The development of experimental procedures for the evaluation of additives to attenuate manure odour, and the impact of these additives on workers, animals and the environment


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Abstract The objective of this project was to develop a laboratory research protocol to evaluate the effect of additives on manure odour and physico-chemical characteristics, and establish conditions that are representative of those found in farm storage structures (temperature, solids content, pH, ventilation above the manure surface, storage period). The results suggested that system configuration might have an impact on additive effect. An open system should be used when it is recommended that additives be applied in the animal diet or the gutters. Additionally, the surface/depth ratio of the gutter should be respected, since it will impact on the relative importance of the aerobic layer and on ammonia volatilization. On the other hand, a closed system should be used when the additive is applied to the manure storage tank, especially if the tank has a cover. Odour analysis still requires fundamental research to establish reliable procedures and protocols, especially in the area sample collection and dilution levels required to decrease H₂S concentration to safe levels for the panellists. Odour analysis should also be conducted in triplicate, because of the possible large experimental error due to dilution, the human factors, and also instrumental error.

Keywords Hedonic tone; manure additives, odours; odour intensity; odour units

Introduction Odours are one of the major environmental problems limiting the growth of the pork industry. Recent studies tend to demonstrate that bad odour is not just a nuisance, but can cause nausea, headaches, sleeping disorders, digestive problems, loss of appetite and depression. A significant increase in respiratory disorders was observed in regions with high animal density (Hinz and Krause, 1987; Hartung, 1992). The expansion of the hog industry will partly depend on how the odour and environmental problems are resolved.

In recent years, various additives for reducing odours from manure storage structures have been commercialized. Some of these additives have been tested in laboratories, according to various research protocols and procedures (Al-Kanani et al., 1992; Martinez et al., 1997; Miner et al., 1995; Patni and Jui, 1993; Ritter, 1981; Warburton et al., 1981; William, 1995; William and Schiffman, 1995; Zhu et al., 1996). However, experimental procedures were not representative of conditions in storage tanks in Eastern Canada, namely temperature, pH, manure composition, surface/volume ratio, and air flow-rate over the manure surface. The effect of the additive on farm workers, animals and the environment was never evaluated. Additives could present high environmental and health risks (Denis, 1997; Lachance, 1998).

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conditions that are representative of those found in farm storage structures (temperature, solids content, pH, ventilation above the manure surface, storage period). Finally, the project proposed to evaluate the potential impact of the additives on the health and safety of farm workers and the environment (this aspect of the project was conducted by a separate research group specializing in workers’ health and safety issues, and results will be presented in a separate article).

**Method**

**The additives**

Four commercially available manure additives were selected to test the experimental protocol: a biological neutralizer, a chemical neutralizer, a chemical agent and a masking agent. Table 1 presents the main characteristics of the four products. When the additive dose was low compared to the manure volume, the product was mixed in distilled water before application.

**The manure storage structure**

Two zones can be distinguished in manure storage structures: (1) a thin aerobic surface layer, populated by facultative anaerobic bacteria that can adapt to aerobic conditions and use oxygen as an electron acceptor, and (2) a deep anaerobic zone populated by strict anaerobes. The contribution of the aerobic surface layer to biological and chemical processes in the manure would be more significant in shallow gutters, while it could be negligible in deep storage tank. Gases and VOCs emitted by the two layers will have different compositions.

The open-system barrels were used to simulate manure conditions in shallow gutters. Manure collected at a hog finishing barn was mixed for 30 min. Ten 220-L plastic barrels (880 mm high by 580 mm diameter) were filled with 100 L of manure. The barrels were covered and connected to diaphragm pumps that ventilated the barrel headspace. Air flow-rate above gutters in commercial barns is difficult to measure. The ventilation rate in the barrels was initially set at 2.5 ml/min. It was later increased so that the NH₃ concentrations measured in the headspace were as close as possible to the NH₃ concentrations measured just above the manure surface in gutters under a slatted floor in a commercial barn (68 to 80 ppm).

