Treatment of Livestock Odor and Pathogens with Ultraviolet Light

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Abstract. *Livestock production systems are associated with aerial emissions of odor, volatile organic compounds (VOCs), other gases, and particular matter including airborne pathogens. Control of those emissions is needed to assure compliance with environmental regulations and long-term viability of the industry. The focus of this research is a novel approach to abatement of livestock odor and pathogens utilizing photocatalysis, i.e., UV irradiation in presence of TiO_2 as a catalyst. A standard gas generation system was built and tested to generate ten odorous VOCs commonly defining livestock odors. These VOCs included methylmercaptan, ethylmercaptan, dimethylsulfide, butylmercaptan, acetic, propanoic, butyric, and isovaleric acid, p-cresol, and H_2S. Our previous research established a reduction of VOCs with UV light only of 60~98% for sulfur VOCs and 91% for p-cresol, but only 20 to 45% removal for volatile fatty acids (VFAs). Titanium dioxide was used in the current research to catalyze UV reactions in the same gas mixtures of VOCs held in a small photoreactor. The reactor was designed to conduct controlled tests with UV light under dynamic (with airflows) conditions that facilitate experiments simulating exhaust from mechanically-ventilated barns. Six 10W lamps with characteristic bands at (185), 254, 312, 365 nm, respectively, and principle output at 254 nm were used as UV source in dynamic system. Solid phase microextraction (SPME) fibers were used to sample VOCs before and after UV treatment and for transfer of samples to a gas chromatography and mass spectrometry olfactometry (GC-MS-O) system. Odor analysis was completed by a forced-choice dynamic-dilution olfactometer in the Olfactometry lab at ISU. Effectiveness of four different treatment options, i.e., UV_{254}, $UV_{185+254}$, $UV_{254}+TiO_2$, and $UV_{185+254}+TiO_2$ was assessed. Effect of light energy, catalyst presence and light wavelength was evaluated. More than 50% in chemical reduction was found for all VOCs tested with a treatment time of 18.5 second. A linearly positive correlation was found between the percent conversion of tested VOCs and light energy dose. TiO_2 showed to greatly improve the treatment effectiveness on VOCs, VFAs in particular, no matter deep UV was used or not. However, when TiO_2 was used, deep UV showed very little improvement in degrading VOCs tested, while significant improvement was observed when no TiO_2 was used. Total odor reduction of 70% by certain energy level indicated the feasibility of odor mitigation by UV light. Continued work includes simultaneous inactivation of airborne pathogens with UV light.*

Keywords. UV photocatalysis, odor, H_2S, ammonia, VOCs, livestock operations, TiO_2, SPME, GC-MS-O.

1. Introduction

Livestock production systems are associated with air emissions of odor, volatile organic compounds (VOCs), ammonia, hydrogen sulfide, other gases, and particular matter including airborne pathogens. With larger and more concentrated livestock production systems coming up, odor as well as other airborne gas emissions, are becoming an issue for agricultural producers receiving more and more attention. Research has shown the nuisance livestock odor was caused by several key volatile (semi-volatile) organic compounds identified from emissions from swine barn (*Bulliner et al., 2006; Lo et al., 2008; Wright et al., 2005*), beef cattle (*Cai et al., 2006; Wright et al., 2005*)., and poultry manure (*Cai et al., 2007).* Three categories of chemicals (indoles, VFAs and methylthiol) were determined as key compounds of pig odor (Willig et al. 2004). Meanwhile, the odor intensity was positively correlated with ammonia concentration (*McGinn et al. 2003*).

Due to the rising odor issue, a need is urged to find an ideal air treatment process that is both cost- and abatement-effective for odor control. Agricultural scientists and engineers have put more effort than ever for a best odor mitigation technology, such as biofiltration (Melse et al. 2005; Hoff et al., 2008; Nicolai et al. 2008; Treloar et al. 2008), diet modification (Sutton et al., 2008), air scrubbers (Melse et al. 2008), setbacks (Stowell et al. 2005), windbreak walls (Ford et al. 2003), vegetable oil sprinkling (Nonnenmann et al. 2003) and biomass filters (Hoff et al. 1996), however, they still cannot satisfy both criteria. Photocatalysis for using ultraviolet light with catalyst present, has been well recognized for its powerful treatment effectiveness and ease of use for liquid-phase pollutant removal, and widely used for industry wastewater treatment. The advantages of photocatalysis, includes low operation temperature, low cost and significantly low energy consumption. Several thousands of papers or patents summarized in reviews (Fox and Dulay, 1993; Herrmann, 2005) and bibliography works (Blake, 1994; 1995; 1996; 1999; 2001) related to treatment of air or water pollutants with TiO_2 photocatalysis showed how intensively this technique has been researched in the last two decades.

