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Abating odour nuisance from pig production units by the use of a non-thermal plasma system

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Non-thermal plasma systems can be used for abatement of odour nuisances. Odour reduction is achieved by radical-initiated oxidation and dust collection in the plasma reactor. This study was conducted to evaluate the efficiency of non-thermal plasma technology towards emissions from pig production units.
Ventilation air from a pig production unit was treated with a non-thermal plasma test unit from Applied Plasma Physics AS. Samples were taken from both the inlet and the outlet of the plasma system and analyzed by thermal desorption gas chromatography and mass spectrometry (TD-GC/MS). The TD-GC/MS used was also equipped with a sniffing port that made it possible to manually record odour-active compounds eluting from the column. Relative amounts of odour-active compounds in the inlet and the outlet flow from the plasma system were compared. Bag samples from inlet and outlet were also analyzed with a one-man-olfactometer, NasalRanger^{TM}. These results indicated an average odour removal efficiency of 97% ($p = 0.06$).
The analysis showed that that the non-thermal plasma system can effectively reduce emissions of odorous compounds from pig production units. The effects on important odour-active compounds such as indoles, phenols and volatile carboxylic acids are presented and discussed.

1. Introduction

Odour emissions from pig production units can have negative effects on the surrounding communities. In order to remain commercially competitive, modern livestock production systems are becoming increasingly intensified and mechanized. Large and dense pig houses may result in reduced air quality on neighbouring properties, which leads to a need for odour abatement technology. Biological air filters for pig farms have been developed at a commercial scale and demonstrated to be able to reduce both odour and ammonia. However, the odour reductions are typically in the range of 20 – 50 % (Melse and Ogink, 2005; Jensen and Hansen, 2006). Biological treatment is not flexible towards variable loading of contaminants and is difficult to control. Chemical acid

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scrubbers have been demonstrated to be very efficient towards ammonia, but have little or no effect on the odour (Melse and Ogink, 2005).

Non-thermal plasma treatment of ventilation air offers a promising alternative technology for odour removal (Oda, 2003; Chang et al., 2003; Jarrige and Vervisch, 2007). Plasma technology has only been tentatively tested for treating air from pig facilities. Although promising results were obtained, with above 97% reduction of odorous compounds such as indole and skatole, further research and development is needed in order to verify the suitability of this technology and optimize the application for air from pig farms.

Odours can be measured with sensory and analytical methods, but difficulties occur as a person's response to an odour is highly subjective. This is further complicated by the fact that many odorous emissions consist of many individual odorants, and the overall odour of complex mixtures cannot easily be predicted (Gostelow et al., 2001). Gas chromatography (GC)–mass spectrometry (MS)/olfactometry (O) offers the advantages of combining sensory assessment with the identification and quantification of compounds (S. Zhang, et al., 2009).

A test system based on the Applied Plasma Physics (APP) odour abatement system was used in this study. The principle of the APP Odour Abatement System is to treat entire emissions in a non-thermal plasma field. The system has previously shown a cleaning efficiency of 75 to 98 % for different process emission, such as emissions from tobacco factories, fish food and pet food production.

In the APP Odour Abatement system the air flow with the odorants are led through a reaction chamber. In the test unit used in this study the reaction chamber consists of one hexagonal cell with a corona wire. A full scale unit consists of 149 of these cells.

The corona wire runs through the cell centrally and is isolated from the rest of the chamber. A high voltage generator distributes a high frequency modulated high voltage to the corona wire which results in a silent discharge between the corona wire and the cell wall.

The discharge leads to emissions of high-speed electrons, which collide with background gas molecules creating chemically active species known as radicals and charge carriers. Reactions subsequently occur with the odorants in the gas to be treated.

2. Method

Air from the pig house was routed through the plasma reaction chamber. At the end of the outlet pipe a suction fan was connected and the flow was adjusted to approximately 138m^3/h during the experiment. The high voltage generator was set to 44 kV and 3.2 mA, and connected to the corona wire inside the reaction chamber.

Sampling for TD-GC-MS/O was done on sorbent tubes packed with Tenax TA and Carbograph 1TD. Before sampling, the tubes were conditioned at 335°C for 20 minutes. Sampling for olfactometry was done in 10 litres sample bags made of Nalophan.

