EFFECT OF LOW OZONE DOSE TREATMENT ON EMISSION AND COMPOSITION OF PIG MANURE

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1 INTRODUCTION

Emission of Ammonia (NH_3), hydrogen sulphide (H_2S) and odour from intensive livestock production adversely affect local air quality as well as the health and well-being of animals and human beings (Aneja *et al.* 2009). The most important odorous component of livestock production is believed to be reduced sulphur compounds, volatile fatty acids (VFAs), phenols and indoles (Aneja *et al.* 2009; Feilberg *et al.* 2010).

The indolic and phenolic compounds (phenol, p-cresol, 4-ethylphenol (4E-phenol), indole and skatole) are degradable by ozone treatment and offensiveness of the manure odour was significantly reduced when doses of 0.5g O_3/L manure where used (Wu *et al.* 1999). High ozone doses (1, 2 and 3g/L manure) can degrade odorous phenolic and indolic microbial metabolites to non-detectable levels, but have not proven effective on e.g. total volatile fatty acids (VFAs) and only slightly on hydrogen sulphide (H_2S) (Watkins *et al.* 1997). However, manure treatment with high doses of ozone is costly due to high power consumption and includes a risk of release of excess ozone, which is toxic to plants and humans. In order to develop cost-effective and safe ozone treatment technologies, there is therefore a need for investigation of ozone treatment at low doses.

The purpose of this work is to investigate effects of ozone treatment on pig manure emissions and composition. The focus was on application of ozone at relatively low doses (0 – 150mg/L manure). Furthermore, the paper also includes results from ozone treatment of flocculated manure with a lower content of suspended solids. Low-dose ozone application is currently being tested at farm level in Denmark.

2 MATERIALS AND METHODS

For the ozonation experiment, pig manure (pH ~8; E_h ~330mV; dry matter content ~ 2%; total ammoniacal nitrogen (TAN) 2.8 g/L) from a research facility were collected. Flocculation was performed by adding 350mL 0.25% C2260 polymer pr litre manure, This was tested to give the best combination of large floc size and fast dewatering of the flocculated sample as well as the lowest turbidity and smallest dry matter content of the liquid fraction (Hjorth *et al.* 2010).

Ozone was generated by passing an oxygen stream though an electrical discharge ozone generator, set to highest ozone output level (~45mg/L O_2). The ozone-enriched oxygen steam was added through a diffuser placed underneath the manure surface. Ozone was added by a gas flow rate of 500mL/min during constant stirring, to a manure volume of 7L, in a laboratory scale reactor. Ozonation was carried out at dosages of 0, 40, 80 and 150mg O_3/L manure. After each ozone addition the headspace was exchanged at a air flow of 2L/min, before dynamic sampling of emissions were carried out; NH_3 on detections tubes (Kitagawa, Japan; range 0.25 – 300ppm); H_2S was measured by gold film H_2S detector (Jerome) and air samples were collected on Tenax/Carbograph sorbent tubes for analysis of Volatile Organic Compounds (VOCs) emission. Moreover pH and Redox potential (E_h) were measured as a function of ozone doses.

Detailed analyses of odorous VOC emissions were carried out by thermal desorption coupled with gas chromatography – mass spectrometry (GC/MS) using the GC/MS method described in Feilberg *et al* (2010). Emission rates were calculated from the measured concentrations and the air exchange rate.

3 RESULTS AND DISCUSSION

Emissions of selected compounds prior to ozonation are presented in Table 1. The study showed that ozonation changed the composition of VOCs in the headspace. Emissions of both phenolic and indolic compounds were clearly reduced during ozonation treatments (Figure 1). After adding 40mg O_3/L manure, indolic compounds were reduced to below detection limit for both manure types.

TABLE 1 **The rate of emission (ng/min) for the phenolic and indolic compounds for untreated manure for raw and flocculated manure respectively.**

Manure	Phenol	*p*-Cresol	4E-phenol	Indole	skatole
Raw	3.0 ± 0.9	52.9 ± 5.2	2.5 ± 0.3	1.03 ± 0.16	3.48 ± 0.33
Flocculated	39.1 ± 3.2	24.6 ± 2.5	9.1 ± 0.9	1.49 ± 0.27	7.61 ± 0.39

Emissions rates (ER) of p-cresol and 4E-phenol from raw manure were strongly reduced even at the lowest ozone dose, whereas higher emissions of phenol were observed following ozonation. Phenol emissions after ozone doses of 80 and 150 mg/L were, however, lower compared to emissions after 40 mg/L, the large variation in phenol emission is tentatively ascribed to low concentrations close to background levels. Surprisingly, ozone treatment of flocculated manure was less efficient compared to raw manure, since reductions at all ozone doses were lower for flocculated manure. Furthermore, flocculated manure gave higher initial emissions of all compounds except p-cresol (Figure 1).