A second set of 10 barrels, called the closed-system barrels, was used to simulate the predominantly anaerobic conditions in deep manure storage tank. The manure was mixed for 30 min, and 100 L was distributed to each barrel. The barrels had tightly closed covers connected to gas sampling ports and metering apparatus. However, some of the barrels

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Agent and dosage used in the experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Category</td>
<td>Dose (ml/m³)</td>
</tr>
<tr>
<td>Biological neutralizer</td>
<td>50</td>
</tr>
<tr>
<td>Chemical neutralizer</td>
<td>5000</td>
</tr>
<tr>
<td>Chemical agent</td>
<td>17</td>
</tr>
<tr>
<td>Masking agent</td>
<td>20</td>
</tr>
</tbody>
</table>

NA: not available

a As described by the manufacturer

b The dose used was determined by the manufacturer after analysis of the experimental manure. The dose recommended on the package was 350 ml/m³
developed slow leaks, and although the conditions inside the barrels remained anaerobic, biogas production could not be accurately measured.

The open system and closed system barrels were placed in two controlled-temperature rooms maintained at 15°C. Each of the four additives was added to two barrels in each room at the dose given in Table 1. Two barrels in each room were kept as controls.

Manure
Manure was collected on two occasions from a commercial hog finishing barn. The manure characteristics presented in Table 2 for the closed and open systems are the averages of 10 samples.

Sample collection and analysis
Manure analysis. One-litre samples were collected from each barrels before and after additive incorporation and on days 7, 14, 28 90, 150 and 280 for the open system barrels and on days 28, 93, 149, and 282 for the closed-system barrels. Manure sample analysis included total, suspended and volatile solids (TS, TSS, and VS), total and soluble chemical oxygen demand (TCOD and SCOD), volatile fatty acids (VFAs), pH, alkalinity and apparent viscosity. On the last sampling day, total Kjeldahl and ammonia nitrogen (TKN and NH₃-N) were measured. All analytical methods were described in Massé et al. (2002).

Gas composition analysis. In open system barrels, air samples were collected every three to 10 days. For the open-system barrels, samples were collected on the gas evacuation line at a rate of 2 L/min and send to Draeger CH₄ detection cells and to an Ultramat NH₃ analyser.

Odour analyses. Gas samples for odour analysis were collected on days 1, 3, 7, 28, 70, 90, 150, 210, and 280 from the open system barrels, and on days 29, 71, 92, 148, 211 and 281 from the closed-system barrels. The samples were collected in 60-L Tedlar bags. The day following air sample collection, odour analysis was conducted at the olfactometric laboratory of the Agriculture and Agri-Food Research Centre. Odour samples were tested by six panellists, who were selected according to the AFNOR NFX 43-101 standard for statistical analysis and the CEN standard (CEN, 1997) for olfactometric analysis.

Air samples had to be diluted to decrease the H₂S concentration before odour intensity

Table 2 Characteristics of the hog manure used in the additive experiment

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Closed system Average</th>
<th>STD</th>
<th>Open system Average</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total COD (g/L)</td>
<td>138.4</td>
<td>5.1</td>
<td>119.5</td>
<td>7.2</td>
</tr>
<tr>
<td>Soluble COD (g/L)</td>
<td>60.9</td>
<td>1.4</td>
<td>61.3</td>
<td>2.6</td>
</tr>
<tr>
<td>Total solids (g/L)</td>
<td>84.0</td>
<td>4.8</td>
<td>57.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Total volatile solids (g/L)</td>
<td>61.1</td>
<td>4.7</td>
<td>39.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Suspended solids (g/L)</td>
<td>68.3</td>
<td>4.7</td>
<td>40.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Volatile fatty acids (g/L)</td>
<td>29.1</td>
<td>1.6</td>
<td>28.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Acetic acid (g/L)</td>
<td>13.6</td>
<td>0.8</td>
<td>13.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Propionic acid (g/L)</td>
<td>4.2</td>
<td>0.2</td>
<td>4.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Butyric acid (g/L)</td>
<td>7.4</td>
<td>0.4</td>
<td>6.9</td>
<td>0.2</td>
</tr>
<tr>
<td>Isobutyric acid (g/L)</td>
<td>1.2</td>
<td>0.1</td>
<td>1.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Valeric acid (g/L)</td>
<td>0.4</td>
<td>0.0</td>
<td>0.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Isovaleric acid (g/L)</td>
<td>1.9</td>
<td>0.1</td>
<td>1.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Caproic acid (g/L)</td>
<td>0.4</td>
<td>0.0</td>
<td>0.7</td>
<td>0.0</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
<td>0.0</td>
<td>7.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Alkalinity (g CaCO₃/L)</td>
<td>34.5</td>
<td>2.6</td>
<td>30.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>93.3</td>
<td>27.6</td>
<td>45.1</td>
<td>1.7</td>
</tr>
</tbody>
</table>
and hedonic tone analyses. The target H₂S concentration was 15 ppm, which represents the maximum concentration to which a worker can be exposed for a period not exceeding 15 min (Quebec Official Publisher, 1999). The odour intensity of air sample was compared to that of butanol. The hedonic tone was determined using pictograms.

