Emission rates of odorous compounds from pig slurries

Taux d'émission de composés malodorants issus du lisier de porc.

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Abstract

Techniques to identify odorous compounds and determine their emission rates from liquid wastes using an odour emission chamber, are described. Odorous compounds, or odorants, were analysed by GC-MS and odour concentration was determined olfactometrically after emission from slurry after 6 weeks storage. We determined a range of emissions for the effects of reduced crude protein diets as compared to a commercial diet and the compounded effects of age and sex. The major odorous compounds were identified as belonging to the sulphide, volatile fatty acid, phenolic and indolic chemical groups. The mean emission rates were 1.35 million Odour Units min^{-1} m^{-2} for odour and 214, 2.15, 0.21, 0.44, 0.068 and 0.02 mg min^{-1} m^{-2} for hydrogen sulphide, ammonia, phenol, 4-methyl phenol, 4-ethyl phenol and indole respectively. The effects of the sex of the pig, age and sex/diet interactions on the emission rates are discussed.

Keywords : *slurry odours, emission rates, pig, diet and crude protein.*

Résumé

Les techniques pour identifier les composés odorants et déterminer les taux d'émission de déchets liquides sont décrits. On a analysé les composés odorants ou odeurs par GC-MS et on a mesuré la concentration odorante avec un olfactomètre après l'émission des effluents utilisant une chambre d'émission odorante. On s'est procuré ces effluents de porcs qui ont ingéré une alimentation commerciale conventionnelle et une alimentation à base de protéines brutes réduite. On a identifié les composés odorants majeurs comme appartenant aux groupes sulfures, acide gras volatils, phénoles et indoles. Les taux d'émission moyens des 200 litres d'effluents agités avec une vitesse d'air de 4 m sec^{-1} étaient 1.35 million unités d'odeur min^{-1} m^{-2} et 214, 2.15, 0.21, 0.04, 0.068 et 0.02 mg min^{-1} m^{-2} pour l'hydrogène sulfuré, l'ammoniac, le phénol, le phénol 4-méthyle le phénol 4-éthyle et indole respectivement.

Mots-clés : odeurs de lisiers, taux d'émission, porc, alimentation, protéine brute.

1. Introduction

Emission rates of odours from farm wastes have not received so much attention as organic compounds of environmental interest, such as hydrocarbons, halogenated hydrocarbons and poly aromatic hydrocarbons. However, at concentrations in the mg l^{-1} range H_2S and methanethiol have been fatal in many cases (Donham 1994). The emission rates from a range of anthropogenic phenols could be considered as a guide for this experiment, however, they are normally determined from natural waterways (Thomas 1990) and not a livestock slurry. Farm wastes have considerably different physical, chemical and biological properties and such analogies are difficult to justify.

In this study, we investigated pig waste using slurry from pigs fed diets containing the minimum and commercial amounts of crude protein. We also considered the age and sex of the pig on the emission rates of odorants and gases from the resulting slurry after six weeks storage. These emission rates would represent those from slurry storage facilities that have an open surface.

2. Materials and methods

2.1. Livestock and diets

Finishing (65 to 95 kg) and growing (35 to 65 kg) pigs of commercial stock were housed in groups and fed *ad libitum* the respective commercial diets (both containing 13.75 MJ digestible energy and 11 $g.kg^{-1}$ lysine) for their age. In this comparative test, a standard commercial diet and a reduced crude protein (RCP) diet were fed to each of the age groups. As a consequence, there were two diets for the growers(G); a commercial (a) and a RCP diet (b) and also a commercial (c) and RCP diet (d) for the finishers(F). The RCP diets were obtained at the least cost according to a commercial feedstuffs database and have synthetic amino acids added. They were formulated to contain approximately same protein as the commercial diet and ratios of lysine to methionine + cystine, threonine and tryptophan at 1 to 0.6, 0.65 and 0.20 respectively. The lysine to digestible energy (DE) ratios were close to the ideal of 0.9 and 0.8 for the growers and finishers respectively (Wang and Fuller 1989). In addition, the diets contained copper sulphate (a growth promoter) at approximately 175 and 100 mg g^{-1} for the growers and finishers respectively.

