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# Field-scale testing of mobile laboratory for mitigation of gaseous emissions from the swine farm with UV-A photocatalysis

## Abstract

UV-A photocatalysis has been investigated to comprehensively mitigate odor and selected air pollutants in the livestock environment. This study was conducted to confirm the performance of UV-A photocatalysis on the swine farm. The objectives of this research were to (1) scale-up of the UV-A photocatalysis treatment, (2) evaluate the mitigation of odorous gases from swine slurry pit, and (3) evaluate the effect of suspended particulate matter (PM). We tested UV-A photocatalysis at a mobile laboratory-scale capable of treating  $\sim 0.2 - 0.8 \text{ m}^3 \cdot \text{s}^{-1}$  of barn exhaust air. The targeted gaseous emissions of barn exhaust air were significantly mitigated ( $p < 0.05$ ) up to 40% reduction of measured odor; 63%, 44%, 32%, 40%, 66%, and 49% reduction of dimethyl disulfide, isobutyric acid, butanoic acid, p-cresol, indole, and skatole, respectively; 40% reduction of  $\text{H}_2\text{S}$ ; 100% reduction of  $\text{O}_3$ ; and 13% reduction of  $\text{N}_2\text{O}$ . The PM mitigation effect was not significant. Formaldehyde levels did not change, and a 21% generation of  $\text{CO}_2$  was observed. The smell of benzoic acid generated in UV-A treatment was likely one of the compounds responsible for the less-offensive overall odor character of the UV-treated emissions. Results are needed to inform the design of a farm-scale trial, where the interior barn walls can be treated with the photocatalyst, and foul air will be passively treated as it moves through the barn.

## Keywords

Air pollution control, air quality, volatile organic compounds, odor, environmental technology, advanced oxidation, UV-A, titanium dioxide

## Disciplines

Agriculture | Bioresource and Agricultural Engineering | Environmental Chemistry | Environmental Health

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## *Field-scale testing of mobile laboratory for mitigation of gaseous emissions from the swine farm with UV-A photocatalysis*

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**ABSTRACT.** *UV-A photocatalysis has been investigated to comprehensively mitigate odor and selected air pollutants in the livestock environment. This study was conducted to confirm the performance of UV-A photocatalysis on the swine farm. The objectives of this research were to (1) scale-up of the UV-A photocatalysis treatment, (2) evaluate the mitigation of odorous gases from swine slurry pit, and (3) evaluate the effect of suspended particulate matter (PM). We tested UV-A photocatalysis at a mobile laboratory-scale capable of treating  $\sim 0.2 - 0.8 \text{ m}^3 \cdot \text{s}^{-1}$  of barn exhaust air. The targeted gaseous emissions of barn exhaust air were significantly mitigated ( $p < 0.05$ ) up to 40% reduction of measured odor; 63%, 44%, 32%, 40%, 66%, and 49% reduction of dimethyl disulfide, isobutyric acid, butanoic acid, p-cresol, indole, and skatole, respectively; 40% reduction of  $\text{H}_2\text{S}$ ; 100% reduction of  $\text{O}_3$ ; and 13% reduction of  $\text{N}_2\text{O}$ . The PM mitigation effect was not significant. Formaldehyde levels did not change, and a 21% generation of  $\text{CO}_2$  was observed. The smell of benzoic acid generated in UV-A treatment was likely one of the compounds responsible for the less-offensive overall odor character of the UV-treated emissions. Results are needed to inform the design of a farm-scale trial, where the interior barn walls can be treated with the photocatalyst, and foul air will be passively treated as it moves through the barn.*

**Keywords.** *Air pollution control, air quality, volatile organic compounds, odor, environmental technology, advanced oxidation, UV-A, titanium dioxide.*

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## Introduction

Ultraviolet (UV) light ranges between 200 to 400 nm in the electromagnetic spectrum adjacent to the purple band, invisible to the human eye. The UV range is conventionally separated into wavelength ranges, labeled A, B, and C, corresponding to progressively shorter wavelengths. UV-A (~315–400 nm) is considered the least toxic and is used in consumer product applications such as commercial indoor tanning. UV-C (200–280 nm) is considered the most effective to inactivate microorganisms. In practical applications, UV-C is typically associated with 'germicidal' 254 nm irradiation, though formally, it stretches to the shortest wavelengths in the range.

