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The effect of slurry treatment including ozonation on odorant reduction measured by in-situ PTR-MS

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ABSTRACT

The emission of odorous compounds from intensive pig production facilities is a nuisance for neighbors. Slurry ozonation for odor abatement has previously been demonstrated in laboratory scale. In this study, the effect of slurry ozonation (combined with solid–liquid pre-separation and acidification) on emissions of odorous compounds was tested in an experimental full-scale growing pig facility using Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) for online analysis of odorants. The measurements were performed to gain a better understanding of the effects of ozone treatment on emissions odorous compounds and to identify potential options for optimization of ozone treatment. The compounds monitored included volatile sulfur compounds, amine, carboxylic acids, ketones, phenols and indoles. Measurements were performed during nearly a one-month period in summertime. The compounds with the highest concentrations observed in the ventilation exhaust duct were acetic acid, hydrogen sulfide, propanoic acid and butanoic acid. The compounds with the highest removal efficiencies were hydrogen sulfide, 3-methyl-indole, phenol and acetic acid. Based on odor threshold values, methanethiol, butanoic acid, 4-methylphenol, hydrogen sulfide and C_5 carboxylic acids are estimated to contribute significantly to the odor nuisance. Emissions of odorous compounds were observed to be strongly correlated with temperature with the exception of hydrogen sulfide. Emission peaks of sulfur compounds were seen during slurry handling activities. Discharging of the slurry pit led to reduced hydrogen sulfide emissions, but emissions of most other odorants were not affected. The results indicate that emissions of odorants other than hydrogen sulfide mainly originate from sources other than the treated slurry, which limits the potential for further optimization. The PTR-MS measurements are demonstrated to provide a quantitative, accurate and detailed evaluation of ozone treatment for emission reduction.

1. Introduction

Emissions and discharges from agriculture may have adverse impacts on the quality of the air, water, soil and long-term sustainability of agricultural ecosystems and have been recognized by growing public and regulatory concerns (e.g., Aneja et al., 2009). Specifically, intensive pig production is a source of offensive malodorous compounds and a major cause of nuisance for neighbors in the local surroundings (e.g., Feilberg et al., 2010B; Schiffman et al., 2005). Emissions from intensive pig production facilities must be reduced in order to prevent negative health (Schiffman et al., 2005) and environmental effects (Hartung and Phillips, 1994). Innovative techniques to reduce odorants associated with intensive livestock farms are therefore needed. Several techniques that could be implemented in order to meet regulations include e.g. slurry oxidation and biological air cleaning (e.g., Wu et al., 1999; Feilberg et al., 2010A).

Ozonation has previously been demonstrated to be beneficial in water and wastewater treatment (e.g., von Gunten, 2003; Ternes et al., 2003; Huber et al., 2005). When applied to pig slurry, ozone has shown a potential for oxidizing phenolic and indolic compounds (Wu et al., 1999). Ozone is found to be very reactive with indolic compounds, whereas it reacts somewhat slower with phenolic compounds. On the other hand, ozone reacts very slowly with volatile fatty acids and has no apparent effect on emissions of these (Wu et al., 1998). Total sulfides are found to be reduced effectively and rapidly by ozonation from manure slurry with no observed influence on the sulfate concentration (Wu et al., 1999, 1998). Furthermore, ozonation has been demonstrated to reduce emissions of total odor (measured by olfactometry) significantly

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when applied to manure slurry (Wu et al., 1998). When ozone is applied to room air (up to 0.1 ppm of ozone in the room) instead of manure slurry, it shows similar effects with indolic compounds being removed effectively, but with no significant effects on phenolic compounds and volatile fatty acids (Kim-Yang et al., 2005). However, no significant effects are observed on odor emission and sulfur compounds concentration, when ozone is applied to room air in a pig building at a similar concentration (Elenbaas-Thomas et al., 2005). At the same time, ammonia concentration is observed to be increased and pig average daily gain is decreased.

Previous studies of slurry ozonation were mainly carried out by laboratory or pilot-scale treatment of slurry batches. In one study, reduction of odorant emissions by means of slurry ozonation has been demonstrated at production unit level (Lyngbye et al., 2008) with an average reduction in odor emissions (measured by olfactometry) of ∼50%.

In the present study, Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) was used to test the effect of treatment by slurry ozonation on emissions of odorous compounds in an experimental full-scale growing pig facility. A three-step slurry ozonation treatment system (with intermittent two-step acidification treatment) was used in this study and the system has been demonstrated by a previous parallel study (Jonassen et al., 2010) to give an average reduction in odor (measured by olfactometry) as well as a 40% reduction of ammonia emissions. The aim of the current study was to gain a better understanding of the effects of ozone treatment on emissions of specific odorous compounds using PTR-MS and to identify potential options for optimization of ozone treatment. PTR-MS allows a low detection limit (10–200 pptv) and a fast time response (1–10 s) when measuring odorous organic compounds in real time. It has become an essential tool for a wide variety of fields, including measurement and monitoring of VOC in the atmosphere and VOC emitted from animal houses (Feilberg et al., 2010B; Hewitt et al., 2003; Shaw et al., 2007; Ngwabie et al., 2008).