However, not much is known about the effects of UV light on gas phase VOCs emitted from concentrated animal feeding operations (CAFOs) and so far no research has been reported to utilize TiO_2 photocatalysis to control VOCs/odor emissions from agricultural facilities. Our previous work (Yang et al, 2007) on VOC photolysis was done without adding TiO_2. Benefits or potential benefits of UV mitigation technology include ease of use and low maintenance cost, ability to treat both exhaust/inlet air, simultaneous treatment of odor and pathogens, and potential to treat green house gases as well. Meanwhile potential challenges exist, including the short treatment time consistent with fast air flow in a mechanically ventilated barn, treatment of complex organic mixtures, the abundant presence of NH_3 and H_2S. Airborne dust emissions may potentially lead to catalytic deactivation adding to the difficulty of maintenance.

Solid phase microextraction (SPME) has established a big name for its sensitivity, reusability and ease of use (Koziel and Pawliszyn 2001, Koziel and Novak, 2002). Several researchers have shown the use of SPME and gas chromatography mass spectrometry (GC-MS) or GC-Olfactory or GC-MS-Olfactory analysis (Frank et al. 2004, Xiong et al.2004) for the analysis of VOCs related to livestock odor (Bulliner et al. 2006, Cai et al. 2006, Cai et al. 2007, Kim et al. 2002, Koziel et al. 2006, Lo et al. 2008). In this work, GC-MS coupled with headspace (HS) SPME was used for chemical analysis, while a forced-choice dynamic-dilution olfactometer was used for odor analysis.

The main objectives of this work were: 1) to evaluate the feasibility of applying TiO_2 photocatalysis to treat mixtures of VOCs associated with livestock odor; 2) to evaluate the effect of light energy dose on treatment effectiveness; 3) to evaluate the need of applying TiO_2; 4) to

evaluate the effect of UV light wavelength. A special batch photoreactor was designed capable of evaluating effects of different factors that would directly affect treatment effectiveness.

2 Experimental

2.1 Chemicals-standard gas mixtures

A standard gas generation (SGG) system generated VOCs/H_2S as simulation of air emissions from swine barns (Yang et al. 2007). Chemicals used include reduced sulfur-containing compounds (H_2S, methylmercaptan, ethylmercaptan, butylmercaptan and dimethylsulfide or DMS), volatile fatty acids or VFAs (acetic, propanoic, butyric and isovaleric acid, respectively), and phenolic compound (p-cresol). Each chemical was carried by one permeation tube (made in house or from KIN-TEK™ Laboratories, La Marque, TX). The permeation tube technology has showed the capability of generating constant VOCs emissions at trace concentrations (Koziel et al. 2004). The gas system was controlled by mass flow controllers under constant flow. The carrier gas was 99.9% pure air. Exhaust from the system was connected to the photoreactor. The system can generate VOCs/H_2S at different concentrations by varying flow rate. Moreover, further experiments to assess the effect of NH_3 presence or moisture can be conducted easily by adding NH_3 or water vapor into the SGG system.

2.2 Photoreactor and UV sources

A batch reaction chamber was designed for simultaneous destruction of VOCs and pathogens, shown in Fig. 1. With this reaction chamber connected to SGG system, we can test the effect of several variables on the destruction efficiency of VOCs, including treatment time, UV light energy dose, RH, T, initial VOCs concentration, gas flow rate, presence of TiO_2, light wavelength, presence of other gas species and carrier of medium gas as well.
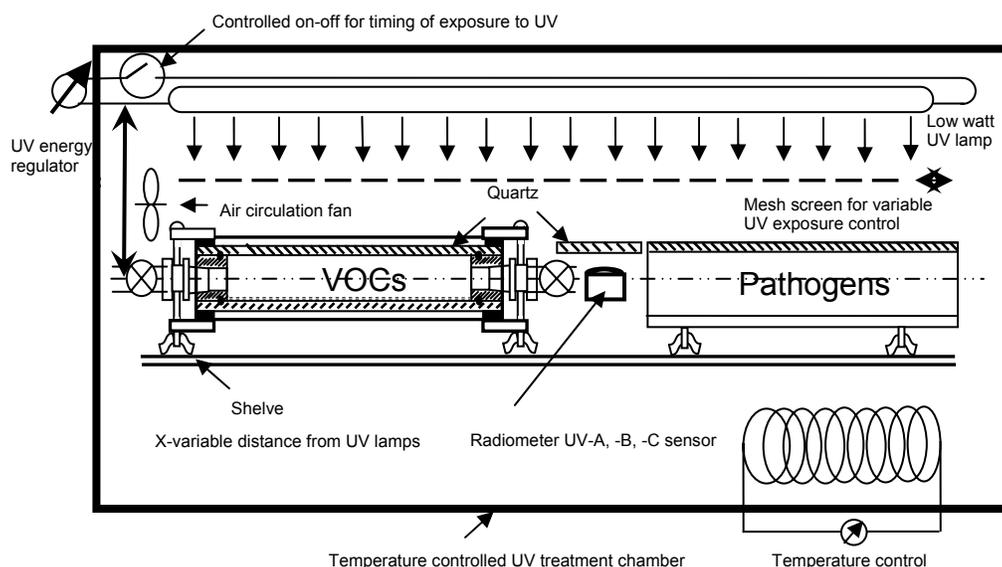

Fig.1. Schematic of reaction chamber: the sealed photoreactor holding VOCs or pathogens made from PTFE with quartz windows (on the top) for UV transmission and glass sheets (on the bottom) for TiO_2 film coating. It also has two toggle valves for filling with standard gases from the SGG system.