UV treatment can be considered for both 'end-of-pipe' (treating a point-source exhaust air from mechanically-ventilated barns) and source-based (e.g., improving the indoor air quality inside the barn) applications. UV treatment can be classified as either direct photolysis (i.e., mitigation primarily via direct absorption UV light by the ambient gases) and photocatalysis (i.e., mainly via surface-based reactivity based on catalyst activation by the UV light). With its relatively long wavelength, fewer pollutants directly absorb UV-A, and thus it is generally less effective than using the same wavelengths with a photocatalyst designed to operate by UV-A absorption (Lee et al., 2020a; Lee et al., 2020b;). Photocatalysis is commonly facilitated on surfaces coated with nanosized titanium dioxide (TiO<sub>2</sub>), which is considered reasonably durable and cost-efficient (Hashimoto et al., 2005; Zaleska, 2008; Schneider et al., 2014).

Selected publications report developing and testing UV treatment of selected odorous gases on a lab-scale for both UV-A (Alonso-Tellez et al., 2017; Brancher et al., 2016; Lee et al., 2020a; Portela et al., 2008; Wu et al., 2014; Yao & Feilbeg et al., 2015; Zhu et al., 2017;) and UV-C (Koziel et al., 2010; Nguo, 2011; Rockafellow et al., 2012;). In the lab-scale experiments, the percent reduction varied depending on the coating's thickness, the coating material, temperature, relative humidity, dust accumulation, and the UV wavelength. Statistically significant mitigation of NH<sub>3</sub>, H<sub>2</sub>S, N<sub>2</sub>O, O<sub>3</sub>, and VOCs was shown (Alonso-Tellez et al., 2017; Brancher et al., 2016; Lee et al., 2020a; Portela et al., 2008; Rockafellow et al., 2012; Wu et al., 2014; Yao & Feilbeg et al., 2015; Zhu et al., 2017;). Pilot-scale studies with UV-A photocatalysis showed effective mitigation of measured odor (~63%), p-cresol (~49%), skatole (~49%), indole (~66%), H<sub>2</sub>S (~40%), butan-1-ol (~41%), O<sub>3</sub> (~100%), N<sub>2</sub>O (~14%), and NH<sub>3</sub> (~11%) in the swine and poultry barn (Maurer & Koziel, 2019; Koziel et al., 2019; Lee et al., 2020b; Lee et al., 2021a; Lee et al., 2021c; Yang et al., 2020;).

Only two studies have been conducted at a farm-scale (Guarino et al., 2008; Costa et al., 2012;) for evaluating the mitigation of NH<sub>3</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and PM concentrations inside swine nurseries by utilizing UV-A. While these pioneering tests conducted in Italy showed auspicious results, it is still necessary to test whether UV-A photocatalysis is effective for other swine housing types and management systems farm conditions. We have been scaling up the UV-A technology to farm-scale trials to provide the necessary data on the performance (e.g., the percent reduction) and treatment economics.

Lee et al. (2021c) designed, built, and tested a UV mobile laboratory for treating up to 1.25 m<sup>3</sup>·s<sup>-1</sup> of air with UV-A and TiO<sub>2</sub> photocatalyst. The next step was testing UV-A photocatalysis to mitigate fast-moving gases emitted from swine manure using the mobile laboratory (Lee et al., 2021a;). Significant percent reduction for measured odor (~63%), p-cresol (~41%), indole (~20%), butyric acid (~48%), propionic acid (~51%), butan-1-ol (~41%), N<sub>2</sub>O (~14%), and NH<sub>3</sub> (~11%) were reported.

Thus, the next logical step was to test the UV mobile lab at a farm-scale. We used TiO<sub>2</sub>-based UV photocatalysis by connecting the mobile lab to one of the continuous fans that remove gaseous emissions from stored manure pit under slatted-floor swine barn. We aimed to evaluate the on-farm-scale efficacy of UV photocatalysis performance in mitigating odorous gaseous emissions using swine barn exhaust air. Results are needed to inform the design of farm trials and applications, where the interior barn walls are sprayed with the photocatalyst, and the foul indoor air will be passively treated as it moves through the barn inside a poultry barn.

