Odor

Identification and Quantification of Odorants from Livestock Production by Sampling on Adsorption Tubes and Analysis by Thermal Desorption and Gas Chromatography with Mass Spectrometry

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Abstract

Odour nuisance is a major barrier to the further development of livestock production in Denmark and other livestock-dense areas, and there is an urgent need to develop odour abatement technologies in this field. A first and necessary step is to identify the major odour contributors from livestock production. Three techniques have been chosen for further development: (i) sampling on adsorption tubes with subsequent thermal desorption and analysis by gas chromatography and mass spectrometry (TD-GC/MS), (ii) membrane inlet mass spectrometry (MIMS), and (iii) sampling on adsorption tubes with subsequent thermal desorption and separation by gas chromatography whereby the sample stream is split into a mass spectrometer and a sniffing device with two ports (TD-GC/MS/O). The latter two techniques are presented in other papers; this paper will focus on TD-GC/MS. The objective was to develop a robust and cost-effective technique whereby the sampling can be done by a technician after a very brief period of training and the tubes are sent by mail to the laboratories for further analysis. The result is a method of active sampling on stainless steel adsorption tubes packed with Tenax TA, Carbograph 1TD and Carbograph 5TD or Unicarb. A calibration standard solution containing 40 compounds selected on the basis of their odour contribution values, i.e. typical concentration values divided by their odour threshold concentrations, has been set up and tested. The compounds represent the following chemical groups: sulfides, terpenes, aldehydes, ketones, alcohols, phenols, indoles and volatile fatty acids. The maximum calibration amounts were 100 ng for all compounds except acetic, propanoic, butanoic and pentanoic acids, where 1000 ng were spiked on the adsorption tubes. Twenty to 100 ng were loaded on the analytical column due to a cold trap outlet split of 1:4. The sample separation was performed using a polar polyethylene glycol capillary column. Dimethyl sulphide, methanethiol and trimethylamine were purchased as certified ultra pure gases in nitrogen and added to the adsorption tubes using a gastight syringe. Data for break-through volumes, storage recoveries, desorption efficiencies, method detection limits and GC/MS parameters will be presented. The developed method was used to establish livestock production emission data for the odorants and to evaluate odour abatement technology, e.g. biofilters, wet scrubbers and changes in the feedstuff composition.

Characterization of Dairy Manure Odor Using Headspace Solid Phase Microextraction and Multidimensional Gas Chromatography - Mass Spectrometry - Olfactometry Analysis

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Abstract

Livestock operations are associated with emissions of odor, gases, and particulate matter. The majority of previous livestock odor studies focused on swine operations. Relatively few relate to dairy cattle. Dairy industry in Iowa is sizable (~250,000 head) and modernizing. In Israel, dairy is one of the main livestock production sectors. Thus, there is a need to characterize emissions of odor and odorous gases associated with dairy cattle to enable researchers, industry, and policy makers to better address such aerial emissions. Finding compounds which constitute the primary odor impact is among the most demanding of analytical challenges because critical odor components frequently present at very low levels in a complex matrix of numerous insignificant volatiles. In this study dairy manure odor was characterized using a novel multidimensional gas chromatography - mass spectrometry - olfactometry (MDGC-MS-O) system allowing for simultaneous chemical and sensory analyses of dairy odors. Manure samples were collected from the ISU Dairy Farm in Ankeny, Iowa. Headspace solid phase microextraction (HS-SPME) was used to collect volatiles from 3 mL manure enclosed in 20 mL vials held at 30 ºC. A total of 25 extractions ranging from 15 sec to 11 h using DVB/Carboxen/PDMS fibers were completed. These were followed by chemical-olfactory analyses on the MDGC-MS-O system. Multidimensional capability of the analytical system enabled the isolation and identification of key characteristic odorants. To date, more than 50 distinct odors/aromas and over 150 compounds were found emitted from dairy manure. Of these, about 20 odor-compounds matches were already resolved and more are underway. Several key characteristic odorants were matched and identified. These include S-containing compounds (i.e. dimethyl sulfide / onion; dimethyldisulfide / sweet; dimethyltrisulfide / garlic), volatile fatty acids (i.e. butanoic acid / cheesy, body odor; pentanoic acid / body odor) and phenolic compounds (i.e. p-cresol / medicinal, barnyard; indole / phenolic, body odor; skatole / phenolic, body odor). Both short and long HS-SPME exposure times resulted in clear separations of MS and aroma peaks that were also important odorants. At very short extraction times sulfuric and phenolic compounds were most dominant. Odor intensity and the number of compounds identified were generally proportional to the SPME extraction time. Compound competition and displacement was delineated for several VOCs particularly during longer extraction times. Different relationships between compound concentrations (MS peak area) and intensity of their matched odor (aroma peak area) were also observed. These relationships were more strongly dependent at short extractions.

Quantification of Odor and Odorants at Swine Facilities and Assessment of Their Impact Downwind

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Abstract

Confinement swine production has been developed to increase productivity and to make efficient use of land and facilities. However, complaints of malodors are reported with increasing frequency in some communities near confined swine operations. The purpose of this paper is threefold: 1) to describe methods for quantifying odor and odorants emitted at swine operations, 2) to show how the odor is typically dispersed downwind, and 3) to elucidate the potential impact on human health from exposure to odor (and odorant) levels to which a neighbor is typically exposed. Methods used to quantify odor and odorants include: a) human assessments of the odors and irritation associated with gaseous emissions and particulates, and b) instrumental measurements of the concentrations of total volatile organic compounds (called VOCs), hydrogen sulfide, ammonia, particulates, and endotoxin present in the air during the odor assessments. Human evaluations of odor and irritation in the field are obtained with portable threshold devices (e.g. Scentometer, Nasal Ranger®, Duke University lateralization device), comparison with butanol standards, and ratings of overall odor intensity, irritation intensity, pleasantness, and odor character. Air samples are also obtained in the field in Tedlar® bags which are taken to the laboratory for olfactometry to determine how many times the odorous air needs to be diluted to reach threshold. The olfactometer utilized has a variety of testing modes including Triangular Forced Choice and meets the requirements of the CEN odor testing standard, EN13725:2003 and ASTM International E679-91. VOCs are measured in two ways. Real-time monitoring of VOCs at ppb levels is performed with a photo-ionization detector (PID) that can detect VOC concentrations down to a few ppb. Air samples are also obtained in canisters and analyzed in the laboratory by GC/MS and GC/FID. Hydrogen sulfide is measured with a gold film sensor selective for hydrogen sulfide. Ammonia is measured with a chemiluminescence NH_3 analyzer and Draeger tubes. Total suspended particulate concentrations are measured in real time by a monitor that utilizes aerodynamic particle sizing and an in-line filter cassette for gravimetric sampling (HAZ-DUST EPAM-5000). Endotoxin is collected on fiberglass filters and quantified using a Limulus Amebocyte Lysate (LAL) assay. Human measurements are correlated with instrumental measurements to determine the best predictors of odor. Dispersion modeling is used to predict the intensity of odor and concentration of odorants downwind under a variety of atmospheric conditions. Levels downwind predicted by dispersion modeling are compared with results from exposure studies to determine potential health effects.

