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IDENTIFICATION OF KEY ODOUR COMPONENTS FROM PIG BUILDINGS FOR MODELLING PURPOSES

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ABSTRACT Three biotrickling filters are installed in bench-scale pig chambers to study potential ways of optimizing the performance of these kinds of reactors in reducing odour emissions from swine production facilities. Though mathematical models are known to be useful tools in describing and simulating performance of reactors, it would be impossible to simulate the removal of hundreds of components in the exhaust air from pig buildings. However, modelling the removal of key components, those that are mainly responsible for the unpleasant odour might be sufficient to describe the overall odour reduction. Thus, air samples at the inlet and exhaust of the biotrickling filters were collected to identify the main odorants that are removed by the system as well as those that remained after the treatment. Samples were collected by means of carbotrap tubes and analyzed by GC-MS coupled with an olfactory port (GC-MS/O). This system identifies the different odour components as well as the odour intensity of each component. A total of 176 volatile organic compounds (VOCs) were identified at both the inlet and exhaust of the bioreactors. The key odour components in swine gas were identified using the odour index of each component. The odour index was estimated as the geometric mean of intensity and hedonic tone of the individual component. The compounds having the highest odour indices in the samples taken at the inlet of the bioreactors are 2,3-butanedione, 2-methylbutanoic acid, 2-methylpropionic acid, 3-methylbutanoic acid, acetic acid, butanoic acid, dimethylsulfide, and p-cresol while those measured at the exhaust are p-cresol and dimethylsulfide.

Keywords: Swine odour, Key odour components, Odour index, Biotrickling filter, Modelling study.

INTRODUCTION

Odour emissions from livestock operations have become an important social problem due to its negative impact on the local economy, human health, and quality of life (Blanes-Vidal et al., 2009). With the emergence of larger livestock operations, there has been an increasing concentration and intensity of odours as well as a change in the unwillingness

of neighbours to accept livestock odours (Hogberg et al., 2005). Concerns have been directed at a broad spectrum of livestock production operations, however, the swine industry has received the highest attention from both public health and public policy standpoint (Thu, 2002). An increase in public awareness has led to the stimulation of development of better legislation (Sheridan et al., 2003) and technologies to control the release of malodorous gases from swine facilities.

Although many technologies exist for odour control, biological treatment (e.g. biofilters, biotrickling filters and bioscrubbers) was found to be cost-effective for the treatment of large volume of waste gases containing readily degradable contaminants in relatively low concentrations such as those emitted from farm facilities (Park and Jung 2006; Iliuta and Larachi 2004; Sheridan et al. 2002). However, even if biological methods have shown to effectively treat odour from livestock productions (Martens et al. 2001; Sheridan et al. 2002; Mann et al. 2002), bioreactors have not yet been efficiently incorporated into the barn system (Ozis et al., 2005). Despite its advantages over the other methods, biological treatment is limited by some operational problems. Nevertheless, the development of mathematical models for predicting and simulating the performance of the bioreactors, which allows for a better design and process optimization, helps reduce the impact of these limitations (Devinny et al., 1999).

The objective of this paper is to present the process on how the key odour components of swine barn air were selected for a modelling study. The odour emitted from pig production facilities is caused by the hundreds of odorous components present in the building exhaust gas (O'neill and Phillips 1992; Schiffman et al. 2001). This huge number of contaminants made it difficult, if not impossible, to simulate their removal in biotrickling filters. However, a hypothesis was formulated that if the compounds that are mainly responsible for the unpleasant odour could be well identified, then simulation on the removal of these components might be sufficient to describe the overall odour reduction.

Several studies have attempted to identify the main odorants responsible for the malodour emitted from pig buildings (Wright et al. 2005; Blanes-Vidal et al. 2009; Spoelstra 1980). Blanes-Vidal et al. (2009) suggested that in order to develop cost effective strategies for reducing odour nuisances from livestock production, it is important to determine what compounds are mainly responsible for the unpleasant odour. With this, measurements could be then focused on limited number of chemical compounds which could simplify the quantification of odours. Though the odour perceived by humans in a livestock facility cannot be easily predicted from the concentration of individual compounds in the waste air due to the interaction effects between individual compounds (Blanes-Vidal et al. 2009), it would be more reasonable to work on the removal of those few components, which are well-identified as the ones that carry much of the overall odour impact.