## Materials and Methods

### Experimental reactor setup

The mobile laboratory (7.2 × 2.4 × 2.4 m) designed for evaluating the performance of UV photocatalysis was used in this study. The mobile laboratory (Lee et al., 2021c;) consisted of a series of 12 flow-through and connected chambers (7.2 × 0.9 × 2.4 m), and each chamber (0.5 × 0.9 × 2.4 m) was divided by vertical baffles to maximize the UV dose. Each chamber was equipped with 11 wall panels coated with TiO<sub>2</sub> (nanostructured TiO<sub>2</sub> anatase at 10 μg·cm<sup>-2</sup> from PureTi, Cincinnati, OH, USA) on all sides. Two fans (I-Fan Type 40, Fan-com, Panningen, The Netherlands) were installed to control the treated airflow through the mobile laboratory. The airflow was measured with the anemometer fan (ATM, Fancom, Panningen, The Netherlands), and the internal airflow was controlled in real-time using the fan monitoring system (Lumina 20/21, Fancom, Panningen, The Netherlands), the two fans, and the anemometer fan.

The mobile laboratory and filtration unit were installed at the swine farm (illustrated in Lee et al., 2021b; Figure 1). The rationale for using the filtration ahead of UV treatment was to separate UV and filtration effects on the mitigation of odorous gases. While farm-scale UV treatment is relatively novel, mechanical filtration is also rarely researched. It is essential to note that the PM is a carrier of sorbed odorous compounds (Cai et al., 2006;) and pathogens. The filtration kept the UV

chambers clean for the initial phases of this research.

The mobile laboratory was connected to the airflow from the pit fan to a T-shape connector capable of discharging the excess air. A flexible duct was used to channel the treated air into the filtration unit and the mobile lab. The minimum treated airflow was  $0.28 \text{ m}^3 \cdot \text{s}^{-1}$  (facilitating 52 s UV treatment time from inlet to outlet in the mobile laboratory). The maximum treated airflow was  $0.78 \text{ m}^3 \cdot \text{s}^{-1}$  (enabling 19 s UV treatment time from inlet to outlet in the mobile laboratory).

The UV-A (light-emitting diode; LED) lamps installed inside the mobile lab were the same as the previous pilot-scale experiment (Lee et al., 2021c;). Additional 110 lamps were installed in chambers #2 and #3, and a total of 50 lamps were installed in the remaining ten chambers (#1 and #4 - #12). The treatment was controlling the UV dose (a product of treatment time and UV irradiance).

## Swine farm

Testing was conducted at the university AG450 Farm (Ames, IA, USA). The swine farm was a finishing operation facility with about ~ 350 pigs. Pigs started at ~ 18-23 kg (40-50 lbs) a few weeks before the study initiation and followed the finishing diet. Animal stocking density was  $0.56\text{-}0.62 \text{ m}^2 \cdot \text{head}^{-1}$ . The farm used a manure pit ventilation system in which fans' flowrate was not controlled. The manure pit of the experimental farm was divided into four independent headspaces. The approximate manure depth in the pit was 2.4 m (8 ft). While the animals were present inside the barn, the study did not use animals, nor were they exposed to UV light.

## UV sources

The mitigation of targeted gases was investigated using four different light sources (UV-A: 367 nm and UV-C: 254 nm, 222 nm, or 185+254 nm). Two low-pressure mercury sources (American Ultraviolet Co, Lebanon, IN, USA) were used, both of which emit strongly at 254 nm, but one additionally contains a small 185 nm component because the bulb is made from special materials that allow transmission of that line. The emission spectrum of low-pressure Hg lamps is well known, and these sources both also contained small emissions at 365 nm and other wavelengths common to all of these bulbs. Nonetheless, we refer to these as 254 nm or (185 + 254) nm light sources. An excimer source (Ushio America Inc., Cypress, CA, USA) emitting at 222 nm was the third source. The fourth source was an LED with emission centered at 367 nm lamps (T8 LED, Eildon Technology, Shenzhen, China), near the 365 nm range that Hg lamps commonly were used for, but without disadvantages of Hg-based lamps.