Two groups of six similar 10W UV mercury lamps (American UV Co., Lebanon, IN), were used in parallel. Both groups of lamps have principal outputs at 254nm, with other characteristic bands at (185), 312, 365 nm, respectively, and one group had 185nm output while the other did not.

The chamber was controlled at 25 ºC for all the experiments in this work.

2.3 Catalyst preparation

Commercial Degussa P25 TiO_2 (Degussa, Germany, 75% anatase and 25% rutile, BET surface area ~50m^2 g^{-1}) powder was mixed in a proportion of 25mg with 4ml methanol. The TiO_2-MeOH suspension was then stirred by an ultrasonic cleanser for 5 minutes. Thereafter, the suspension was transferred evenly to the tape-framed glass (5"x7") surface using a thin drawn glass tube. The coated film was dried under atmospheric conditions in a fume hood. Finally, the air-dried glass surface was irradiated with UV for two hours. Each time after UV treatment, photoreactors were opened, cleaned, and baked for future use.

2.4 Analytical methods

2.4.1 SPME extraction

HS-SPME extractions were performed with a SPME fiber coupled with a manual fiber holder from Supelco (Bellefonte, PA, USA). For our application, 85µm Carboxen/PDMS SPME has shown the best extraction efficiency among all four commercially available SPME coatings (Yang et al., 2007), hence this coating was selected to do all the extractions in this study. Before use, each fiber was conditioned in a heated GC splitless injection port under helium flow. After conditioning, SPME fiber was then quickly moved to the sampling points and performed extractions at desired time. Once extraction was done, the SPME fiber was removed and immediately transferred to the injection port of GC for analysis. The desorption time of SPME fiber was 40 minutes at 260 ºC.

SPME extractions were done at constant temperature (fume hood) for both the control and treatment samples. The sampling time for all extractions in this work was 5 minutes.

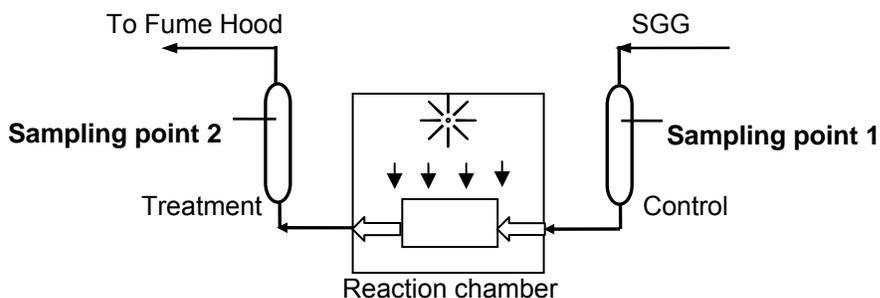Fig. 2 shows the sampling points for control and treatment with airflows in the system.

Fig.2. Schematic of sampling points (SP), connection of SGG to reaction chamber. SPME fiber extracted gas samples from SP1 and SP2.

2.4.2 GC-MS and forced-choice olfactometer

Multidimensional GC–MS (Microanalytics, Round Rock, TX, USA) was used for the analyses (Cai et al, 2006; Lo et al, 2008). The system integrates GC–O with conventional GC–MS (Agilent 6890N GC/5975 MS from Agilent, Wilmington, DE, USA) as the platform with the

addition of an olfactory port and flame ionization detector (FID) (however, in this work odor analysis was not done by this system but instead performed by a forced-choice olfactometer in the Olfactometry Lab at ISU). The system was equipped with a polar column as well as system automation and data acquisition software. Full HC mode was used for all analyses in this research. The oven temperature was started at 40 ºC and held for 3 min then increased at 7 ºC /min to 220 ºC , and finally held for 7 min at 220 ºC. Helium was used as the carrier gas. Mass/molecular weight-to-charge ratio (m/z) range was set between 33 and 280. Spectra were collected at 6 seconds and electron multiplier voltage was set to 1000V. The MS detector was auto-tuned weekly. VOCs/H_2S abundance was measured as area counts under the MS peak, and odor was accessed by a forced-choice, dynamic-dilution olfactometer at a total odor basis with four panelists' sniffing for each sample collected in a 10L Tedlar bag.

2.5 Procedures

TiO_2 film was coated on the clean and dry glass surface by the coating method described above. The VOCs holder, the photoreactor, was then sealed after the TiO_2 coated glass was fixed to its bottom. The photoreactor was checked for leaks and flushed with pure air. Under constant airflow in SGG system, the photoreactor was placed in the reaction chamber connecting to SGG for a continuous flow through long enough for adsorption of VOCs to TiO_2 surface to reach equilibrium. UV lamps were then kept on for a time period (about 4 hours) for the reactions to reach steady state. SPME extractions were then done at two sampling points, for control and treatment, respectively. Meanwhile, gases were collected at two sampling points by 10L Tedlar bags, which were transferred to the Olfactometry lab at ISU and analyzed by four trained panelists within 24 hours.

Removal fraction was calculated as below.