2. Experimental methods

2.1. Measurement location and pig facility

In-situ measurements of odorants were performed at the outlets of two identical sections (treated section and control section) from an experimental pig production facility located at Grønhøj (55° 20′ 00′ N, 11° 23′ 00′′ E), Denmark. Each section contained two identical pens (2.4 m × 4.8 m) and each pen housed 16 growing pigs with an average weight of 64.2 kg at the start of the measurement period (06/07/2009). The pig house was equipped with mechanical ventilation via a duct with a fan through the roof and with diffuse air intake through the ceiling insulation. The ventilation system was controlled by the room temperature, which was attempted to be maintained at 18 °C during the measurement period. However, the ventilation system can only cool the indoor temperature to a few degrees (3–5) above outdoor temperature and at an outdoor temperature of 14 °C the ventilation system is running on maximum. When the outdoor temperature exceeded 14 °C, the pigs could be cooled by water from a sprinkling system above the dunging area. The two pens shared a simple dry feeder, and each pen was equipped with a nipple drinker. Feed was supplied *ad libitum*. In order to avoid recirculating the air from the exhaust duct, the air intake of the ventilation system was extended to 5 m above the roof ridge. The floor in each pen consisted of 2/3 slatted floor and 1/3 drained floor as well as a 60 cm deep slurry pit. Ventilation rates were measured by a measurement wing (Fancom, Holland) at 5 min intervals. Room temperature was measured with a VE 10 temperature sensor (VengSystem A/S, Denmark) situated below the ventilation duct.

In one of the two sections, the slurry was treated (treated section) as described below, and in the other section (control section) the slurry was discharged once during the measurement period (see Table 1). A batch of growing pigs was placed in the sections on 25/05 and delivered to the slaughterhouse on 18/08. In this period (25/05–18/08) their weight increased from 32 to 113 kg.

2.2. Slurry handling activities and ozonation treatment system

A three-step slurry ozonation treatment was performed once a week after the slurry in the pit had been flushed into a concrete tank located outside the building. In the first step of the treatment, the slurry was separated in a Volute separator (Amcon Inc., Japan) using a polymer to obtain an efficient separation. Approximately 40 g polymer was used per m^3 of treated slurry. The solid fraction was removed mechanically, and the liquid fraction was pumped into a plastic container for further treatment. In the next step the liquid fraction was treated with ozone at a rate of ca 2 $m^3\ h^{-1}$ of liquid as the second step. During the process, around 75 g ozone was applied to the slurry per hour, resulting in 40 g ozone per m^3 of treated slurry. The slurry ozonation treatment was done by means of a venturi injector in a closed system and the volatilization of compounds in the slurry was expected to be very small during the treatment. Finally in the third step, the liquid fraction was acidified with 96% sulfuric acid until a pH level of 5.5 in the third step. This normally required between 0.75 and 1.2 l of acid per m^3 of treated slurry. After treatment, the liquid fraction was recirculated into the slurry pit in order to reduce the ammonia emission from the fresh manure. The reduction of odorant emissions is expected to be obtained by ozonation, whereas the main purpose of the pre-separation is to reduce the ozone consumption (and hence the cost). Post-treatment by acidification is used for reducing ammonia emissions. However this paper focuses on odorant abatement, and for clarity we refer to the treatment as ozonation treatment in the following. Where appropriate, the effects of pre- and post-treatment are discussed.

A two-step treatment in which the slurry was flushed out once, separated and acidified to pH 5.5 was performed between the weekly three-step slurry ozone treatment. The amount of slurry recirculated into the pits was between 4.5 and 5 m^3 per section, resulting in a height of ∼20 cm slurry. Surplus slurry was transferred to storage tank.

The treatment activities carried out in the slurry pits during the measurement period are shown in Table 1.

Table 1
Manure slurry treatment for both sections during the measurement period in 2009.

Date and starting time	Activities for treated section	Activities for control section	Height of slurry in treated section (cm)	Height of slurry in control section (cm)[d]
30/06; 09:30	–	–	20.5	36.0
03/07; 06:30	Sep. + Acid.[a]	–	21.0	39.0
06/07; 08:30	Sep. + Ozon. + Acid.[b]	–	24.0	42.3
10/07; 06:00	Sep. + Acid.	–	21.0	47.0
13/07; 08:00	Sep. + Ozon. + Acid.	Discharge[c]	18.0	2.0
20/07; 06:00	Sep. + Ozon. + Acid.	–	18.0	16.5
24/07; 08:00	Sep. + Acid.	–	22.0	19.5
27/07; 08:00	Sep. + Ozon. + Acid.	–	22.0	25.0

[a] Separation and acidification treatment of manure slurry (two-step slurry acidification treatment).
[b] Separation, ozonation and acidification treatment of manure slurry (three-step slurry ozonation treatment).
[c] The slurry was discharged from control section pit.
[d] See Fig. S1 in supplementary data file for more information.