MATERIAL AND METHODS

Biotrickling filters Three biotrickling filters were treating the exhaust air from the three bench-scale pig chambers of the Research and Development Institute for the Agri-Environment (IRDA) at Deschambault, Québec, Canada. Each chamber (1.14 m wide, 2.44 m long, 2.44 m high, and fully slotted) housed four grower/finisher pigs. Each biotrickling filter has a total volume of 0.8 m^3. The packing is made of a synthetic material. A liquid was continuously recirculated through the packing during the

operation. Two sets of trials were conducted: one in winter (December 2008) and one in summer (June 2009). The bioreactors were treating air at flow rates around 35 and 100 L/s under winter and summer conditions, respectively. Each trial lasted for four weeks.

Sample collection The air samples for the analysis of VOCs were collected once every week during the last two weeks of each trial. They were taken from both the inlet and exhaust of the three bioreactors. A total of 24 samples were collected from the two trials (inlet and exhaust of three bioreactors; two weeks of sampling per trial; two trials), however, four of them were not included in the analysis of this study. The air samples were collected using carbotrap tubes and three tubes were collected at each sampling point. The air was pumped through the tubes using SP330/SP350 Sidepak personal sampling pumps for two hours at an average flow rate of 0.2 L/min. The samples collected in the tubes were subjected to GC-MS/O analysis to identify the different odour components as well as the odour intensity of each component. Simultaneously, another set of samples were collected in Nalophan bags for odour concentration measurements which were analyzed by olfactometry.

Gas chromatography–mass spectrometry–olfactometry system The samples were analyzed using a GC-MS-O system (6890N GC, 5975 MS detector, and Gerstel olfactory detector port (ODP2)) from Agilent Technologies. It is also equipped with a thermal desorption system (TDS) and a cooled injection system (CIS). The TDS temperature was set at 325^{o}C for 7 min while the CIS temperature was set at -150^{o}C. At the exit of the CIS, the sample was separated by chromatography. The initial oven temperature was set at 35^{o}C for 10 min. The temperature was programmed by certain increments until the final temperature reached 325^{o}C with 3 min. hold. The injection temperature was at 325^{o}C. Helium gas was used as carrier gas at a flow rate of 2 mL/min. Molecular weight-to-charge ratio (m/z) range was set between 33 and 450.

As the compounds exit the chromatograph, they were simultaneously directed to two detectors: the mass spectrometer and the olfactory detection port. The mass spectrometer identifies each compound while the olfactory detection port is where the odour intensity of each component was rated (from 1 to 10) by three experts.

Selection of key odour components The components were selected based on their odour indices. The odour index was estimated as the geometric mean of the odour intensity and hedonic tone of each component (equation 1; Qu et al., 2010).

$$OI = \sqrt{I * H} \tag{1}$$

where OI is the odour index, I is the intensity, and H is the hedonic tone. The hedonic tone was determined by giving numerical value to the odour character of the component. Using the odour wheels presented by Sheffield and Ndegwa (2008); McGinley et al. (2000) as guides, numbers were assigned to the different types of odour. A value of 1 was given to the natural pleasant odours e.g. fruity, vegetable-like, floral; 2 to the earthy odours e.g. mushroom, grassy, peaty; 3 to the chemical odours e.g. plasticizer, solvent, metallic, paint; 4 to the disinfectant or medicinal odours e.g. alcohol, vinegar, ammonia, phenolic, chlorinous; and 5 to the unpleasant or offensive odours e.g. sulphide, fishy, rancid, faecal, burnt, manure, sour, vomit, rotten eggs.