For chemical reduction,

Removal = (Control AC – Treatment AC) / Control AC and expressed as a percentage,

Where AC stands for the area counts under the MS peak

For odor reduction,

Removal = (Control ODT – Treatment ODT) / Control ODT and expressed as a percentage,

Where ODT stands for the odor detection threshold

3. Results and discussion

3.1 Effect of UV/TiO_2 photocatalysis on VOCs removal

The power of UV/TiO_2 photocatalysis to decompose tested VOCs can be illustrated easily by the comparison of total ion chromatograph (TIC) of control and treatment samples, as shown in Fig. 3.

With 18.5 second UV treatment, all VOCs tested achieved conversion of more than 50%, as shown in Table 1. It was believed most of VOCs were converted into CO_2 and H_2O, which would be the most favorable feature to apply this technique for pollutant removal. However, when the light energy is not enough for complete mineralization of VOCs into terminal products including CO_2, SO_2 and H_2O, new products or intermediates that are potentially hazardous and odorous such as acetone, will also be generated.
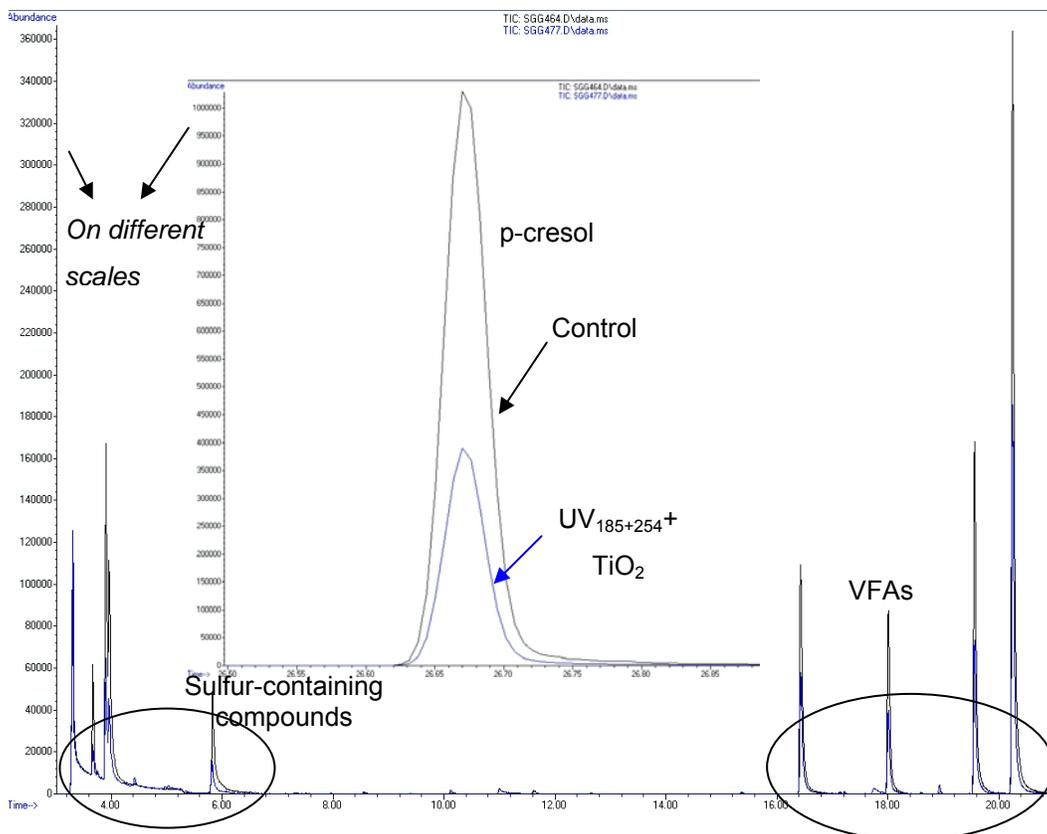
Fig. 3 Comparison of TIC of control and treatment samples: illustration of the effect of $UV_{185+254}$ with TiO_2 on destructing VOCs associated with livestock odor

Treatment: 18.5 second treatment time with airflows; Light intensity at 254nm =0.25mW.cm^{-2};

5 min HS-SPME extraction; T=25ºC; analyzed by GC-MS

Table 1. Chemical reduction% of VOCs tested by 18.5 second $UV_{185+254}$ + TiO_2 treatment