This paper will present research findings that compare odor dispersion from swine facilities that used a variety of alternative and conventional waste technologies. Nineteen different sites were included in the study; some sites included more than one technology to be evaluated. The trajectory and spatial distribution of odor and odorants downwind of each of the facilities (the alternative technologies and two controls) under two meteorological conditions (daytime and nighttime) were predicted using a Eulerian-Lagrangian model. The odor modeling was based on a mathematical model to predict long distance dispersion (Hsieh et al. 1997; Katul and Albertson, 1998; Nathan et al., 2002; Hsieh et al., 2003) but was modified to be consistent with experimental odor dispersion data at swine operations in North Carolina (Schiffman et al., 2003a; Schiffman et al., 2003b; Schiffman et al., 2005). Modeling was performed using all significant odor sources at a facility. This model was strengthened during the course of the study with an increased number of testing sites and observations. For the farms with animals, the computations were performed with and without the swine houses to determine the odor contribution from the animals themselves along with the technology components. The potential health consequences of the levels of odors dispersed downwind will be addressed as well.

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1000 Olfactometry Analyses and 100 TD-GC/MS Analyses to Evaluate Methods for Reducing Odour from Finishing Units in Denmark

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Abstract

Odour from pig production is one of the biggest barriers to expanding pig production units in Denmark. There is a great need to develop methods to reduce odour emission. However, it is very important that the solutions are economically feasible. During the last four years, the National Committee for Pig Production has carried out approximately 1000 olfactometry analyses of air samples from commercial pig production units. The measurements have primarily been carried out in finishing units because approximately 70% of odour originates from this part of an integrated pig production unit.

The aim was to evaluate different methods for reducing the odour emission. Case-control studies were performed to test different methods, and an intensive campaign measurement programme was conducted to investigate whether an idea for odour reduction has a potential for development.

In the case-control studies, the farms were visited every second week over a period of six months. Each time, the following samples and registrations were made: 1) air sample was collected in 30-litre tedlar bags during a 40-minute period, and analysed in accordance with European CEN standard for olfactometry the following day, 2) ventilation rate was determined using calibration measuring fans from Fancom and 3) ammonia and carbon dioxide concentrations were measured using detection tubes from Kitagawa and electronic equipment from the Veng system. During the last year of the project, the measurement protocol was enlarged to include sampling on adsorption tubes and analysis by gas chromatography and mass spectrometry (TD-GS/MS).

The overall conclusions of the tests were that 1) The odour emission is 3-5 times higher during the summer than during the winter, 2) There is a linear correlation between air exchange and odour emission, 3) The odour emission from a finishing unit with slurry system is the same before and after delivery of pigs as long as the ventilation rate is maintained, 4) Management factors are essential for controlling the odour emission from finishing units. 5) Biological purification of exhausted air is the only odour-cleaning technique that can be recommended, 6) Scrubbers with one filter using sulphuric acid can only be used for ammonia reduction and not for odour reduction, 7) comparison of odour strengths determined by olfactometry and TD-GS/MS indicated that phenols, indoles and volatile fatty acids do not play a major role for the odour emission. This part will be discussed in the presentation, however not in the proceedings.

Introduction

Denmark is a small country in Europe that produces 25 million pigs annually, corresponding to the number of pigs raised in Iowa. However, in terms of land area, the country is only 1/3 of the size of Iowa and has twice the human population.

As in every other industrial country with a high pig density compared with the human population density, odour has become an increasing problem. If production levels are to be maintained or even increased, it is essential to develop methods for reducing odour.

Meat-exporting countries such as Denmark cannot add the cost of reducing odour to the retail price. Importing countries will not pay for odour reduction in Denmark. Therefore, odour reduction in industrial countries with high pig densities compared with human population densities has to be financed by achieving a higher level of productivity within pig production, enhancing the quality of the meat and, last but not least, improving the country's veterinary health status and food safety standards. If these criteria cannot be met, the pig production sector will move to countries with lower human population densities and fewer environmental regulations.

In the light of this scenario, the National Committee for Pig Production, Danish Bacon and Meat Council, has conducted and financed a number of campaign measurements and specific tests aimed at following new technology and shortening the path from idea to reliable and cost-effective odour reduction method.

Today, ammonia emissions can be reduced by 90%. When odour from pig housing facilities can be reduced by more than 90-95% and demands for operating efficiency and cost-effectiveness have been met, there will be a strong potential for growth in pig production.

Aim

The aim of the paper is to present the results from a number of projects that were conducted in order to evaluate different methods for reducing odour from finishing units in Denmark. The proceeding will involve analyses of:

- Feed experiments
- Ventilation rate
- Chemical air purification
- Biological air purification
- Odour source

Besides the tests of odour reduction technologies, some supplementary experiments were conducted in order to answer the following questions:

- Is it possible to mail odour samples in Tedlar bags from a post office near the farm to the olfactometry laboratory during the cold winter period, when there is a risk of condensation forming inside the bags?
- How many odour measurements need to be taken in a case-control study in order to demonstrate a difference of 50% between the emissions from two sections?

Materials and Methods

The odour tests of different techniques were performed in commercial pig herds around Denmark, and the feed experiments and cooling experiment were performed at a test station owned by Danish Bacon and Meat Council.

All measurements were taken in finishing units, since 70% of the odour from an integrated production facility comes from the finishing unit. This can be seen both in the use of current standard data for odour emissions from pig units, which are based on measurements taken in German housing units in the 1980s, and in the future standard data for odour emissions from pig units, which are based on Danish measurements taken in 2005 (reference 1).

Two different test protocols were used in the testing of the different technologies:

- One of the protocols is referred to as campaign measurements, which are designed to show whether an idea for odour reduction has a potential for development. The evaluation is based on an intensive measurement programme spread over a period of one and a half months.
- The other protocol is referred to as a case-control study, which is designed to demonstrate to the environmental authorities and the pig producers the capability of a technology. This study is spread over a period of at least six months so that different seasonal variations and operating efficiencies can be included. During this period, odour concentrations were measured every two weeks.

The primary test parameter was the odour emission. The odour concentration was measured by collecting exhausted air in a 30-litre Tedlar bag during a 40-minute period.

The following day, the air bags were analysed at the Danish Meat Research Institute to determine the odour concentration using the olfactometric method in accordance with the European CEN-standard (reference 2).

In connection with the odour samplings, the following data were registered in all the case-control studies and some of the campaign measurements:

- Ventilation rate (using Fancom measure wings)
- Carbon dioxide concentration in the chimney (using Kitagawa tubes and pump)
- Ammonia concentration in the chimney (using Kitagawa tubes and pump)
- Outdoor temperature and the temperatures in the chimneys
- Number of pigs at pen level and visual assessment of the weight of the pigs
- Chemical substances sampled together with some of the odour samplings (TD-GC/MS)

In the case-control studies, the temperatures, ammonia concentrations, carbon dioxide concentrations, and in some cases, ventilation rate were also measured online once an hour using the Danish Veng system.

This equipment consisted of pumps, that pumped approximately two litres of air per minute from the air inlet and chimneys through Teflon tubes to instruments that analysed the ammonia and carbon dioxide content of the air. To measure the ammonia concentration, a Polytron 1 from Dräger with a measuring range of 0-100 ppm was used, and to measure the carbon dioxide concentration, a Vaisala with measuring range of 0-5000 ppm was used.

A manifold placed immediately before the ammonia and carbon dioxide instruments ensured that the air from each pump was sent separately to the two instruments. The air from each pump was analysed for a period of ten minutes, and the last recorded value was stored.

During every second measuring period, outdoor air was pumped through the ammonia and carbon dioxide instruments. All the air that was analysed was preheated to 34 °C, before being pumped into the measuring instruments.

The reason for choosing to send the outdoor air through the instruments every second time and to preheat the air from the measuring points in the pig unit was to make the ammonia sensor stable.

There had previously been problems maintaining the calibration, especially when the relative humidity in the unit was high. The preheating was carried out by placing the manifold in a steel box that could be heated electrically.