Three parallel samples were taken on the sorbent tubes from the inlet and the outlet pipe. The sampling was done simultaneously in the inlet pipe and the outlet. For the first sample pair, chemical components from 10 liters of the flow were collected on the tubes. Portable sample pumps with a set flow rate of 200 ml/min were used for the field

samples. For two of the sample sets 5 litres were collected on the tubes. A sample to check for breakthrough was also taken.
Humidity, temperatures and ozone level were also measured during the experiment. Humidity was measured in the inlet and the temperature was measured in both the inlet and the outlet. A multifunctional measuring instrument, Testo 435-4, was used for these measurements. The ozone level was measured in the outlet with a Dräger tube. The Nalophan sample bags were filled with 10 liters from the inlet and the outlet. These were analyzed by four human operators by using a one-man-olfactometer, NasalRanger^{TM}. The time from sampling to analysis was about 3 hours.
The samples on the sorbent tubes were analyzed with a thermal desorption GC-MS/O. Blank samples were run before the analysis. The TD system consisted of a Markes International Unity 2^{TM}. The GC-MS system was an Agilent Technologies 7890A GC System and an Agilent Technologies 5975B VL MSD. The odour of the separated compounds was assessed at the sniff port simultaneously with the chemical analyses.
For semi-quantification of the chemical concentrations the integrated TIC-signals were compared directly with a standard 1 litre 10 ppb toluene reference.

3. Results

Humidity was measured to 70 % in the inlet pipe. The temperature was measured to 13.2 °C in the inlet and 10.5 °C in the outlet in the beginning of the experiment. Before the last sample was taken the temperature in the inlet was 13.0 °C and 12.2 °C in the outlet. The ambient temperature were the equipment was located was measured to 8.1 °C. Moderate levels of ozone were measured in the outlet; below 2 ppm, which can be addressed separately with a catalyst if there are concerns regarding toxicity.
The results from the NasalRanger^{TM} measurements are shown in the table below.

Table 1: Results from olfactomety analysis.

Person	Inlet sample bag*	Outlet sample bag*	Odour reduction
1	60	2	97%
2	7	<1	100%
3	15	<1	100%
4	30	2	93%

*The highest dilution factor for detection of odour

Person no 2 and 3 could not detect any odour in the samples from the outlet. The results from this test gave average odour abatement efficiency of 97±3 %.

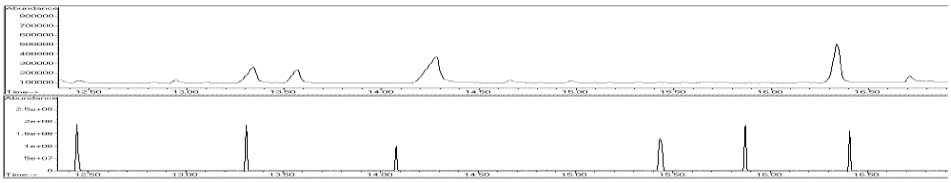

Figure 1: Part of the chromatogram and aromagram for a 5 litre inlet sample. The size of the signal in the aromagram only indicate when odour was detected, not the strength of the perceived odour.

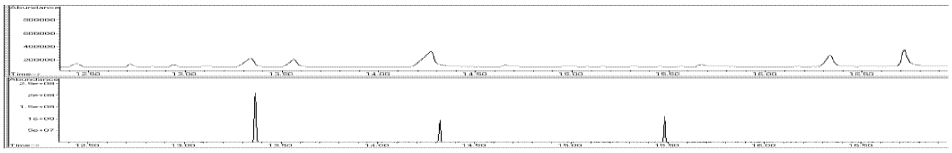

Figure 2: Part of the chromatogram and aromagram for a 5 litre outlet sample. The size of the signal in the aromagram only indicate when odour was detected, not the strength of the perceived odour.

Table2: Results from TD-GC-MS/O.