2.2. Experimental Design

Experiments were performed with pens containing pigs of different sex and age, each age was fed their respective RCP and commercial diet. There were twelve pigs in each of the eight pens, four pens contained entire males(m) and four pens contained females(f). The amount of feed offered to the pigs was 0.95 of the calculated *ad libitum* DE intake based on the pig liveweight during an acclimatisation period. The *ad libitum* DE intake, measured in MJ per day was calculated using the equation 4.1 $xW^{0.5}$ (where W is the liveweight of the pig in kg).

Slurry was accumulated separately under each pen for one month. During month one mG were fed either diet a or b; month two mF were fed either diet c or d; month three fG were fed either diet a or b and month four fF were fed either diet c or d to acquire slurry from each diet and age group. A slurry volume of 200 litres was taken from each slurry store after thorough mixing to determine emission rates in the odours emission chamber (OEC). Emission rates for the eight slurry samples were determined to after six weeks storage under anaerobic conditions at 15^{o}C, after four weeks accumulation beneath slatted pens.

2.3. Odour Emissions Chamber

The odour emissions chamber (OEC), was designed by Cumby *et al* (1995) and has an initial headspace volume of 40 m^3 of air. A slurry container with a capacity of 200 litres enabled the slurry to be stirred to expose a new surface to the laminar airflow. Minimal splashing and particulate emission occurred during slurry stirring throughout the experiment. The temperature of the slurry and the air were controlled at 15 and 20^{o}C respectively so that the higher air temperatures would minimise condensation onto the internal OEC surfaces. The OEC consists of stainless steel U-shaped ducting (0.5 m x 0.5 m internal section) whose ends were connected by a Tedlar bag. Adequate pressure was applied to the air in the OEC by the bag wrapping around a roller moving down rails under gravity to prevented external air being drawn through any leaks. This was necessary to prevent dilution of the odorants in the OEC volume.

2.4. Sampling and analysis of odorants

Headspace samples were taken at seven preset time periods during the 225 minute experiment to measure odorous and non-odorous emissions by passive sampling using a Teflon FEP gas sampling bags.

Slurry samples, of 500 ml, were taken before and after the experiment for every sample for the analysis of the usual parameters, including pH, ammonium-N, nitrate-N, total N and solids and the odorants were quantified by GC-MS analysis.

Volatile compounds were concentrated from a 600 ml sample of the headspace volume above the pig slurry by adsorption onto silica (Orbo 52, Supelco Inc. Supelco Park, Bellefonte, PA, 16823-0048 USA) and carbon (Orbo 32) based adsorbents. The concentrated odorants were then thermally desorbed from the adsorbents into the GC-MS system for identification and quantification.

Liquid or slurry samples were stored at 3^{o}C and analysed within three days of arriving at the laboratory to minimise the likelihood of further or different microbiological processes occurring. An accurate standard of each odorant in a mixture was prepared in distilled water with the pH adjusted to 8.3 and used for calibration (also stored at 3^{o}C). Samples volumes of between 50 and a 100 ml of slurry were centrifuged at 5000 G for 30 minutes. The concentration of selected odorants was determined by the direct injection of 0.5 µl of supernatant liquid from the centrifuged slurry sample into the GC-MS system.

A Hewlett Packard (hp) 5890 II Series GC and a 5972A mass selective detector (MSD II) were used to analyse all the samples. A fused silica (cross linked methyl siloxane) hp-1 column (25 m; i.d. of 0.2 mm and a 1.00 µm film) with a 1 m deactivated fused silica guard column was employed to analyse the sulphide component. A hp-1 column with a film thickness of 0.34 mm was used to analyse the headspace and slurry samples. Retention time was used to identify odorants and confirmed by matching the mass spectra with that from the NIST library.

Non-odorous methane and carbon dioxide emission rates were determined by GC-flame ionisation detection and infrared spectroscopy respectively.

The olfactometric response was determined using dynamic dilution. Each olfactometer had two sniffing ports and was of the forced choice type, with odourless air being presented to the panellist through one port and diluted odorous air through the other as described in Hobbs *et al* (1995).

2.5. Operational and computational parameters

The effects of diet on odorants in the slurry, in terms of sex of pig for both age groups were determined and expressed as a difference in the concentration, usually as a quadratic equation. The emission rates were calculated at zero time of the OEC run. The reasons for this are threefold. First, suppression of emission by the mass present in the headspace would be minimal, as Henry's Law infers an increasing headspace concentration would reduce the chemical potential, or energy for emission to occur. This would not reflect the real situation where odorants are rapidly removed. Second, physical and chemical interactions with other odorants, which are polar and reactive, will unnecessarily complicate the results. Third, oxidative processes that occur in the slurry because of stirring may introduce another factor into the calculation that is difficult to evaluate. The emission rates are expressed as mass emitted per unit area.