## Measurement of odor

Gas samples were collected from the inlet and outlet sampling ports (illustrated in Lee et al., 2021b; Figure 1) in-side the UV mobile lab into 10 L Tedlar bags using a Vac-U-Chamber and sampling pump (both from SKC Inc., Eighty-Four, PA, USA). Tedlar bags were pre-cleaned by flushing with clean air three times before use. Odor samples were analyzed using a dynamic triangular forced-choice olfactometry (St. Croix Sensory Inc., Stillwater, MN, USA). Four trained panelists at two repetitions each were used to analyze each sample, presented from low to increasingly lower dilutions to the point of consistent odor detection.

## Measurement of odorous VOCs

The VOC samples were collected in 1 L gas sampling glass bulbs from gas sampling ports. An internal standard (hexane) was used to minimize variability in sampling and sample preparation. All the samples were analyzed with a GC-MS within 12 h of sample collection. A 2 cm DVB/Carboxen/PDMS solid-phase microextraction (SPME) fiber (Supelco, Bellefonte, PA, USA) was used to extract VOCs from the glass bulbs for 50 min, then the SPME fiber loaded with VOCs inserted in the GC injector set at 260 °C. The analysis was completed using a custom multidimensional gas chromatography (GC, Microanalytics, Round Rock, TX, USA) built on Agilent 6890N (G1530N) (Agilent Technologies, Santa Clara, CA, USA), mass spectrometer (MS, same manufacturer), olfactometer (mdGC-MS-O). The GC oven temperature was programmed at the initial 40 °C for 3 min, followed by ramping up to 240 °C at  $7 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ , maintained for 8.43 min. The quadrupole MS used 70 eV ionization energy and the 34 - 350 m/z scan range.

For evaluating the performance of UV photocatalysis on targeted VOCs, treated gas samples were analyzed in the selected ion mode (SIM mode) because of its higher sensitivity and lower detection limit, compared to the total ion chromatogram (TIC) mode. Pure standards of all 15 VOCs were analyzed and calibrated to verify the VOCs' retention time. The VOC concentrations were not quantified. A surrogate metric of VOC abundance (measured with peak area counts) was used to assess UV treatment performance by comparing the VOC abundance in the treatment and control.

## Analysis of aromas and odors in UV-treated gas

UV treatment changes the characteristic smell of barnyard air into a less offensive overall odor. Chemical analysis by GC-MS was used to evaluate the gas compounds and linking them to the aroma generated or mitigated after the UV

photocatalysis. The sample collection and analysis were similar to that described in the previous paragraph. The trained panelist's nose evaluated separated compounds eluting from the sniff port to record and build the aromagram. The chemical analysis data were analyzed using Chemstation ver. D.02.00.275 (Agilent Technologies, Santa Clara, CA, USA). The aroma characterization was done using AromaTrax ver. 10.1 (Microanalytics, Round Rock, TX, USA). The mdGC-MS-O system was used in full heartcut mode with a total run time of 40 min for TIC and SIM. The olfactometry part of the instrument was used during this analysis. Aromagrams for odor intensities were generated using AromaTrax software, recorded, and generated by the three panelists. The odor intensity reported was on a scale of 0–100%, where 0% was the minimum, and 100% was the maximum. Odor characters recorded/reported by the panelist were verified with published odors descriptors (Banik et al., 2020; Cai et al., 2006).

### Measurement of ozone concentrations

An O<sub>3</sub> detector was connected to the monitoring system (Series 500 monitor, Aeroqual, New Zealand) and installed at the gas sampling ports when in use. The detector was factory-calibrated to the 0 - 50 ppb detection range (Gas Sensing, IA, USA) and certified before use.

### Measurement of greenhouse gas (GHG) concentrations

Methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and nitrous oxide (N<sub>2</sub>O) were measured as those are often mitigated or generated by UV treatment. GHGs samples were collected using syringes and 5.9 mL Exetainer vials (Labco Limited, UK) and were analyzed for concentrations on a GC equipped with FID and ECD detectors (SRI Instruments, Torrance, CA, USA). Samples were analyzed on the day of collection. Standard calibrations were constructed daily using 10.3 ppm and 20.5 ppm CH<sub>4</sub>, 1,005 ppm and 4,010 ppm CO<sub>2</sub>, and 0.101 ppm and 1.01 ppm N<sub>2</sub>O. 99.999% He was used for calibrating the 0 ppm baseline (Air Liquide America, Plumsteadville, PA, USA).