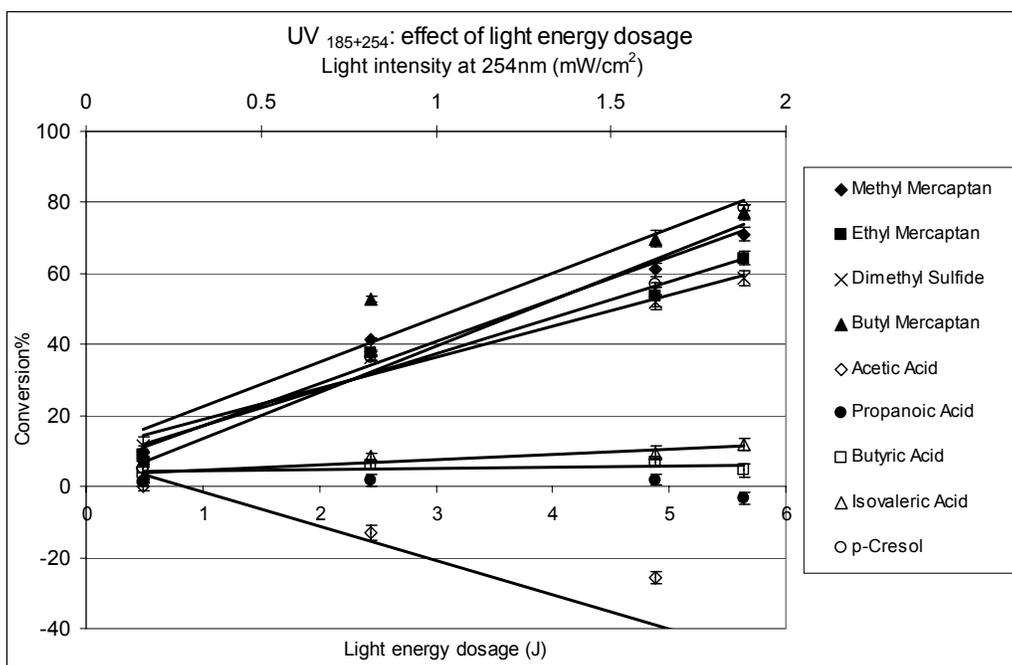| Compounds	Chemical reduction%
Methyl Mercaptan	70.9
Ethyl Mercaptan	66.0
Dimethyl Sulfide	63.6
Butyl Mercaptan	65.8
Acetic Acid	51.4
Propanoic Acid	59.9
Butyric Acid	56.7
Isovaleric Acid	51.7
p-cresol	64.6

3.2 Effect of UV energy dose (light intensity)

The following experiment was conducted to evaluate the effect of light intensity (energy dose) while keeping all other factors such as treatment time (37 second), initial gas concentrations, T, and RH unchanged. Considering the possibly more oxidant deep UV, we used UV lamps with 185nm output for both cases whenever TiO_2 was added or not. Three replications were taken

for each control and treatment samples. The chemical reduction percentages for tested VOCs over different light intensities (energy doses) were plotted in Fig. 4.
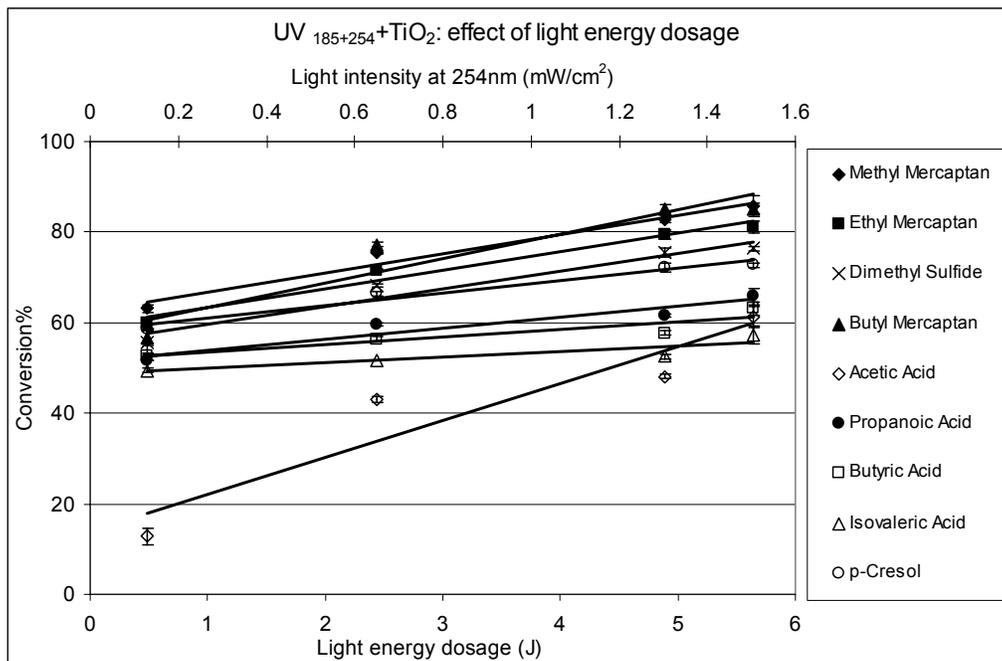
(a) $UV_{185+254}+TiO_2$

(b) $UV_{185+254}$

Fig. 4 Effect of light intensity at 254nm on chemical reduction of tested VOCs

Accordingly, Table 2 shows how the percent conversion of tested VOCs is linearly correlated with light energy dose.