3. Results

The OEC was found to function effectively when quantifying major gases to determine the emission rates. However, VFA's and skatole gave variable concentrations because they were at or below the limit of detection, even with preconcentration onto adsorbents.

Emission rates are presented in Tables 1 and 2 for growing and finishing pigs respectively. The mean and standard deviation (sd) of the emissions for all samples are presented in Table 3 to give a range of expected emissions from 200 litres of slurry with a 1 m^2 surface area that was replenished by stirring. The mean emission rate was 1.35 million Odour Units (OU) min^{-1} for odour and 214, 2.15, 0.21, 0.44, 0.068 and 0.02 mg min^{-1} for hydrogen sulphide, ammonia, phenol, 4-methyl phenol, 4-ethyl phenol and indole respectively.

	Male		Female		
	diet a	diet b	diet a	diet b	Sed
OC in OU m-3 min-1	6.17E+05	3.23E+05	5.70E+0.5	6.53E+05	1.77E+05
carbon dioxide	1017	1362	1224	879	57.9
methane	6.67	12.92	5.68	4.82	1.07
hydrogen sulphide	110	105	198	232	14.1
ammonia	2.69	0.35	2.37	1.25	*
phenol	0.011	0.012	0.007	0.576	0.024
4-methyl phenol	0.012	0.042	1.065	0.941	0.058
4-ethyl phenol	0.0001	0.0048	n.d.	0.1817	0.0078
indole	0.0016	0.0000	0.3790	0.0919	0.0291

Units of mg m^{-2} min^{-1} unless otherwise staded.
ns not significant P>0.2
* not determined as two measurements at the end of the run were used.

Table 1
Emission rates from growing pigs fed commercial (a) and RCP (b) diets

	Male		Female		
	diet a	diet b	diet a	diet b	Sed
OC in OU m-3 min-1	2.50E+06	1.04E+06	2.49E+06	2.65E+06	1.87E+05
carbon dioxide	1003	1660	757	549	49.4
methane	6.43	6.08	17.9	13.2	1.08
hydrogen sulphide	173	337	274	289	12.1
ammonia	2.79	0.87	5.85	1.04	*
phenol	0.48	0.17	0.01	0.45	0.058
4-methyl phenol	0.49	0.33	0.54	0.13	0.0341
4-ethyl phenol	0.11	0.04	0.07	nd	0.0466
indole	0.48	0.01	0.21	0.40	0.0498

Units of mg m^{-2} min^{-1} unless otherwise staded.
ns not significant P>0.2
* not determined as two measurements at the end of the run were used.
nd not detected

Table 2
Emission rates from finishing pigs fed commercial (c) and RCP (d) diets.

	Emission rate	Standard deviation	min.	max.
OC in OU m^{-2} min^{-1}	1.36E+06	1.01E+06	3.23E+05	2.65E+06
carbon dioxide	1056	352	548.7	1660
methane	9.22	4.80	4.8	17.9
hydrogen sulphide	214.7	83.9	105	337
ammonia	2.15	1.75	0.35	5.85
phenol	0.21	0.0247	0.0068	0.58
4-methyl phenol	0.44	0.397	0.0125	1.06
4-ethyl phenol	0.07	0.069	0.0001	0.182
indole	0.20	0.199	0.00001	0.475

Units of mg m-2 min-1 unless otherwise staded.

Table 3
Range of emission rates of all pigs and diets.

Odorants id and magnitude of concentrationTo establish if Henry's Law was obeyed, we looked for a relationship between the emission rate and the concentration in the slurry. For the odorants that were quantified in both air and slurry, ammonia, the VFAs, the phenols and indole showed no relationship (P>0.1). Physical and chemical parameters may affect the emission rate, with, for example, dry matter (DM) (Fig 1) ranging from 8.4 to 4 % by weight. The chemical composition of the slurries also varied. The VFA's, total N and ammonia were generally less for the RCP diets than for the corresponding commercial diets for

both age and sex of the pigs.

Relationships of individual odorants in the slurry to the olfactory response was investigated. This was linear for 4-methyl phenol [4-mp] (r^2=0.6509, P<0.10), described by equation 1 where x is the odour emission rate (OU m^{-2} min^{-1}).