Statistics for Case-Control Studies

Emissions of ammonia and odour were determined by multiplying the odour concentrations by the ventilation rate.

For each batch, the average and standard deviation were determined for the temperature in the chimney, ventilation rate, carbon dioxide concentration, and the concentration and emission of ammonia.

For the latest case-control studies, the log-transformed odour emission was analysed statistically using a variance analysis in the MIXED procedure in SAS. The group and batch were included as a systematic effect.

Supplementary Experiment 1 – Condensation

Since the odour samples were taken in Tedlar bags at different pig units around Denmark, it would have been time-consuming for the technicians to deliver the samples to the olfactometry laboratory. Instead, the samples were sent to the institute by express mail. However, according to the CEN-norm condensation is not allowed in the bags, and there was a risk of condensation at low outdoor temperatures. A supplementary experiment was therefore performed to investigate what effect the condensation would have on the actual analysis.

The simulation was carried out as follows. Three double samples were taken between 12 pm and 1 pm, 1pm and 2 pm, and 2 pm and 3 pm, respectively. At 4 pm, one of the double samples was placed in a freezer at a temperature of -3°C, while the other sample was kept at 22°C. At 9 am the following morning the bags were taken out of the freezer and placed next to the other bags. The odour analysis was started at 12 pm. The experiment was repeated the following days.

Supplementary Experiment 2 – Panel Variation

Generally speaking, there has been a lot of scepticism about panel variation when analysing odour from pig units. For this reason, a comparative study of the two panels was conducted.

The air samples were analysed twice, first by a panel in the morning and then by a panel in the afternoon. The analysed samples were taken from the chimney in two identical housing sections for finishing pigs. A total of 36 measurements were analysed twice by different panels.

Supplementary Experiment 3 – Statistically Significant Difference Between Two Systems

Before starting an experiment, it is necessary to know how many measurements need to be taken to prove a statistically significant difference between systems.

Over a period of one year, odour measurements were taken at regular intervals in two identical sections for finishing pigs. A total of 4 batches were included in the experiment. For each batch measurements were taken on 5 to 7 occasions and each time odour measurements were taken between 12 pm and 1 pm, 1pm and 2 pm, and 2 pm and 3 pm. Besides odour, the registration parameters mentioned previously were also recorded.

In the statistical calculations, the percentage difference between the odour emission in the two sections was considered. A variance analysis was performed in order to determine the number of measurements needed to record a difference of 50, 30 and 20% between the sections, depending on the number of measurements taken each day.

Results and Discussion of Supplementary Experiments

Results and discussion for the supplementary experiments will be given before the odour reduction technologies, because the supplementary experiments form the basis of the overall measurement strategy.

Supplementary Experiment 1 – Condensation

In supplementary experiment 1, in which condensation in the Tedlar bags was simulated, visible condensation on 1/5-1/2 of the inner surface of the bag was recorded, when they were taken out of the freezer at 9 am. At the start of the odour analysis at 12 pm, the temperature in all of the bags was 22.5 °C, so no condensation was present at the time of analysis. The results of the odour analysis are illustrated in Figure 1. The odour analysis showed, that at the specified temperature and humidity levels, the presence of condensation had no effect on the result of the odour analysis.

Provided there is no condensation when the samples are taken in the pig unit and at the time of analysis, then it makes no difference if there is condensation in the period between sampling and analysis. It was therefore concluded that odour samples can be sent by express mail to the olfactometry laboratory.

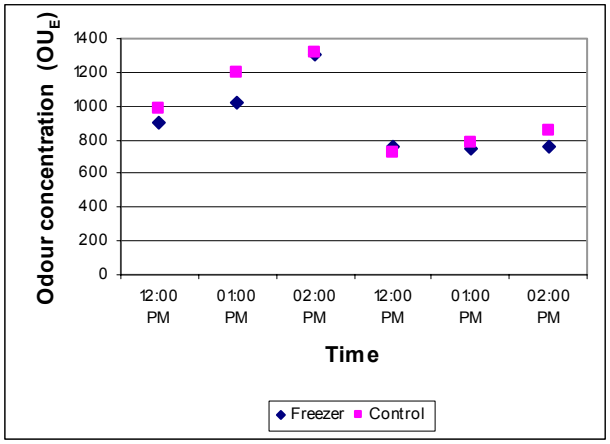

Figure 1. The odour concentration in Odour Units (OU_E) for the double air samples, one of which was kept in a freezer at – 3°C and the other at 22 °C. When the samples were analysed, the temperature was 22.5°C. The samples were taken over a period of two days between 12 pm and 1 pm, 1pm and 2 pm, and 2 pm and 3 pm, respectively. The temperature in the pig unit was 18°C and the relative humidity was 68%.

Supplementary Experiment 2 – Panel Variation

The results of double olfactometry analysis for 6 days' odour measurements in two sections for finishing pigs are shown in Table 1.

The log-transformed odour concentration was analysed statistically using a variance analysis in the MIXED procedure in SAS. The time of day and section were included as a systematic effect, and the date and panel within the day were included as a random effect.

The estimate of the covariance parameter shows that 79% of the variance of the odour concentration is caused by the date, 10% is caused by the section, and that the panels do not contribute to the variance.

After this calculation, the percentage difference between the odour concentration recorded by the morning panel and the afternoon panel was calculated for each bag with odour.

Then the calculated differences were then analysed statistically using a variance analysis in the MIXED procedure in SAS. The time of day and section were included as a systematic effect, and date was included as a random effect. The result showed that 95% confidence interval for the percentage difference between the panels was -10 – 9%.

It can be concluded that, compared to the variance of date and compared to the difference of the sections, the variance of the panels can be neglected. It can also be concluded that 95% of the differences between the panels were within the interval of -10 – 9%.

Table 1. Odour concentration analysed twice by a morning panel and an afternoon panel, respectively.

	Time	12 pm – 1 pm		2 pm – 3 pm		4 pm - 5 pm	
	Section	1	2	1	2	1	2
3 Sept	Morning	577	869	633	654	745	739
	Afternoon	633	630	702	770	604	680
18 Sept	Morning	1272	950	1275	948	1142	782
	Afternoon	1219	776	1329	1078	1521	707
2 Oct	Morning	716	618	618	750	908	471
	Afternoon	811	594	871	746	748	668
16 Oct	Morning	1512	2258	2602	1629	1998	2041
	Afternoon	1851	1918	2345	1578	1853	1318
30 Oct	Morning	1105	1029	1145	1035	993	1392
	Afternoon	1025	1145	993	893	1002	1502
11 Nov	Morning	623	817	724	701	658	754
	Afternoon	722	744	812	865	744	981

Supplementary Experiment 3 – Statistically Significant Difference Between Two Systems

Odour emissions from two identical sections for finishing pigs over a period of one year are shown in Figure 2. Figure 3 shows the percentage difference in odour emission between the two sections. As can be seen in the graph in Figure 3, the percentage differences vary around 0, and in table 2 the average and standard deviation are shown for each batch.