Table 2. Linearity of conversion% as a function of light energy dose from Fig. 4

Compounds	$UV_{185+254}+TiO_2$			$UV_{185+254}$		
	m	b	R^2	m	b	R^2
Methyl Mercaptan	4.23	62.5	0.971	11.8	5.42	0.969
Ethyl Mercaptan	4.07	59.4	0.968	10.1	7.14	0.971
Dimethyl Sulfide	3.94	55.7	0.947	8.79	10.0	0.976
Butyl Mercaptan	5.39	58.0	0.883	12.5	10.0	0.924
Acetic Acid	8.18	13.8	0.885	**-0.937**	8.16	0.817
Propanoic Acid	2.39	51.6	0.912	-	-	-
Butyric Acid	1.72	51.7	0.852	-	-	-
Isovaleric Acid	1.24	48.6	0.770	1.54	2.92	0.903
p-Cresol	2.76	58.2	0.966	13.1	0.282	0.968

Where conversion % = m * (energy) + b

Fig. 4 shows an obvious positive linear correlation (except VFAs in $UV_{185+254}$ treatment) between percent conversion and light intensity (energy dose), with $R^2 > 0.85$ for most of the compounds except isovaleric acid in $UV_{185+254}+TiO_2$ treatment, and $R^2 > 0.9$ for all VOCs except VFAs in $UV_{185+254}$ treatment. Absence of TiO_2 resulted in irregular decomposition of VFAs, among which acids with smaller carbon numbers, i.e., acetic and propanoic acid, increased instead of being degraded. However, one interesting observation was that acetic acid, with the smallest carbon numbers among all four VFAs tested, increased linearly with the range of light energy tested. This is possibly caused by the incomplete degradation of isovaleric acid, butyric acid and even propanoic acid (which were degraded more with light intensity increased) into acetic acid. The effect of TiO_2 will be discussed in details in section 3.3.
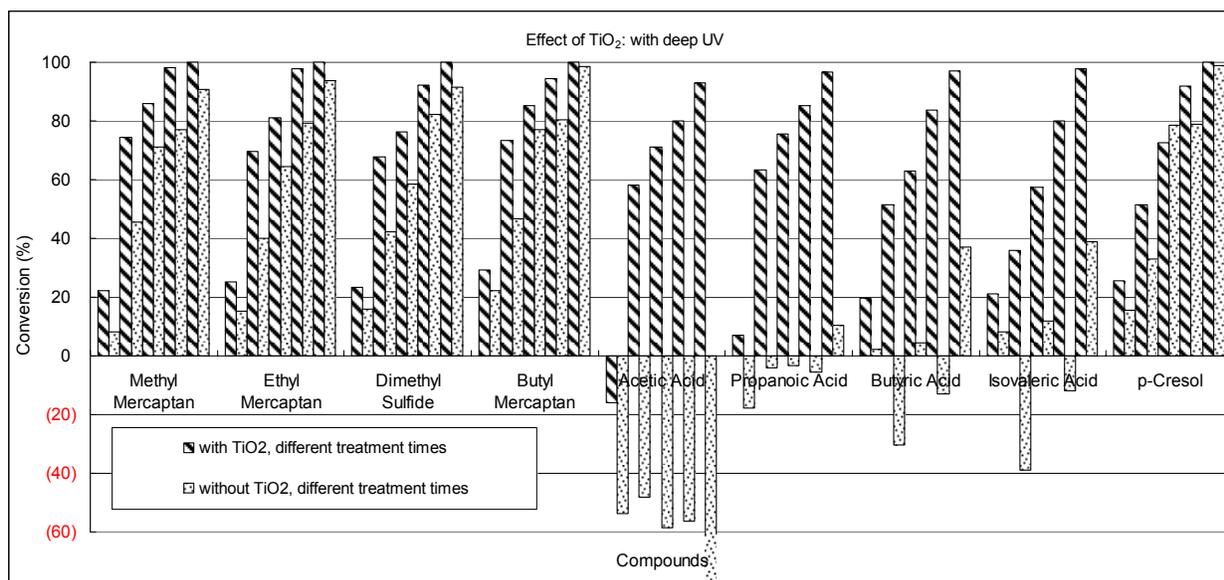
3.3 Effect of TiO_2 catalysis

Fig. 5 Effect of TiO_2 on treatment effectiveness when deep UV was used at different treatment times, 2.5 second, 18.5 second, 37 second, 56 second, 112 second.
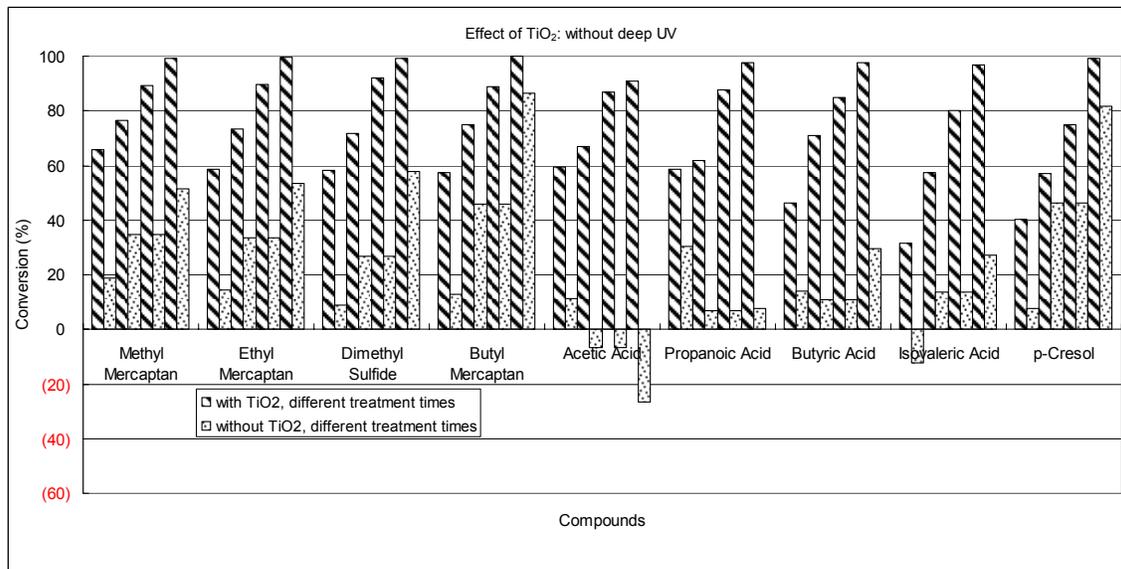
Fig. 6 Effect of TiO$_2$ on treatment effectiveness when deep UV was NOT used at different treatment times, 18.5 second, 37 second, 56 second, 112 second.