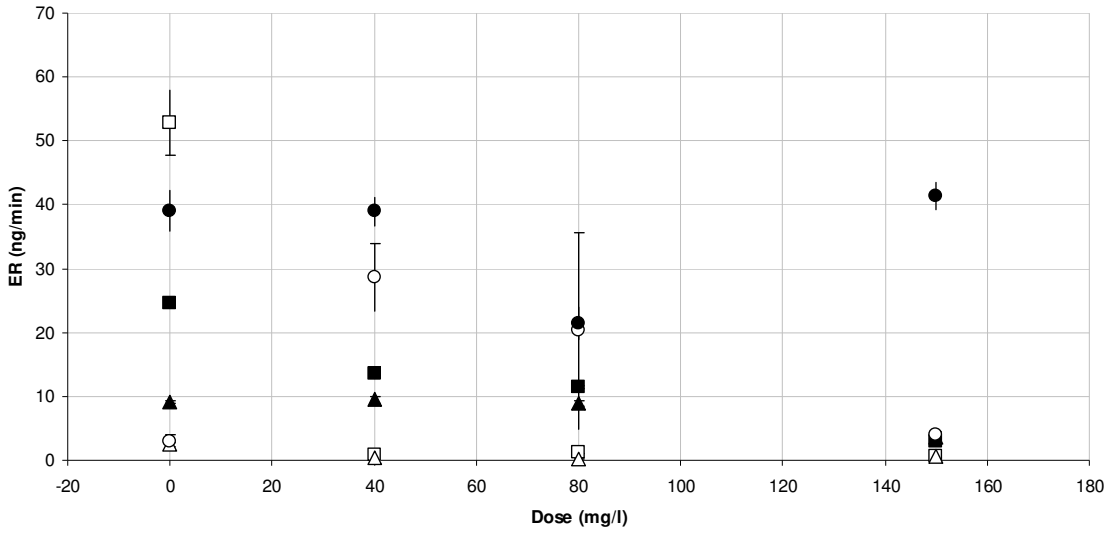

FIGURE 1 **Emission rates (ng/min) for the phenolic compounds for the raw manure (open symbols) and the flocculated manure (black symboles) for the different amount of O_3 (mg) added pr litre manure. Circles represent phenol, squares *p*-cresol and triangles represent 4E-phenol.**

VFA emission (Table 2) was in consistence with other work (Watkins *et al.* 1997) not decreased during ozonation and were not affected by observed changes in E_h, in agreement with Guenzi and Beard (1981). In fact, total VFA emissions increased at ozone doses up to 80 mg/L for raw manure and up to 150 mg/L for flocculated manure. The results indicate that VFA are formed as by products of ozone treatment of manure. The reason for the difference between raw and flocculated manure is presently not resolved.

TABLE 2 **Changes in emission rate of H_2S (mg/min), NH_3 (mg/min) and total amount of VFAs (µg/min) and E_h for all doses, for raw and flocculated (sep) manure respectively.**

Dose	E_h (mV)		H_2S (mg/min)		NH_3 (mg/min)		VFA_{total} (µg/min)	
(mg/l)	raw	sep	raw	sep	Raw	Sep	raw	sep
0	-330	-380	7 ± 2	25 ± 3	134 ± 13	92 ± 9	0.1 ± 0.1	0.1 ± 0.2
40	-0.17	25	0	0	134 ± 13	64 ± 6	0.2 ± 0.05	0.2 ± 0.06
80	25	37	1.4 ± 0.1	0	117 ± 11	72 ± 7	0.3 ± 0.1	0.15 ± 0.05
150	50	50	0	0	141 ± 14	71 ± 7	0.2 ± 0.1	0.2 ± 0.04

H_2S emission was reduced to below background level for both manure types even at the lowest ozone dose. Initial emission rates are presented in Table 2. Formation of sulphur compounds (e.g. H_2S) in cattle manure is

E_h dependent and mainly occurs under anaerobic conditions when E_h is below 0 mV (Beard & Guenzi 1983). For the present data, the inverse correlation between H_2S emission and E_h is in agreement with the literature and shows that the same is likely to be true for pig manure.

pH was stable at approximately 8, and consequently no significant increase in NH_3 emissions as a function of ozone dose was observed. For flocculated manure, a small but non-significant, decrease was observed upon ozonation.

4 CONCLUSIONS

This study of ozonation at relatively low doses has shown that concentrations of phenolic and indolic compounds in general are easily reduced, the indolic compounds already at ozone levels below 40mg O_3/L manure. H_2S emission is E_h dependent and disappears when E_h becomes positive, which occurs at the lowest ozone dose applied. Total VFA emission increased during ozonation.

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