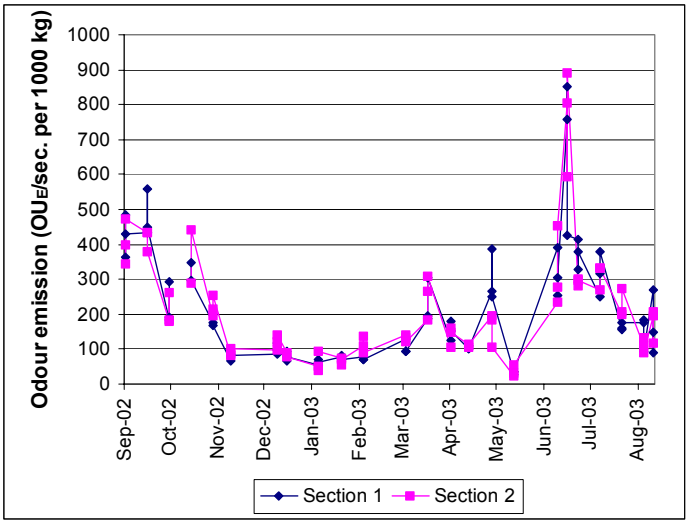

Figure 2. Odour emission in OU_E/sec. per. 1000 kg animal. On one measurement day (18 June), the odour emissions were inexplicably high. Presumably, the measurements taken on this day are incorrect.

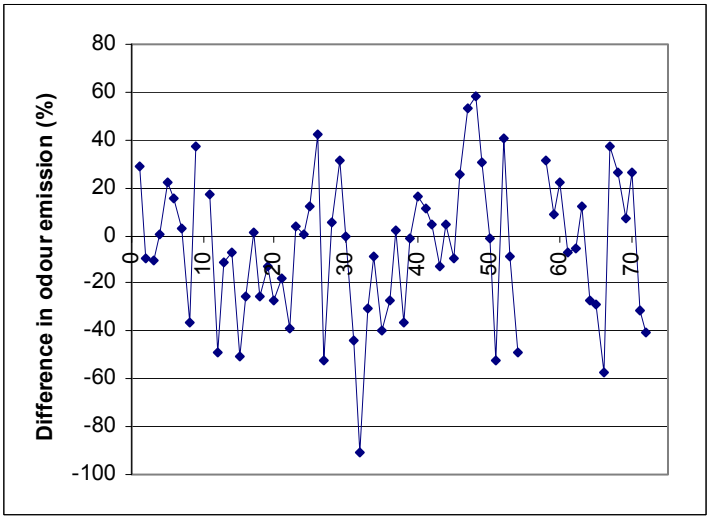

Figure 3. Differences in odour emissions between the odour samples taken in the two sections at the same time. A total of 144 odour measurements were taken, i.e. 72 pair-wise registrations. Data from 18 June are not included in the figure, because of the inexplicably high values on this day.

Table 2. Odour emissions from two identical sections for finishing pigs.

Batch	Average of odour emissions		Average of percentage difference between the odour emissions registered at the same time in section 1 and 2	Standard deviation of the percentage difference between the odour emissions taken at the same time in section 1 and 2
	(OU_E/sec. pr. 1000 kg)		(%)	(%)
	Section 1	Section 2		
1 Sep-Nov	284	280	1.4	26
2 Dec-Feb	78	90	-15	34
3 Mar-May	157	140	9	30
4 June-Aug	310	314	-1.2	38
4 Without the divergent measurements the 18 June	248	238	-2.4	31

Despite the large differences in odour emissions from batch to batch shown columns 2 and 3 in Table 2, it was interesting to observe that the standard deviations of the percentage differences between the odour emissions from the two sections were at the same level for each batch throughout the year.

If the three percentage differences in odour emissions from the same day are seen as repetitions, and the entire data set is taken into account, the variance between days is 234 and the variance within the day is 675. This means that 74% of the variance of the percentage differences in odour emissions from the two sections is due to the variation within the day.

Measurements taken over a period of one year can be used to predict the number of measurements needed to determine whether a given treatment is capable of reducing odour emissions by 50, 30 and 20%, respectively. If the variation between days is set to 27 and the standard deviation is set to 35, then, for example, 10 days with one measurement in each section, or 6 days with triple measurements in each section are needed to test a 50% reduction (see Table 3).

Table 3. Number of measurements needed to test a difference in odour emission from two identical sections with different treatments

Reduction (%)	1 sample in each section per day	2 samples in each section per day	3 samples in each section per day
50	10	8	6
30	24	16	13
20	50	33	28

Results and Discussion of Test Concerning Odour Reduction Technologies

Feed Experiments

Three feed experiments were carried out at the test station owned by Danish Bacon and Meat Council. Before describing the results in detail, it should be mentioned that none of the feed experiments had an effect on the odour emission. However, as expected the experiments resulted in reduced ammonia emissions.

Crude Protein

The odour and ammonia concentrations in two sections with finishing pigs weighing between 33 and 113 kg were compared. In one of the sections, the pigs were fed a diet containing a reduced level of crude protein. The feed was delivered to the farm in two batches. The analyses showed that the first delivery for sections 1 and 2 contained 16.1 and 14.2% crude protein, respectively, and the second delivery contained 15.1 and 14.0%, respectively.

The ammonia concentration and the secondary registration parameters using the Veng system were taken every half hour. Three odour samples were collected in the chimney in each of the two sections on 6 measurement days spread over the whole production cycle.

The ammonia emission was reduced by 33% in the section with the reduced level of crude protein. With the given number of measurements, it should be possible to prove whether treatment with reduced crude protein could reduce the odour emission by 50%, but in this experiment it was not possible.´

Table 4. Average of ammonia and odour emission together with supplementary records in the experiments with different levels of crude protein

Section	Ambient temperature Celsius	Outlet temperature Celsius	Ventilation rate m^3/hour per pig	NH_3 ppm	CO_2 ppm	Ammonia emission g NH_3-N/hour	 kg NH_3-N	Odour Emission OU_E/sec. per 1000 kg
Control	-0,1	17.3	27	19.8	2316	0.304	0.533	78
Reduced crude protein		16.3	29	12.5***	2232	0.209***	0.366***	90

*, **, ***: Statistically significant difference, *: P<0.05; **:P<0.01; ***:P<0.001

Benzoic Acid

The feed containing 1% benzoic acid was tested on pigs weighing between 30 and 100 kg, while feed containing 3% benzoic acid was tested on pigs weighing between 65 and100 kg.

Batch 1: Control feed versus control feed containing 1% benzoic acid.

Batch 2: The same as batch 1, though the treatments in the sections were interchanged.

Batch 3: Control feed versus control feed containing 3% benzoic acid.

Batch 4: The same as batch 3, though the treatments in the sections were interchanged.

The ammonia concentration and the secondary registration parameters using the Veng system were recorded every half hour.

For both batches 1 and 2, three odour measurements were taken in the chimney in each of the two sections on 6 measurement days spread over the whole production cycle. For both batches 3 and 4, three odour

measurements were taken in the chimney in each of the two sections on 6 measurement days spread over the two production cycles. This means that, a total of 108 odour measurements were taken.

The addition of benzoic acid to the feed did not result in a statistically significant differerence in the odour emission.

In batch 1, the ammonia emission was 10% higher from the section with the feed containing 1% benzoic acid compared with the control section, where benzoic acid was not added to the feed ($p<0.05$). The reason that there was an increase rather than a reduction is that, according to the feed analyses, the crude protein content in the feed was 0.9% higher in this group. Furthermore, the results of the analysis showed that the concentration of benzoic acid was not 1%, as expected, but rather 0.83%.

In batch 2, the feed mixtures were identical, except for the addition of 1% benzoic acid to the feed in the treatment group, and the experiment showed that the ammonia emission was 5% lower from the unit where the pigs were given feed containing benzoic acid. However, the reduction was not statistically significant.