### Measurement of ammonia and hydrogen sulfide concentrations

NH<sub>3</sub> and H<sub>2</sub>S concentrations were measured with a real-time analyzer (OMS-300, Smart Control & Sensing, Daejeon, Republic of Korea) calibrated with high precision standard gases (5-point dilution, R<sup>2</sup>=0.99). The analyzer was equipped with NH<sub>3</sub>/CR-200 and H<sub>2</sub>S/C-50 electrochemical gas sensors (Membrapor, Wallisellen, Switzerland), NH<sub>3</sub>/CR-200 (0 to 100 ppm), and H<sub>2</sub>S/C-50 (0 to 50 ppm), respectively.

### Measurement of formaldehyde concentration

Formaldehyde (a carcinogenic air pollutant) is of concern in the context of photochemical reactions, and thus, was incorporated into the list of targeted gases. A gas sampling pump kit (model GV-100S, Gastec Corp., Tokyo, Japan) was used for formaldehyde gas detection. The concentration of formaldehyde was measured by a detector tube (Ivyland, PA, USA) within the 20 - 400 ppb range.

### Measurement of particulate matter concentration

PM's concentration was measured using TSI Dusttrak (Monitor 8533, Shoreview, MN, USA). The PM concentration was measured simultaneously while the targeted gas was being measured. At 5 s intervals, airborne PM concentration was recorded by size (PM 1, PM 2.5, 'respirable' size = PM 4 - PM 10, PM 10, and total PM).

### Data measurement and analysis

Gas samples were collected after 30 min of equilibration time under each treatment condition. The overall mean % reduction (mitigation) for each measured gas was estimated using:

$$\% \text{ Reduction} = \frac{E_{con} - E_{Treat}}{E_{con}} \times 100 \quad (1)$$

where

E<sub>Con</sub> and E<sub>Treat</sub> = the mean measured concentrations in control and treated air, respectively

Emission rates were calculated as a product of measured gas concentrations and the total airflow rate through the wind tunnel, adjusted for standard conditions and dry air using collected environmental data. The overall mean mitigation of each measured gas emission was estimated using:

$$\text{Mitigation of emission} = \left( C_{con} \times V \times \frac{273.15 \times MW}{(K_{con}) \times 2.24 \times 10^4} - C_{Treat} \times V \times \frac{273.15 \times MW}{(K_{Treat}) \times 2.24 \times 10^4} \right) \quad (2)$$

Where:

Mitigation of emission (g min<sup>-1</sup>) = the mitigation of gas emission

C<sub>Con</sub> and C<sub>Treat</sub> = the mean measured concentrations in control and treated air (mL m<sup>-3</sup>), respectively

V = the ventilation rate (m<sup>3</sup> min<sup>-1</sup>)

MW = the molecular weight of target gas ( $\text{g mol}^{-1}$ )

$K_{\text{Con}}$  and  $K_{\text{Treat}}$  = the temperature in control and treated air (K), respectively

$2.24 \times 10^4$  = an ideal gas conversion factor for liters to moles at 273.15 K.

UV dose (Eq. 3) was estimated using measured light intensity (I) at a specific UV wavelength ( $\text{mW}\cdot\text{cm}^{-2}$ ) and treatment time (ts, s).

$$\text{UV dose} = I \times t_s \quad (3)$$

### Statistical analysis

All measurements are replicated with at least three samples. The R studio (version 3.6.2) was used to analyze the mitigation of the targeted standard gases. The UV dose and treatment time parameters between control concentration and treatment concentration were analyzed using one-way ANOVA. The statistical difference was confirmed by obtaining the p-value through the Tukey test. A significant difference was defined for a p-value  $< 0.05$ .