[4-mp] = $3.37e^{-5}x$ + 10.52 - Eq-1

3.1. Emission rates for slurry from growing pigs

The OC, which could be interpreted as the total odorant content, as well as including the effects of non-odorous emissions on the odorous components, was shown to differ between the sexes (P=0.097). Carbon dioxide, hydrogen sulphide, phenol, 4-ethyl phenol and indole showed a strong sex/diet interaction (Table 2). Reduction in concentration of nitrogen components in slurry from pigs fed the RCP diet was greater for male than female pigs (Fig 2). Ammonia emission rates from the slurry were lower for the RCP diet fed to pigs of both sexes (Table 2).

3.2. Emission rates for slurry from finishing pigs

Higher OC emission rates were observed from slurries from finishers than from growers (Table 3). Effect of diet was only evident for slurry from male pigs with a decrease in odour emission rate for pigs fed RCP diet. Generally, the emission rates of OC, hydrogen sulphide, phenol and indole all showed a sex/diet interaction. Although there was a higher OC emission rate for the slurries from the male pigs fed the commercial diet, the major odorant hydrogen sulphide was emitted at a lower rate than that from the slurry of the pigs fed the RCP diet. The other odorants demonstrated a higher emission rate from the slurry of the male pigs fed the commercial diet than the slurry of the female pigs fed the RCP diet.

4. Discussion

In order to determine their emission rates we require concentrations near 1 ppm(v) which are higher than those found around normal livestock practices. The aim was to determine the range of emission rates (Table 3) using slurries produced from different diets. Stirring the slurry did have effects, for example, an increasing stirring rate increased emission of odorants (unpublished data) although Cumby (1997) found that ammonia emission rates decreased with stirring. Increasing slurry temperature physically increases emissions and bacterial biogenesis of odorants. Odour emissions may be increased as more carbon dioxide and methane are produced with increasing temperature (Husted 1994) to strip the odorants from the waste.

The biogenesis of methane will generally be greater in a larger store per unit volume because the greater volume to area ratio creates a more stable and necessary anaerobic environment. Physical effects are also noticeable. Methane

was emitted quickly after biogenesis because of a low solubility, however there is evidence of some physical inhibition of emission (Hobbs *et al* 1997). In contrast the larger phenol molecule, present at about 50 mg l^{-1}, was emitted at 0.21 mg m^{-2} min^{-1} and would take over 200 minutes to deplete assuming no regeneration. VFAs demonstrated ambiguous emission behaviour giving a variable concentration in the headspace with no discernible pattern. Phenols were at a higher concentration than the VFAs in the headspace although the phenol concentration in the slurry was less by an order of magnitude than that of the VFAs. Henry's law states that a thermodynamic equilibria exists between the concentration in the headspace and the slurry and that the chemical energy driving emissions is proportional to the concentration in the slurry. Phenols and indoles (the latter when measurable) demonstrated characteristic concentration curves increasing and commensurate with Henry's Law. However, Henry's Law applies to pure solutions rather than the complex mixture present in slurries. Electrolytes and surfactants in the form of polymeric proteins, saccharides and lipids all contribute to deviations from this law (Thomas 1990). A ratio of the concentration in the slurry to the emission rate did not reveal any consistent results, with the exception of 4-methyl phenol, due to the large variation of concentration in the headspace of several orders of magnitude.

We identified a relationship between OC and the concentration of 4-methyl phenol in the slurry despite hydrogen sulphide being the major odorant in the headspace. However, emission rates for methane were lower than expected, possibly because the methanogens which are strict anaerobes were inhibited by oxygen infusing into the slurry during stirring. Hydrogen sulphide is not highly soluble in water and additional stirring may have induced rapid biogenesis of this gas. Rapid emissions of hydrogen sulphide have been shown to cause fatalities (Donham 1994) and this set of criteria may be reproduced in the OEC.

The effects of age, sex and diet of the pig on the emission rates were varied, of the eight emission rates for the growers five showed a sex/diet interaction, in addition there was a sex effect for the OC. The finishers had four sex/diet interactions, 3 sex effects and a diet effect where methane biogenesis was reduced for the RCP diet. A common factor was that the RCP diets reduced the ammonia emission rates (Tables 1 and 2) and concentrations in the slurries for pigs of the same sex and age. This was also true of the total nitrogen content in the slurry.

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6. References

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