For all five treatment times, comparison of treatment effectiveness in the processes with/without TiO$_2$ indicated TiO$_2$ played an important role in improving the VOCs degradation. TiO$_2$ even brought more significant reduction to VOCs when deep UV was absent. One more critical observation was TiO$_2$ facilitates the degradation of VFAs. The reason might be that the electron-hole pairs generated on the catalyst surface help produce more radicals that can oxidize VOCs. However, the degradation of p-cresol, which is the priority odorant responsible for swine barn odor nuisance, was not greatly improved with the use of TiO$_2$ when the treatment time was longer than 37 second when deep UV was used. In other words, when deep UV was used, if light energy reached to a certain barrier, there was no significance in degrading more p-cresol even TiO$_2$ was applied.
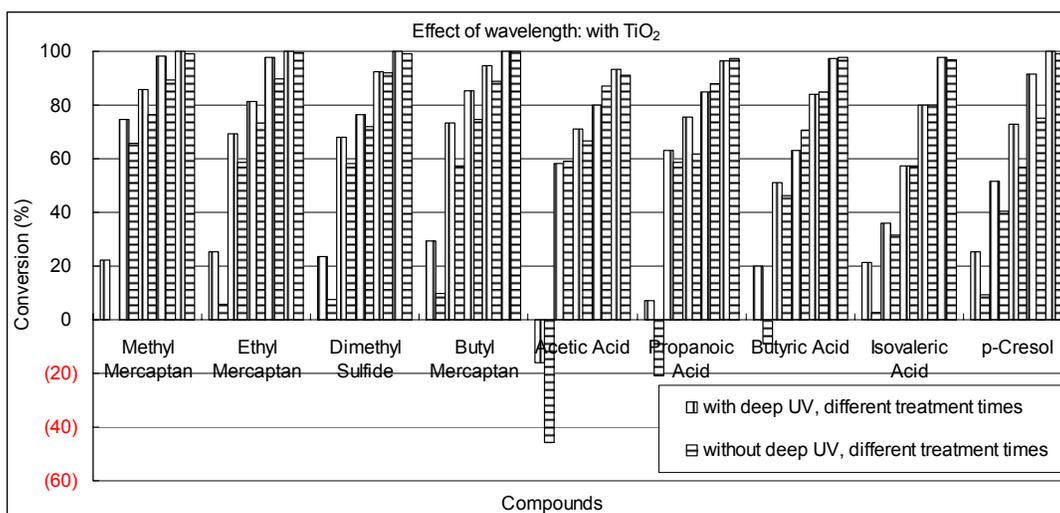
3.4 Effect of light wavelength

Fig. 7 Effect of deep UV (185nm) on treatment effectiveness when TiO$_2$ was used at different treatment times, 2.5 second, 18.5 second, 37 second, 56 second, 112 second.
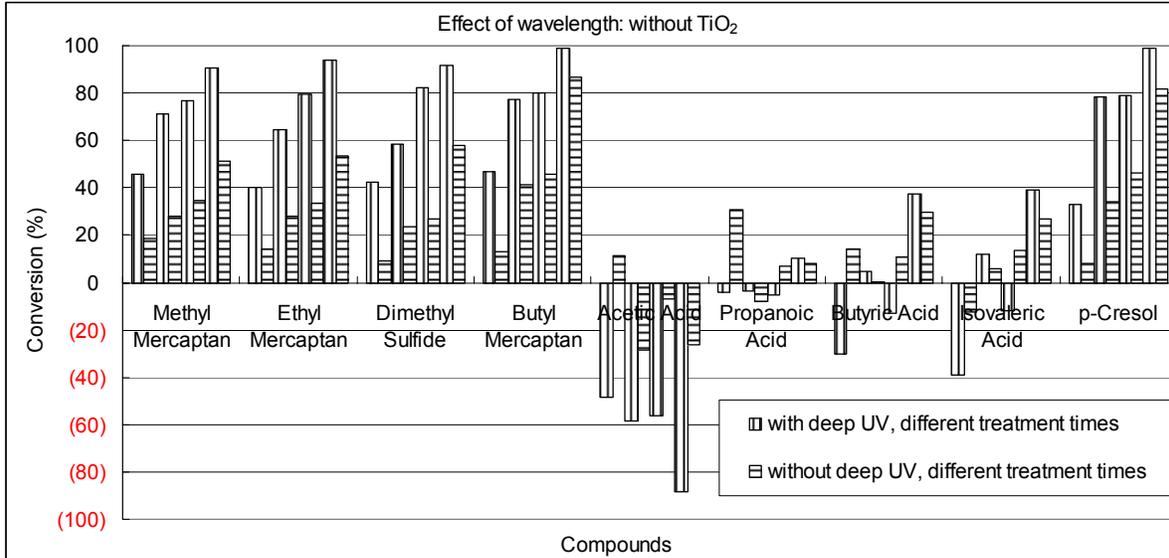
Fig. 8 Effect of deep UV (185nm) on treatment effectiveness when TiO_2 was NOT used at different treatment times, 2.5 second, 18.5 second, 37 second, 56 second, 112 second.