RESULTS AND DISCUSSION

A total of 176 VOCs were identified. Table 1 presents the frequency of appearance of these compounds at the inlet and outlet of the bioreactors. Of the 176 VOCs, only few could be considered significant based on the frequency of their appearance in the samples and odour intensity. As shown in table 1, some compounds were only occasionally present in the samples or they might be present but in concentrations below the detection limit of the instrument or their odour threshold. Some even appeared only at the exhaust of the bioreactors, which would indicate that these compounds were only produced during the biological treatment process.

The average odour indices of those components which appear quite often in the samples were calculated (table 2). Initially, regression analyses were conducted between the logarithm of odour intensity and odour concentration values and between the logarithm of odour index and odour concentration values (data not presented in this paper). However, none of the compounds gave significant correlation coefficients. Thus, the key odour components were then selected based on the strength of their odour indices. As shown in table 2, 2,3-butanedione, 2-methylbutanoic acid, 2-methylpropionic acid, 3-methylbutanoic acid, acetic acid, butanoic acid, dimethylsulfide, and p-cresol have the highest odour indices in the samples collected at the inlet of the bioreactors. As previously mentioned, the air entering the bioreactors was directly coming from the bench-scale pig chambers. Thus, this would indicate that these compounds are the ones mainly responsible for the unpleasant odour of exhausted swine ventilation air.

The finding is in agreement with those cited by other studies. Yasuhara as cited by O'neill and Phillips (1992) found that 2-methylpropanoic, butanoic, 3-methylbutanoic, pentanoic, p-cresol, indole, 3-methylindole, dimethylsulfide, dimethydisulfide, butanol, and 3-methylbutanol produced an odour very similar to swine odour. Eniola et al. (2006) quoted that p-cresol, ethylphenol, and 3-methylbutanoic acid have been identified as the most persistent and most significant contributors to swine odour. Spoelstra (1980) stated that p-cresol and volatile fatty acids might be good indicators of swine odour. Blanes-Vidal et al. (2009) found that odour concentrations were strongly related to the sulphur containing compounds. The study of Wright et al. (2005) showed that p-cresol appears to be the key odour character of swine gas.

However, with these set of significant malodorous components found in the exhaust air from a bench-scale pig barn, most of them were successfully removed in the biotrickling filters except p-cresol and dimethylsulfide (table 2). These two compounds still appear to have high odour indices at the exhaust of the bioreactors. The volatile fatty acids (e.g. butanoic acid, 3-methylbutanoic acid, 2-methylbutanoic acid), for instance, were almost completely removed by the treatment system. One factor that could explain the result would be the relatively high solubility of these compounds in water, as compared to p-cresol and dimethylsulfide, which made them easier to be absorbed into the recirculation liquid. Though, it cannot be concluded as well that these highly soluble compounds were completely biodegraded in the reactors.

Since what is more important is to reduce the odour nuisance of the gas released to the environment from swine facilities, it would be more relevant to study the optimum conditions on the removal of p-cresol and dimethylsulfide, which might still have significant contributions to the malodour of the treated air from the bioreactors. By doing

this, the performance of the bioreactors to reduce odour emissions could still be further improved.

Table 1. Frequency of appearance of the compounds identified in the samples collected at the inlet and exhaust of the biotrickling filters.