Table 5. Average of ammonia and odour emission together with supplementary records in the experiments with different levels of benzoic acid added to the diet

Section	Ambient temp. Celsius	Outlet temp. Celsius	Ventila-tion rate m^3/hour per pig	NH_3 ppm	CO_2 ppm	Ammonia emission		Odour Emission
						g NH_3-N/hour	kg NH_3-N	OU_E/sec. per 1000 kg
Batch 1			0					
Control	5.7	17.9	36	16	2154	0.216	0.430	122
1% benzoic acid		17.5	41	14	2030	0.237* (26-100 kg)	0.471*	114
Batch 2								
Control	16.7	21.1	84	4	820	0.171	0.332	255
1% benzoic acid		21.4	79	4	908	0.163 (27-100 kg)	0.317	255
Batch 3								
Control	7.3	17.6	55	15	1518	0.461		207
3% benzoic acid		16.7	59	6	1259	0.182*** (86-100 kg)		288
Batch 4								
Control	5.3	15.5	56	14	1582	0.424		127
3% benzoic acid		16.3	48	7	1665	0.191*** (80-100 kg)		128
Batch 3+4								
Control	6.2	16.5	56	14	1556	0.440		
3% benzoic acid		16.5	53	7	1485	0.187*** (86-100 kg)		

*, **, ***: Statistically significant difference, *: P<0.05; **:P<0.01; ***:P<0.001

In batches 3 and 4, where 3% benzoic acid was added to the feed given to the treatment group, there was a 58% reduction in the ammonia emission during the last part of the production cycle. The difference was statistically significant ($p<0.001$).

The experiment was not designed to prove a difference in production results. However, it should be mentioned that the lowest production results were found in the group fed a diet containing 3% benzoic acid. In the EU, benzoic acid is approved for use in feed for finishing pigs in doses up to 1%. Dispensation was given for the experiment with 3% benzoic acid.

Coarsely Ground Meal Feed Compared with Finely Ground Pelleted Feed

Coarsely ground meal feed (5 mm hammer mill) was compared with finely ground pelleted feed with regard to odour and ammonia emission. Two batches of pigs weighing between 65 and 100 kg were included in the experiment. The ammonia concentration was measured every half hour. For both batches, three odour measurements were taken in the chimney in each of the two sections on 6 measurement days spread over the two production cycles.

The results of the experiment show that the ammonia emission was higher for coarsely ground meal feed than for the finely ground pelleted feed. On average, the ammonia emission was 20% for the meal feed. The difference was statistically significant ($p<0.001$). There was no effect on the odour emission.

Table 6. Average of ammonia and odour emission together with supplementary records in the experiments with comparison of coarsely ground meal feed and finely ground pelleted feed (control)

Section	Ambient temperature Celsius	Outlet temperature Celsius	Ventilation rate m^3/hour per pig	NH_3 ppm	CO_2 ppm	Ammonia emission g NH_3-N/hour	Odour Emission OU_E/sec. per 1000 kg
Batch 1							
Control	0.5	17	31	18	2646	0.31	225
coarsely ground meal feed		16	34	21	2404	0.40***	198
Batch 2							
Control	4.8	16	44	13	1826	0.33	178
coarsely ground meal feed		17	40	17	2003	0.39***	146
Batch 1+2							
Control	2.7	16.5	38	16	2236	0.32	200
coarsely ground meal feed		16.5	37	19	2204	0.40***	170

*, **, ***: Statistically significant difference, *: $P<0.05$; **:$P<0.01$; ***:$P<0.001$

Ventilation Rate

The odour emission from the finishing unit with a slurry system is generally 3-5 times higher in the summer than in the winter. This is presumably because of changes in the air exchange in the sections. An experiment was therefore carried out to demonstrate the effect of the air exchange on the odour emission. A constant ventilation rate of 100 m^3/hour per pig (maximum ventilation in finishing unit in Denmark) was compared with a ventilation rate of 50 m^3/hour per pig for two batches of pigs weighing between 64 kg and 104 kg.

A cooling system was installed to cool the inlet air to the section with the reduced ventilation rate so that the desired temperature in the sections could be maintained.

In this experiment, the same measurements as in the feeding experiments were taken.

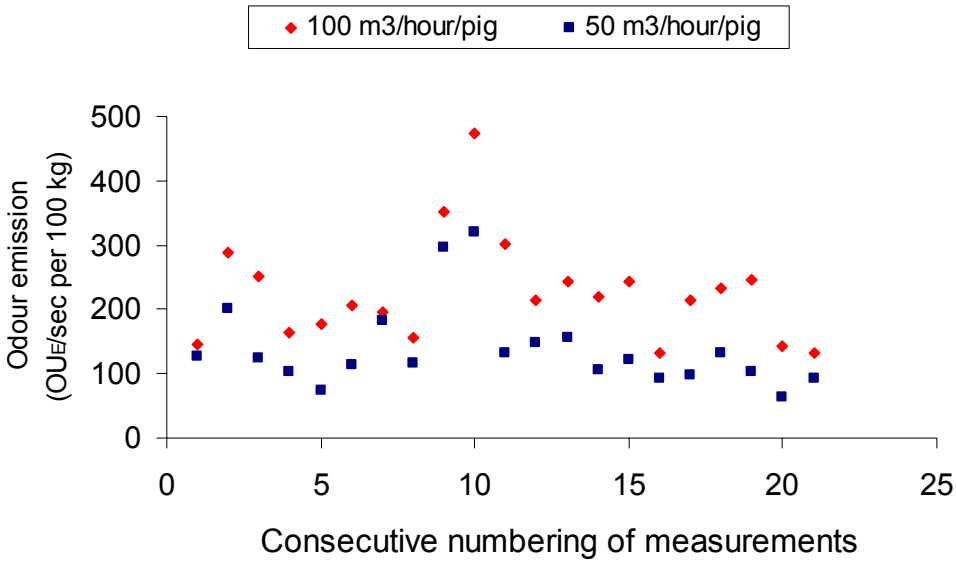

Figure 4. The odour emission from the trial section (50 m^3/hour per pig) with reduced air exchange and the control section with maximum ventilation (100 m^3/hour per pig) for two batches of pigs

On days with odour measurements, the ventilation rate in the trial section was reduced by an average of 50% in batch 1, and this resulted in an odour reduction of 33% with a 95% confidence interval [21 - 45] compared with the control section. In batch 2 the ventilation rate was reduced by an average of 56% on the odour measuremens days, and this resulted in an odour reduction of 47% with a 95% confidence interval [39 - 54].

The effect of the reduced ventilation rate on the ammonia emission was not as great as on the odour reduction. The ammonia emission from the trial section was reduced by 11% with a 95% confidence interval [8 - 13], while for batch 2 the ammonia emission was reduced by 8% with a 95% confidence interval [4 - 11] compared with the control section.

Chemical Air Purification

Purification of the air with scrubbers using a sulphuric solution has been widely tested in Europe and, for many types, the reduction of ammonia is 90-95%. The companies are also trying to develop the systems, with a view to reducing the odour emission. Also, a number of new chemical liquids for the scrubbers have been introduced. However, campaign measurements before and after the air cleaning system show that the chemical scrubbers have no effect - or a minor effect - on the odour emission (see Figure 5).

A new type of chemical air cleaner based on membrane technology is under development. The idea of the system was last year introduced by four Danes and campaign measurements have shown that the system has considerable potential as a method for reducing odour, as long as the system can be developed at a realistic price. The ammonia and hydrogen sulphide were reduced by more than 95% and the results of the odour measurements are shown in Figure 6.