## Results

### Measured Odor

UV-A photocatalysis significantly mitigated odor emissions from swine barn. UV dose  $\geq 4.0 \text{ mJ}\cdot\text{cm}^{-2}$  showed a statistically significant 40% reduction of odor (illustrated in Lee et al., 2021b; Table 1). There was no significant improvement between  $4.0 \sim 5.3 \text{ mJ}\cdot\text{cm}^{-2}$  doses, suggesting that a low dose is economical. The likely reason for the lack of apparent improvement for the higher dose is the odor measurement method itself (by dilution only), which accounts for the odor 'intensity' without considering VOCs' actual photochemistry and changes to the odor offensiveness. UV is also known to generate VOCs, and therefore, the overall odor intensity is not sufficient to evaluate the mitigation effect. Evaluation of targeted odorants and linking them to specific aromas is shown in the subsequent sections.

### Volatile organic compounds

UV-A photocatalysis showed a significant odorous VOCs mitigation (illustrated in Lee et al., 2021b; Table 2). UV dose  $\geq 4.0 \text{ mJ}\cdot\text{cm}^{-2}$  partially removed four to six targeted VOCs. The highest dose ( $5.3 \text{ mJ}\cdot\text{cm}^{-2}$ ) resulted in a statistically significant percent reduction of dimethyl disulfide (62%), isobutyric acid (44%), butanoic acid (32%), p-cresol (40%), indole (66%), and skatole (49%). The mitigation of odorous VOCs was consistent with the results presented for odor (illustrated in Lee et al., 2021b; Table 1). A statistically significant odor reduction was found for higher UV doses in which several targeted VOCs were reduced, e.g., the phenolic compounds. It is important to highlight the generation of some targeted compounds for all UV doses. Generated compounds (several in the VFAs group, DMDS, and phenol) are odorants that are considered slightly less impactful than p-cresol, skatole, and indole. Thus, it is feasible to hypothesize that the generated compounds offset the overall odor's mitigation (illustrated in Lee et al., 2021b; Table 1).

### Greenhouse gases

The 9-13% reduction of  $\text{N}_2\text{O}$  was statistically significant for UV-A dose  $\geq 2.9 \text{ mJ}\cdot\text{cm}^{-2}$  (illustrated in Lee et al., 2021b; Table 3). There was no significant increase to the percent reduction between 4.0 and  $5.3 \text{ mJ}\cdot\text{cm}^{-2}$  dose. Remarkably, UV-A mitigates this potent GHG at the farm-scale up to 13%. The results are consistent with the earlier work at the lab- & pilot-scales at swine & poultry barns (Lee et al., 2020a; Lee et al., 2020b; Lee et al., 2021a; Lee et al., 2021c).

$\text{CO}_2$  was generated under all UV-A doses (illustrated in Lee et al., 2021b; Table 4) up to 34%. The  $\text{CH}_4$  concentrations showed a considerable variation between control (5~20 ppm) depending on the sampling day, and there was no statistically significant effect on treatment (illustrated in Lee et al., 2021b; Table S1).

### Hydrogen sulfide and ammonia

Interestingly,  $\text{H}_2\text{S}$  showed a significant percent reduction (26%) at the highest UV-A dose. No mitigation effect for  $\text{NH}_3$  was observed (illustrated in Lee et al., 2021b; Table S2). The results for  $\text{NH}_3$  are consistent with earlier work at the lab- and pilot-scales (Lee et al., 2020a; Lee et al., 2020b; Lee et al., 2021a; Lee et al., 2021 c), where there was a slight ( $\leq 10\%$ ) percent reduction. On the other hand, no mitigation effect for  $\text{H}_2\text{S}$  was observed in earlier work. Thus, the mitigation at the farm-scale is remarkable and deserves further investigation. The average concentration of  $\text{H}_2\text{S}$  in the emitted (control) was 1.2 ppm, and  $\text{NH}_3$  was 22 ppm.

### Formaldehyde

Formaldehyde was not detected in both the control and treatment sample groups (illustrated in Lee et al., 2021b; Figure

2). Therefore, formaldehyde was not produced above the detectable 20 ppb as a by-product of the UV-A photocatalyst's reaction. These findings should be further investigated with a more sensitive detection method as formaldehyde is classified as a carcinogenic air pollutant.

### **Particulate matter**

The PM percent reduction ranged from 9 to 55% for all tracked particulate size ranges, except for PM-1; however, the mitigation effect was not significant (illustrated in Lee et al., 2021b; Table 6). The measurements showed variation in PM concentration in the swine barn exhaust, which likely affected the lack of statistical significance. The significant reduction of PM with UV-A photocatalysis was demonstrated in the pioneering study by Costa et al. (2012) and deserves to be investigated further, especially in the context of airborne pathogens.