Compounds	Frequency[1]		Compounds	Frequency[1]	
	In[2]	Out[3]		In[2]	Out[3]
1,3-di-tert-butylbenzene	2	0	Acetone	5	0
111-trichloroethane	1	0	Acetonitrile	3	0
1-butanol	3	1	Acetophenone	7	4
1-dodecene	1	2	Acetyl valerate	2	0
1-heptanol	0	1	Alpha-cumyl alcohol	7	4
1-methoxy-2-propylacetate	1	2	a-pinene	10	10
1-octene	1	0	Benzaldehyde	1	5
1-phenyl-1-butene	0	1	Benzene	2	3
1-propanol	4	0	Benzoquinone	1	0
1-tetralone	0	2	Bicyclohexyl	0	3
2,3-butanedione	10	3	b-pinene	1	2
2,4-dimethylheptene	0	9	Butanoic acid	10	2
2,6-dimethylheptane	2	3	Butylacetate D3	1	0
2-butanone	2	6	Camphene	0	1
2-butoxyethanol	1	3	Carbon disulfide	4	2
2-butylacetate	1	0	Carbonyl sulphide	5	1
2-ethylhexanal	0	1	Carveol	0	2
2-ethylhexanol	2	4	Cumene	8	6
2-hexyl-4,5-dimethyloxazole	4	0	Cyclohexanone	1	0
2-isobutyl-4,5-dimethyloxazole	1	0	Cyclopentane	1	0
2-methyl-1-pentene	0	2	D4 siloxane	3	2
2-methyl-3-oxobutyronitrile	1	0	D5 siloxane	7	7
2-methyl-benzaldehyde	0	1	D6 siloxane	0	2
2-methylbutanoic acid	10	0	D7 siloxane	8	6
2-methylbutanol	1	0	Decahydro-2-methylnaphthalene	0	1
2-methylpropionic acid	10	1	Decanal	0	2
2-nitro-p-cresol	2	0	DEMB	0	1
2-Nitrophenol	4	0	Dichlorobenzene	3	0
2-octene	1	0	Dimethyl sulphide	10	10
2-pentanone	3	0	Dimethyldisulfide	5	5
2-pentylfurane	5	4	Dimethylethoxybenzene	1	2
3- methylbutanal	2	2	Dimethylstyrene	2	3
3-acetyl-4-hydroxy-6-methylpyridone	1	1	Dimethylsulfone	6	0
3-carene	1	1	Dimethylsulfoxide	1	0
3-methylbutanoic acid	10	1	Dimethyltrisulfide	3	2
3-methylbutanol	1	0	D-Limonene	8	4
3-methylbutanol propanoate	1	0	DMEB	2	1
3-methylhexane	1	0	Dodecanal	0	5
3-octene	0	2	Dodecane	2	0
3-pentanenitrile	0	1	Dodecanol	7	7
3-propylacetate	0	1	Ethanol	3	0
5-methyl-indene	1	0	Ethoxyacetylene	0	1
6-Methyl-5heptene-2-one	10	9	Ethylacetate	0	1
Acetaldehyde	10	9	Ethylanisol	0	1
Acetic acid	10	2	Ethylbenzene	4	9
Acetic formic anhydride	0	1	Ethylbutyrate	0	2

Table 1 Frequency of appearance of the compounds identified in the samples collected at the inlet and exhaust of the biotrickling filters (continued).

Compounds	Frequency[1]		Compounds	Frequency[1]	
	In[2]	Out[3]		In[2]	Out[3]
Ethylhexylethanoate	2	1	Nitrostyrene	2	0
Ethyl-m-cresol	0	2	N-methyl-3-nitrobenzamine	1	0
Ethylphenol	8	4	N-methylnitrobenzamide	2	1
Ethylpropylbenzene	0	1	N-methylnitrobenzamine	1	0
Ethylvalerate	1	0	NN-dimethylacetamide	1	0
Ethylxylene	2	0	NN-dimethylpropamide	2	0
Freon11	1	0	Nonanal	0	1
Freon142	4	1	Nonenal	1	0
Furfural	1	0	Octanal	5	7
Heptanoic acid	2	0	Octanoic acid	1	0
Hexahydrocumene	1	0	o-xylene	4	1
Hexanal	2	9	p-Cresol	10	7
Hexanoic acid	5	0	Acetate de p-cresol	2	0
Hexanone	0	1	p-cymene	3	2
Indane	2	0	Pentanal	1	0
Indanol	1	0	Pentanoic acid	10	0
Indene	1	0	Pentyl benzene	0	1
Indole	1	2	Pentylacetate	0	2
Isobutyl acetate	1	0	Phenol	3	0
Isopropanol	2	0	Phenylethyl alcohol	3	0
Isothiocyanatocyclohexane	3	3	p-menthatriene	1	0
m-cresol	0	1	Propanoic acid	10	1
m-cymene	1	2	Propenylbenzene	2	2
Menth-8-ene	0	1	Propylacetate	0	1
Menthane	1	0	Propylbenzene	1	2
Methanamide	1	0	Propylbutyrate	1	0
Methanamine	3	0	Propylcyclohexane	1	1
Methanesulphonyl chloride	2	0	Propylmethylbenzene	1	0
Methanethiol	0	1	Propylpropionate	0	1
Methylformate	1	0	sec-butyl-methylbenzene	0	1
Methylindole	3	2	Styrene	6	9
Methylmercaptan	5	3	Tetrachloroethylene	1	6
Methylmetacrylate	0	1	Tetrahydrofuran	0	1
Methylpropanal	1	0	Tetrahydronaphthalene	0	1
Methylpyrimidine	0	1	Tetralin	3	1
Methylstyrene	2	0	Tetralin2	0	1
m-nitrocresol	2	0	TMB	3	0
m,p-xylene	6	10	Tolualdehyde	0	1
Naphtalene	8	8	Toluene	4	9
N-ethyl propanamide	1	0	Trimethyl silanol	1	0
Nitrilbenzyl	1	0	Trimethylamine	3	0
Nitrosodimethylamine	1	0	Trimethylcyclohexane	0	1