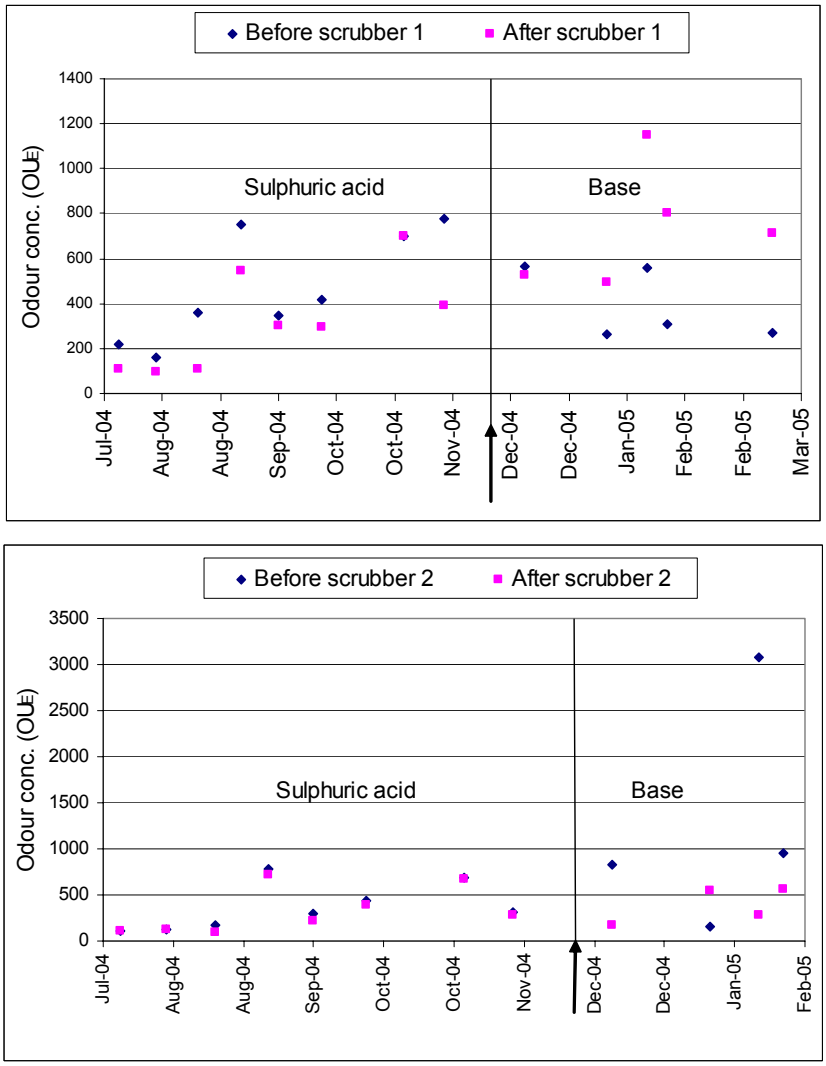

Figure 5. Odour measurements before and after two scrubbers from Scan Airclean A/S. During the first period, a solution containing sulphuric acid was used, and during the last period an alkaline solution was used. The two scrubbers purified the exhausted air from two identical sections at the same farm. However, only one of the scrubbers was able to reduce the odour concentration. In Denmark, the chemical scrubbers using sulphuric acid can only be used for ammonia reduction and not for odour reduction.

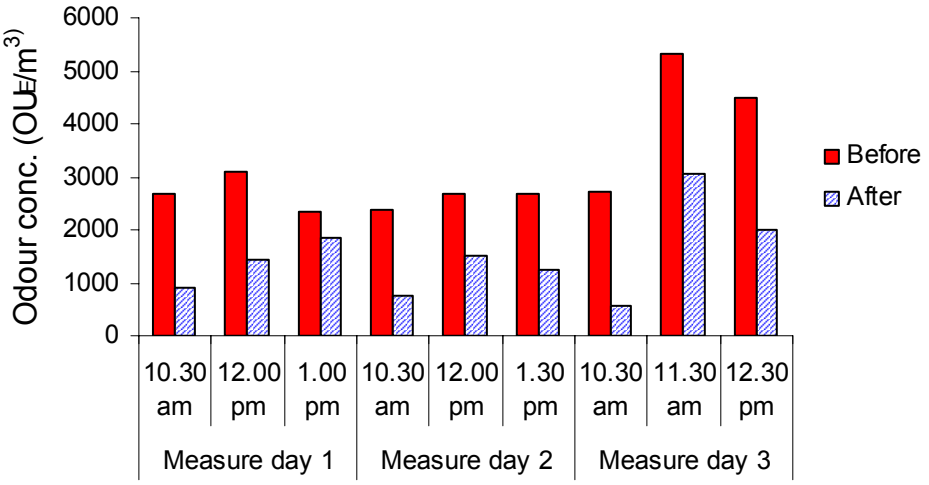

Figure 6. The odour concentration before and after a pilot membrane filter installed after the chimney at a finishing unit. The three measurement days were campaign measurements spread over a 6-weeks period. The positive result demonstrates that the new membrane technology can be used as a odour reduction method in the future.

Biological Air Purification

Two types of biological air purification have been tested. One of the filters is from SKOV A/S and Perstrup Beton Industri A/S and the description and test results are given in the proceeding "A Biotrickling Filter for Removing Ammonia and Odour in Ventilation Air from a Unit with Growing-Finishing Pigs" (reference 3). The other filter is an Oldenburg biofilter, Agrofilter GmbH from Germany.

The Oldenburg biolfilter was installed beside a finishing unit and purified the exhausted air. The biological filter was tested over a period of six months.

The odour reduction is illustrated in Figure 7. The odour reduction was, on average, 49% with a 95% confidence interval [29 – 69]. If the period with problems with the moisture system is excluded the odour reduction was 60% with a 95% confidence interval [37 - 83].

The Oldenburg biofilter required a lot of space. The filter area was 50-60% of the area of the stable. Therefore, the biological filter from SKOV A/S and Perstrup Beton Industri A/S will be more realistic in the future.

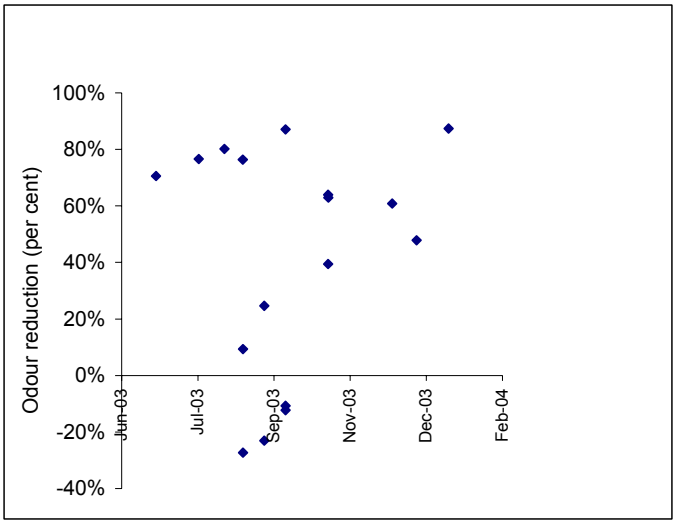

Figure 7. Odour reduction using an Oldenburg Biolfilter, Agrofilter GmbH. The drop in odour reduction was caused by moisture system failure.

Odour Source

To obtain better knowledge of the odour source the odour concentration was measured from two sections before and after delivery of finishing pigs to the slaughterhouse. After the sections had been emptied of pigs, the ventilation rate was maintained at the same level as before delivery.

The measurement results are shown in Figure 8. The odour concentrations before and after delivery of the pigs were approximately the same. This means that most of the odour originates from the slurry pit and manure deposited in the pen.