### **Ozone**

The concentration of O<sub>3</sub> was measured while measuring other targeted gases. Ozone was undetectable in both control and treatment samples. Therefore, O<sub>3</sub> reduction could not be investigated, but neither was it generated. In our earlier research on the lab- and pilot-scales (Lee et al., 2020a; Lee et al., 2020b; Lee et al., 2021c;), we reported up to complete (100%) mitigation of O<sub>3</sub> that was naturally in the unirradiated samples.

## **Discussion**

### **Evaluation of the leading cause of odor reduction with UV-A photocatalysis**

We observed a significant change in the overall odor 'character' (i.e., 'what it smells like') for UV-A-treated swine barn emissions. The research team working at the swine farm test site described the smell of UV-A treated air as a mix of a less-offensive 'disinfectant' or 'swimming pool' scents with a weaker smell of swine manure in the background. Therefore, we investigated which compounds (generated by UV-A treatment) were responsible for adding the less-offensive scents. It should be mentioned that neither the odor measurement (by dilution olfactometry, section 2.4) or the mitigation of targeted VOCs (section 2.5) could answer the key question of why the smell is subjectively less offensive. In general, the 'disinfectant' smell similar to 'ozone and swimming pool' would likely be preferred compared to raw swine manure, even if the odor intensity is the same.

The initial assessment of the simultaneous chemical and sensory analyses (illustrated in Lee et al., 2021b; Figure 4) was consistent with the overall percent reduction of odor and odorous VOCs (illustrated in Lee et al., 2021b; Tables 1, 2, and 11). The overlaid chromatograms (black lines) and aromagrams (red lines) illustrate the difference in the GC-separated peak number, height & areas between the control and UV-treated air for panelist 1 (results for panelist 2 and 3 are presented in Figures S1 and S2). The lower number of aromagram peaks and smaller peak heights are consistent with the weaker (less intense) smell of manure in the UV-A treated air.

The one compound (benzoic acid) generated in the UV-A photocatalysis is known to have the characteristic smell of 'faint, pleasant odor', which appears to be consistent with the panelist's perception. Two panelists indicated that benzoic acid (eluting from GC column at ~15.6 min had a 'toothpaste, mouthwash and pleasant' smell and 'mint, neutral' smell, respectively (illustrated in Lee et al., 2021b; Table 16).

Benzoic acid is the oxidation product of common compounds with the C<sub>6</sub>H<sub>5</sub>-C in the structure, such as a toluene or other (mono) alkylbenzenes. Previous studies report on toluene present in the headspace of slurry pit manure (Lo et al., 2008; Zhang et al., 2019;).

## **Conclusions**

We investigated UV-A photocatalysis treatment to mitigate gaseous emissions at the farm-scale. Specifically, we tested the UV-treatment at a mobile laboratory-scale capable of treating ~0.2 - 0.8 m<sup>3</sup>·s<sup>-1</sup> of barn exhaust air. The targeted gaseous emissions were significantly (p < 0.05) mitigated up to:

- 40% reduction of odor.
- 32~66% reduction of key compounds responsible for downwind odor, i.e., dimethyl disulfide, isobutyric acid, butanoic acid, p-cresol, indole, and skatole.
- 26% reduction of hydrogen sulfide (H<sub>2</sub>S).
- 13% reduction of nitrous oxide (N<sub>2</sub>O).
- The PM mitigation effect was not significant.
- No formation of formaldehyde was detected in these experiments. However, as expected under oxidizing conditions, additional CO<sub>2</sub> was observed (up to 21%, p < 0.05).

The simultaneous chemical and sensory analysis confirmed that UV-A treatment changed the overall nuisance odor character of swine barn emissions into 'toothpaste' and 'mint'. The smell of benzoic acid generated in UV-A treatment was likely one of the compounds responsible for the less-offensive overall odor character of the UV-treated emissions. Results are needed to inform the design of future real farm work, where the interior barn walls will be covered with the photocatalyst, and foul air will be passively treated as it moves through the barn.

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