[1]Frequency of appearance of the compound in the samples (dimensionless). Maximum is ten at each of the inlet and exhaust of the bioreactors.
[2]Inlet of the bioreactors
[3] Exhaust of the bioreactors

Table 2. Average odour indices of some components identified at the inlet and exhaust of the biotrickling filters.

Compounds	Odour Index[4]	
	Inlet	Exhaust
2,4-dimethylheptene	0.0	2.2
2,3-butanedione	5.3	1.2
2-butanone	0.2	1.1
2-methylbutanoic acid	5.9	0.0
2-methypropionic acid	5.5	0.5
2-pentylfurane	1.7	1.2
3-methylbutanoic acid	6.3	0.6
6-methyl-5heptene-2-one	3.7	2.8
Acetaldehyde	3.9	2.7
Acetic acid	4.9	0.6
Acetophenone	3.5	1.3
Alpha cumyl alcohol	3.1	1.4
a-pinene	2.7	2.0
Benzaldehyde	0.3	1.6
Butanoic acid	6.6	0.8
Cumene	2.2	1.2
D5 siloxane	3.3	3.0
D7 siolxane	3.8	2.5
Dimethylsulfide	5.2	3.9
Dimethyldisulfide	2.0	1.6
Dimethylsulfone	1.5	0.0
D-limonene	1.9	0.9
Dodecanal	0.0	1.7
Dodecanol	2.9	3.2
Ethylbenzene	2.3	2.9
Ethylphenol	3.4	1.6
Hexanal	0.8	2.7
Methylmercaptan	1.7	0.8
Mp-xylene	3.1	3.6
Naphtalene	2.7	2.5
Octanal	2.4	2.7
p-cresol	5.8	3.3
Pentanoic acid	4.3	0.0
Propionic acid	4.1	0.5
Styrene	3.1	3.6
Tetrachloroethylene	0.5	2.0
Toluene	1.4	2.5

[4]Dimensionless; maximum is 7.1.

However, it should be noted that what could be simulated in the bioreactors is the reduction of the component concentration, which might not be directly correlated to the overall odour reduction. Nonetheless, the removal of p-cresol and dimethylsulfide from the exhaust air of swine facilities might have a significant impact to the overall odour reduction.

CONCLUSION

The key odour indictors found in the exhaust air from bench-scale pig chambers are 2,3-butanedione, 2-methylbutanoic acid, 2-methylpropionic acid, 3-methylbutanoic acid, acetic acid, butanoic acid, dimethylsulfide, and p-cresol. They were identified based on their odour indices. However, a biological treatment using biotrickling filters was able to

remove most of these compounds except p-cresol and dimethylsulfide. Thus, p-cresol and dimethylsulfide are the swine odour components selected for a modelling study for a performance optimization. Though several studies have revealed that concentrations of the odour components could not be directly related to the perceived odour concentration, the removal of p-cresol and dimethylsulfide from the exhaust air of swine facilities might give a significant impact to the overall odour reduction.

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