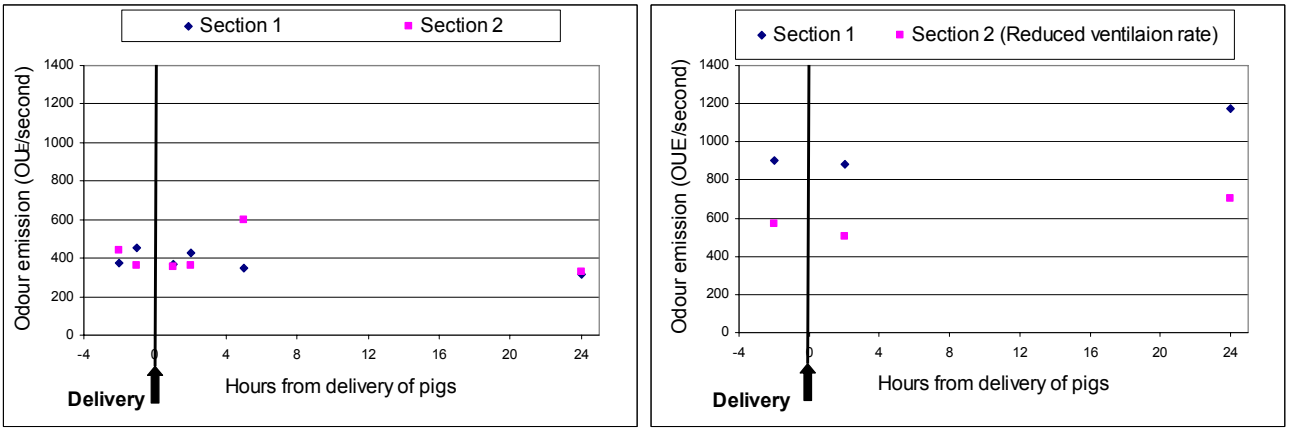

Figure 8. The odour emission from a finishing unit before and after delivery of pigs from two batches. The ventilation rate was the same before and after delivery.

Conclusions

The following conclusions can be given for the supplementary experiments:

- Odour samples can be sent by express mail to the olfactometry laboratory even if there is a risk for condensation in the bags. However, condensation is not allowed during sampling and analyzing.
- When measurements are taken in two identical sections for pigs, the variance of different odour panels can be neglected compared to the variance of the sections and the variance of the date.
- If a 50% difference in odour emission between two sections is to be demonstrated, the measurement programme could involve 10 measurement days with one single odour sample in each section, or 6 measurement days with triple odour samples in each section.

An experiment showed that odour from clean pigs can be neglected, because the odour mainly originates from the manure. This means that it is very important to maintain a good dunging behavior in units with partly slatted floors. In addition, it will mean that the odour emission from finishing units with partly slatted floors is less than from units with fully slatted floors.

The odour emission from finishing units with slurry systems is 3-5 times higher during the summer than during the winter. An experiment showed that the odour emission can be reduced by cooling the inlet air.

Management factors to control the thermal comfort for the pigs are essential, as the ventilation rate must not be too high in relation to the odour emission, and nor too low in relation to the dunging behavior.

A number of feed experiments have demonstrated reduced ammonia emission, but not reduced odour measured by olfactometry.

In the future biological filters will be a solution for the odour problems, and maybe the new membrane technology could be a solution. In Denmark, scrubbers using a solution of sulphuric acid can only be used as ammonia reduction techniques and not for odour reduction.

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Analytical Challenges in Measuring Odorant Emissions from Animal Operations

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Abstract

Accurate measurement of odorant emissions associated with animal agriculture is a challenging undertaking as accurate air concentration data is required. Quantitation of the large number of odorants associated with animal manures is difficult due to the physical/chemical properties of the analytes (highly polar, reactive and volatile), the variability of the ambient air matrix (temperature, relative humidity and dust levels), and the difficulty in creating analytical standards for quantification. Odorants fall into a number of organic compound classes, i.e., sulfides, mercaptans, amines, phenols, indoles and fatty acids, and include inorganic chemicals like hydrogen sulfide and ammonia. The large range of compound classes, polarity, reactivity and volatility require that several analytical methods be used. Many researchers working in this area have operated in an odorant identification mode only or have presented relative concentration data as a means to evaluate emissions from animal operations used to evaluate some odor control technology. In order to accurately determine emission factors for even selected odorants, some basic QA/QC principles are required to validate the effectiveness of a an analytical method. One of the most important factors in assessing the effectiveness of an odorant's analysis is to determine the effect of humidity on analyte collection efficiency and instrument performance. For highly polar analytes such as volatile fatty acids, collection efficiency on a sorbent material may be drastically decreased under high humidity conditions. In addition, recovery and analysis of polar compounds in canisters systems are also affected by ambient humidity levels. Analysis of samples with excess water from high humidity environments will lead to shifts in retention time of analytes and loss of signal intensity during analysis. Another critical issue is the development of accurate calibration curves for analyte quantitation. For example, use of permeation device to create a methyl mercaptan standard gas is complicated by the reaction in the presence of oxygen and light to form dimethyldisulfide, another important odorant. This paper will provide an overview of the current state of the science with respect to odorant analysis, including the limitations of each major approach.

Introduction

Gaseous emissions from animal operations are extremely complex mixtures of organic and inorganic chemicals from numerous compound classes. Some of these gases are relevant from a global warming perspective, i.e., methane, carbon dioxide. Others are important from an air quality perspective; for example some volatile organic chemicals (VOCs) may contribute to the formation of ground-level ozone. However, public concern over animal operations is often focused on the problem of persistent odor emissions which can create a negative physiological and/or psychological response in residents living in downwind areas.

A number of common odorants may elicit an olfactory response at concentrations in the low parts-per-billion level (Table 1). Therefore, scientists investigating these chemicals in the environment must strive to achieve very low analytical detection limits. Existing analytical methods for VOC detection were developed and validated for monitoring of industrial pollutants in urban environments at the parts-per-million levels. Volatile compounds important for agricultural air quality studies are often polar, reactive, and highly sorptive on surfaces; whereas, most validation studies for these different sampling techniques were performed on stable, non-polar hydrophobic compounds. The purpose of this paper is to provide an overview of available methods for sample collection, analysis and quantitation of odorants and to provide a description of research gaps in our critical knowledge.

Table 1. Olfactory detection thresholds for common odorants

Compound	Odor threshold (ppbv)	Compound	Odor threshold (ppbv)
Methyl Mercaptan	1.1	Acetic Acid	145
Ethyl Mercaptan	1.1	Propionic Acid	33.5
Propyl Mercaptan	1.3	Butyric Acid	3.9
Butyl Mercaptan	1.4	Isobutyric Acid	19.5
Carbon Disulfide	95.5	Valeric Acid	4.8
Dimethyl sulfide	2.2	Isovaleric Acid	64
Dimethyl disulfide	12.3	Para-cresol	1.9
Trimethyl amine	2.4		

Sample Collection

Current ambient air sampling techniques used in agricultural air quality studies typically use either a whole air (syringe, Tedlar bags, or stainless steel canisters) sampling approach or pre-concentration (sorbent tubes and solid phase microextraction [SPME] fibers) sampling approach. Each sampling approach and technique has its advantages and disadvantages, but all have one thing in common they were never developed for sampling the types of compounds and environments that are associated with animal feeding operations.

Thermal Desorption

General guidelines on the use of active sampling onto sorbent tubes are found in EPA Compendium Method TO-17 (Woolfenden and McClenny, 1997). This document discusses in detail procedures to follow for sampling and analysis along with supporting reference list. In the appendixes, there are tables listing sorbent material properties, different sorbent tube combinations, and recommendations on the types of sorbent material needed to capture specific compounds. In terms of relevance to agricultural air quality, only two of the 74 compounds listed in the back tables have been identify as agricultural odorants with an additional four compounds listed as major compounds emitted from animal feeding operations. Based on TO-17 three troubling areas emerge as needing validation in agricultural air quality studies: 1) sampling flow rates; 2) safe sampling volumes; and 3) minimizing the interference of water.

