concern (IOA Publications, 2002).

Effect of ozonation on VOCs in the Swine HOUSING Unit

As described in the method section, two air sampling methods (SPME, TD) were used. For each sampling method, two groups of compounds were analyzed; phenolic compounds and VFAs.

SPME air sampling

Volatile Fatty Acids

Short chain VFAs (C2, C3, iso-C4, C4, iso-C5, and C5) were determined. . For the VFAs, peak broadening was observed in chromatogram, however, this is not related to the sampling process, but it is due to the polarity and thickness of the stationary phase on the GC.

For the SPME measurements, the individual VFA concentrations were converted to a carbon basis, added and reported as total carbon. The data shown in the Figure 7 shows the total VFAs recovered. A t-test for data for the control and ozonated rooms showed that ozonation had no significant on total VFA concentrations in the swine building air at the 95% confidence level. The VFA concentrations appeared to decrease over time. This result suggests that generation of VFAs decreases, as pigs get older. However, the effect of pig ages on VFAs generation has not been well documented.