CAS	Name	TH ppb[1]	Ave. od. rem. %[2]	Std. dev. (%)	Ave. content, inlet ppb	Ave. content, outlet ppb	Odour desc.
75-50-3	Trimethylamine	6.0	66*	22	18	7	Rotten fish
431-03-8	2,3-Butanedione	1.0	51	37	23	8	Acid
64-19-7	Acetic acid	564.0	-249	129	78	235	Acid
79-09-4	Propanoic acid	68.6	30	21	131	90	
123-51-3	1-Butanol, 3-methyl-	52.6	32*	12	2	1	
79-31-2	Propanoic acid, 2-methyl- (Isobutyric acid)	10.5	15	9	27	23	Weak odour
624-92-0	Dimethyldisulphide	13.0	78**	7	2	0.51	Cabbage
107-92-6	Butanoic acid	4.2	2	35	186	186	Vomit
66-25-1	n-Hexanal	13.5	-8	11	3	3	
503-74-2	Butanoic acid, 3-methyl- (Isovaleric acid)	0.7	13*	5	29	25	Acid, sweat
116-53-0	Butanoic acid, 2-methyl-	4.8	14*	5	19	17	
109-52-4	Pentanoic acid	7.9	25*	7	65	48	
67-71-0	Dimethylsulfone		-554	91	0.76	5	
108-95-2	Phenol	38.1	-466	214	6	29	Weak
3658-80-8	Dimethyl trisulfide	0.4	100**	0	0.58[3]	n.d.	
124-13-0	Octanal	6.4			n.d.	2	
106-44-5	Phenol, 4-methyl- (p-cresol)	0.3	53*	4	59	28	Strong odour
124-19-6	n-Nonanal	3.2	-903	448	0.66[3]	7	Special plant
90-05-1	Phenol, 2-methoxy- (Guaiacol)	0.8	100**	0	0.29	n.d.	Work-shop
120-72-9	Indole	0.3	100**	0	0.79	n.d.	
83-34-1	1H-Indole, 3-methyl- (Skatole)	0.3	100**	0	2	n.d.	Terrible smell

n.d.: not detected

*: Outlet significantly different from inlet ($p<0.05$); **: Outlet significantly different from inlet ($p<0.001$)

[1]Threshold values from the literature (van Gemert, L. J., 2003) Geometrical average

[2]Average odorant removal, %

[3]Only detected in 2 of 3 samples

The results from the TD-GC-MS/O analysis are shown in the figures and table above. The graph from the human signal is denoted an aromagram. Note that the size of the

peaks in the aromagrams is arbitrary and does not say anything about the intensity of the odour. The peaks only indicate when an odour was perceived by the person doing the sensory part of the TD-GC-MS/O.
Of the odorants investigated in this study, only trimethylamine and dimethyl disulphide were detected in the sample to check for breakthrough, respectively 46 % and 38%.

4. Discussion

The result from the olfactory analysis showed an odour-abatement above 97 %. The results from the analytical measurements showed different degree of abatement of many odorants. Odorants such as dimethyl trisulphide, guaiacol, indole and skatole could not be detected in the outlet; the concentrations were below the detection limit for the instrument. Trimethylamine, which smells like rotten fish, were removed by 65 %, but the results for this compound may not be accurate because of the volatility of the molecule. Odorants such as dimethyl disulphide and 4-methyl-phenol showed also good reduction rates, respectively 78 % and 52 %. Dimethyl disulfide most likely originates from conversion of methanethiol during sampling and analysis (Feilberg et al., 2010). Methanethiol is a potent odorant which has previously been identified in emissions from pig production (Kim et al., 2007; Willig et al., 2004). It should also be noted that hydrogen sulphide (H_2S), which is expected to contribute significantly to odour, is not covered by the analytical method applied. The chromatogram showed some peak fronting for the organic acids due to a low capacity of the DB-VRX column towards polar compounds. Interferences from overlapping carboxylic acids are avoided by using ion-chromatograms for quantifications.
Recent results have demonstrated that volatile sulphur compounds (VSC) are significantly better recovered in Nalophan bags compared to other odorants. High removal efficiency of the plasma reactor towards VSC could therefore hypothetically explain the higher odour reduction as measured by olfactometry compared to compound reductions.
Odour reduction is achieved by radical-initiated oxidation in the plasma reactor, as well as through the electrostatic effect that removes dust from the air stream. Dust can carry large amounts of odorants; hence, trapping the dust will reduce odour.
The analytical analysis showed that some compounds were created in the reaction chamber. This applies to intermediate oxidation products such as acetic acid, octanal and n-nonanal.

5. Conclusion

The analysis from the test unit showed that that the non-thermal plasma system can effectively reduce emissions of odorous compounds from pig units. The olfactometry analysis shows an average reduction in odour concentration above 97 %. The analytical analysis showed a reduction of odorants at different degrees. The overall results show an excellent cleaning efficiency with use of non-thermal plasma for odour abatement in pig houses. This is also in accordance with results presented in the literature.
It is difficult to analyse odour samples, but analyzing inlet and outlet samples by the use of TD-GC/MS is adequate in order to establish the cleaning efficiencies regarding

specific compounds. It is also in contrary to olfactometry, an objective tool for the evaluation of technologies and in optimization of the cleaning process.
Further studies will be conducted due to the complexity of mixes of odorants, perception of odour and challenges with detecting low concentration of odorants. The aim of these studies is to obtain a better understanding of the chemical mechanisms in a non-thermal plasma reaction chamber.

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