When TiO_2 was used, degradation of VOCs by $UV_{185+254}$ was improved by about 10% for VOCs except VFAs, which were abated to similar degree or even less than UV_{254} treatment. However, significant improvement was observed in treatment effectiveness for $UV_{185+254}$ treatment over UV_{254} treatment when no TiO_2 was used. Plus, much more acetic acid was generated by $UV_{185+254}$ treatment.

Among all four treatment options, $UV_{185+254}$ + TiO_2 was the most efficient abatement option, followed by UV_{254} + TiO_2, $UV_{185+254}$, and UV_{254}. This finding was consistent with toluene decomposition (Zhang et al. 2003), reporting the effectiveness of the three processes was in the order of, $O_3/TiO_2/UV_{254}$ > O_3/UV_{254} > TiO_2/UV_{254}. Here $UV_{185+254}$ /TiO_2 worked as well as did $O_3/TiO_2/UV_{254}$.

3.5 Total odor reduction

Odor was accessed by a forced-choice, dynamic dilution olfactometer at a total odor basis with
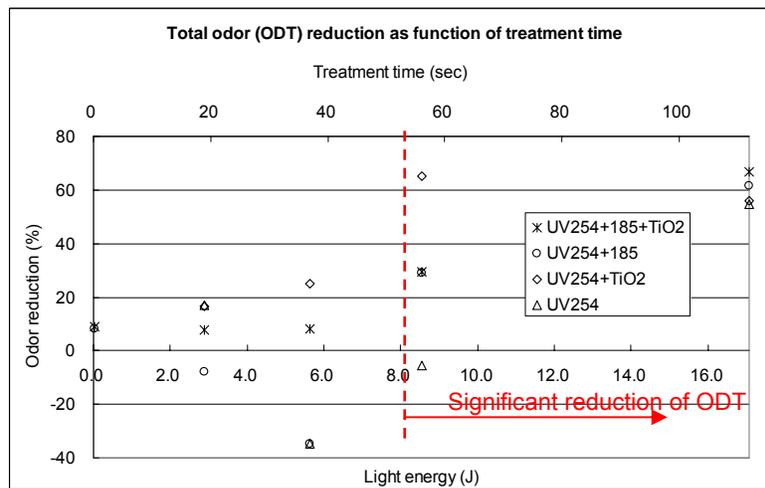

Fig. 9 Total odor reduction by four treatment options at different treatment times

four panelists' sniffing for each sample collected in a 10L Tedlar bag. Total odor reduction was shown in Fig. 10 for all four treatment options at different UV treatment times (light energy dose). Significant odor reduction was observed in $UV_{185+254}$ + TiO_2 and UV_{254} + TiO_2 treatment processes. Negative reduction at shorter treatment times showed some potential odorous (not necessarily bad odor but could detected by human nose) products have been generated when the energy dose is not enough for complete mineralization.

4. Conclusion

The following conclusions can be drawn from this research:

(1) UV/TiO_2 photocatalysis is very effective in removing VOCs/gases responsible for livestock odor in laboratory scale. Total odor reduction of 70% by certain energy level indicated the feasibility of odor mitigation by UV light.

(2) $UV_{185+254}$ + TiO_2 was the most efficient abatement option among all four treatment options involved. In terms of treatment effectiveness, the four treatment options follow an order of $UV_{185+254}$ + TiO_2 > UV_{254}+TiO_2 > $UV_{185+254}$ > UV_{254}.

(3) With airflows, significant removal percentage was observed for treatment times larger than 18.5 second. More than 50% in chemical reduction was found for all VOCs tested with a treatment time of 18.5 second and a complete decomposition for all VOCs tested occurred when the treatment time was about 112 second.

(4) Percent conversion of tested VOCs was linearly positive correlated with the light energy dose, indicating possible solution of challenges caused by short contact time in field conditions by increasing light energy.

(5) TiO_2 showed to greatly improve the treatment effectiveness of VOCs especially VFAs.

(6) Deep UV (185nm) showed significant improvement in treatment efficiency only when TiO_2 was not used.

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