Stainless Steel Canisters

Blunden et al. (2005) recently released characterization of VOC from a swine operation using canister sampling and analysis. They determined that dominate compounds emitted from swine facilities were ethanol, methanol, acetaldehyde and acetone with most agricultural odorants never detected above 7 ppbv. These results are not surprising since Koziel et al. (2005) demonstrated that recovery of the agricultural odorants (i.e., volatile fatty acids, 4-methylphenil, 4-ethylphenol, and indole) from 6 L SUMMA canisters were less than 5% after 0.5 hour of storage and dropped to less than 1% following 24 hours of storage. Ochiai et al. (2002) has shown that increasing relative humidity levels in the canisters lowers recovery of oxygenated (alcohols) compounds. These results are as expected since canister sampling was designed for sampling VOC with vapor pressures greater than 10^{-1} torr at 25^{o}C and 1 atm (McClenny and Holdren, 1999); whereas, many of the agricultural odorants have vapor pressures less than 10^{-1} torr resulting from their polar nature that creates large cohesive energy between molecules (Castellan, 1983) . However, new developments in fused silica lined canisters and heated inlets have the potential to extend the range compounds to include semi-volatiles (Robinson et al., 2004).

Solid Phase Microextraction

SPME has become a widely-used technique for the pre-concentration of volatile and semi-volatile organic chemicals in both liquid and gas-phase samples (Zhang and Pawliszyn, 1993, Lord and Pawliszyn, 2000, Beltran et al., 2000). SPME is a one-step extraction procedure where the compounds of interest are absorbed by a thin polymer film or by porous carbonaceous materials that are bonded to a fused silica fiber. SPME is based on an equilibrium process, and at equilibrium the mass of analyte on the fiber is

proportional to its concentration in the sample matrix (Pawliszyn, 1997). This technique can also be used under non-equilibrium conditions to determine concentrations as long as the exposure time for the fiber is the same for standards and samples. This approach is especially sensitive for gas phase samples as matrix interferences are minimized versus liquid samples. Another advantage of SPME is that no pumps or mass flow meters are required during sample collection. SPME fibers can be used to sample headspace vials, Tedlar bags or canisters, or they can be used for ambient air sampling. However, the mass transfer rate of analytes into the fiber matrix is influenced by temperature and air flow rate, and adsorption can be reduced by high humidity conditions and by the presence of high concentrations of competing VOCs. In addition, there is no one SPME fiber coating that provides adequate adsorption for all odorant compound classes, and there are serious challenges in attempting to calibrate SPME fibers for quantitative analysis of gas phase samples.

Analytical Methods

Gas chromatography-mass spectrometry (GC-MS) is the most sensitive and useful analytical method available for the detection of VOCs. A 30-60-m megabore capillary column with a thick film (1 um), non-polar stationary phase is generally used to retain and efficiently separate the traditional analyte set of non-polar industrial VOCs. However, chromatographic peak shape for the more polar VOCs of interest in an animal agriculture setting, i.e., sulfides, mercaptans, amines, phenols, indoles and fatty acids, is extremely poor when using a typical "Volatiles" column. A more polar stationary phase such as Carbowax or a Porous Layer Open Tubular (PLOT) column is required to maximize separation and signal-to-noise ratios.

In many cases, odorants are small components within a complex air sample matrix containing both polar and non-polar constituents. Critical odorants may become "buried" beneath enormous co-eluting, non-odorous hydrocarbon peaks of similar volatility. Scientists have utilized a number of strategies to tease out and identify these critical odorants. A "sniffer port", or GC-olfactometry (GC-O) approach has been utilized, especially in the food and flavors industry, to monitor the effluent from a GC column using a human operator to identify chemicals which create an olfactory response and to describe the character and intensity of the odorant (Jordán et al., 2001, Ferrari et al., 2004). This approach alone, however, does not address the chromatographic peak shape problem.

The use "heart cutting" techniques or multi-dimensional GC-MS has been successfully applied to odorant analysis whereby, a preliminary separation is performed on a non-polar column. Portions of the effluent from this column are cryo-focused onto the head of a second, more polar column for further separation and analysis by mass spectrometry and sniffer port (Wright et al., 2005). While methods development for a large analyte list is challenging with MD-GC-MS, this approach does provide sufficient sensitivity and selectivity to detect polar VOCs at environmentally relevant concentrations.

Quantitation Methods

One of the most challenging aspects of odorant VOC analytical method development is detector calibration. This challenge stems from the difficulty in creating stable, traceable standard mixtures. Significant variations in chemical and physical properties of the different odorant compound classes necessitate the creation of separate standards for each group. Volatile fatty acids, for example, are created in an aqueous solution of pH <2. Amines on the other hand must be created in an alkaline solution. Some analytes are only soluble in an organic solvent which may cause significant chromatographic co-elution problems, while still others are in the gaseous state at room temperature.

Three potential approaches may be utilized in gas or liquid standard creation. High purity chemical standards may be acquired, and standard solutions may be created by the analyst. However, handling and storage of pure odorant chemicals presents potential worker safety hazards due to their generally poisonous and corrosive nature. This work may also create serious nuisance odors in a laboratory building. The use and handling of pure standards is most appropriate for those chemicals which are solids at room temperature.

For highly volatile chemicals, certified gas standard mixtures may be purchased from a few specialty companies. Since the constituents of the mixture and the proportion of the constituents within the cylinder are set, this approach is most appropriate for a routine analysis method where the sample concentration

ranges and the analytes of interest are well-established. Certified gas mixtures are also costly and may have a very limited lifetime before degradation begins to occur within the cylinder.

Alternatively, certified permeation devices may be used to create standard gases. Permeation devices are generally a sealed Teflon tube containing the pure chemical. The length of the tube and the thickness of the membrane dictate the mass of chemical emitted. Permeation devices are certified at a particular temperature by monitoring the change in mass of the device over time, and this certification process may take several weeks for devices with low emission rates. These devices also require an instrument containing a thermostated chamber with accurate gas flow control through the chamber. Gas flows from several permeation chambers may be combined to create a mixed gas standard. However, precise control over dilution gas flows must be maintained, and care must be taken when mixing gas standards to avoid reactions which may create additional chemicals within the gas stream. The primary resources required for this calibration method are time and carrier gas. While some units may be able to utilize filtered laboratory air as a carrier gas, scientists may wish to use nitrogen or helium to minimize oxidation reactions of some analytes. Significant time is required to allow the chamber system and associated tubing to equilibrate when altering dilution flow or when changing to new chemicals.

Conclusions

The goal of a single standard sample collection and analysis method to evaluate odorant emissions from animal agriculture is unrealistic considering the enormous number of potential odorants emitted from any one facility. Scientists have begun to identify key odorants associated with particular animal species; however, conditions will vary widely between different facilities and between operations in different regions of the country with different climate conditions. Researchers need to approach sampling and analysis from a multifaceted perspective that considers not only the chemistry of the compounds analyzed but also the matrix in which these compounds exist. While existing methods may be effective at identifying odorants within a particular gas sample matrix, significant work remains to develop quantitative sample collection and analysis methods to accurately measure odorant concentrations under conditions typically found in animal production facilities. These methods should incorporate appropriate quality assurance and quality control procedures such as evaluation of humidity on selected adsorbent tubes with respect to breakthrough volumes. Development of these methods will only be successful if they incorporate a fundamental knowledge of the chemical properties of the analytes and of the sample matrix.

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