**Results and discussion**

**Additive effect on the physico-chemical characteristics of the manure**

In the closed-system barrels, there was no treatment effect on VFA concentration, SCOD, TCOD, solids content, alkalinity, pH and viscosity. In all the closed-system barrels, total VFA concentration increased similarly during the experimental period (Figure 1), mainly due to an increase in the concentration of acetic, propionic and butyric acids. Increases will be mainly due to the acidification of the soluble organics, since there was no significant increase in SCOD during the experimental period.

All open-system barrels showed similar VFA concentrations during the initial 29 days of storage at 15°C. The chemical neutralizer had a significant effect on the VFA concentration thereafter (Figure 2). With all other treatments, total VFAs tended to decrease from about 29 g/L on day 0 to 22 g/L on day 289, partly because of volatilization of the VFAs due to air movement above the manure surface, although, at a pH above 7, the concentration of un-ionized VFAs would be low compared to VFAs in ionic form. The reduction in VFAs would be mainly due to the biological activity in the facultative anaerobic zone. In the manure treated with the chemical neutralizer, the VFA concentration tended to remain constant, maybe indicating inhibition of the VFA-oxidizing bacteria.

**Figure 1** Total VFA concentrations in the closed-system barrels during the 420-day storage period

**Figure 2** Total VFA concentrations in the open-system barrels during the 420-day storage period
The analysis of the individual VFAs indicated that, in the barrels treated with the chemical neutralizer, the acetic acid concentration increased during the initial 148 days, and decreased thereafter. In all other open-system barrels, the acetic acid concentration started to decrease after 29 days of storage. The propionic, isobutyric, butyric and valeric acid concentrations increased throughout the experimental period in the barrels treated with the chemical neutralizer, while they decreased or remained constant in all the other treatments. Soluble COD also decreased in all treatments, from about 62 g/L on day 0 to 43 g/L on day 289, while it remained stable throughout the experiment in the barrels treated with the chemical neutralizer. Other parameters (pH, alkalinity, solids content and viscosity) were similar in all treatments during the storage period.

Ammonia–N concentration in the manure at the end of the experimental period is presented on Figure 3 for the closed and the open systems. The significantly lower NH$_3$–N concentration in the open than in the closed system barrels indicates volatilization of important volume of ammonia during the experimental period in the open system. In the closed system, there was no significant additive effect on NH$_3$. The NH$_3$ concentration averaged 9,368 ± 160 mg/L. In the open system, on the other hand, NH$_3$–N concentration was significantly lower in barrels treated with the biological neutralizer than in the control, while it was significantly higher in barrels treated with the chemical neutralizer than in the control.

**Additive effect on gas composition**

Methane content in the headspace of the closed-system barrels, over the experimental period, ranged from 2 to 22%. There was no consistent treatment or time effect on methane content.

During the experimental period, the air ventilation rate in the headspace of the open-system barrels was adjusted (Figure 4) so that the NH$_3$ concentrations were similar to those measured above the gutters in a commercial hog barn (68 to 80 ppm). The ventilation rate was kept at 2.5 L/min for two days. It was then increased to 5 L/min until day 7, to 8 L/min until day 142, and finally to 17 L/min until the end of the experiment. Average NH$_3$ concentration in the control decreased from 314 ± 99 to 135 ± 40 ppm as the ventilation rate was increased from 8 to 17 L/min. However, because of pump capacity limitations, it was not possible to further increase the air flow-rate to reduce NH$_3$ concentrations in the 70 to 80 ppm range.

The chemical neutralizer significantly decreased the NH$_3$ concentration in the headspace, especially between days 42 and 152 of the storage period. Lower NH$_3$ concentration in the headspace would explain the significantly higher NH$_3$–N concentration in the manure treated with the chemical neutralizer, compared to the control, at the end of

![Figure 3](https://iwaponline.com/wst/article-pdf/50/4/257/421665/257.pdf)
the experimental period. After day 152, at a ventilation rate of 17 L/min, there was no observable difference in NH$_3$ gas concentration between the control and the chemical neutralizer.

With all open-system barrels, a small peak in methane concentration was observed with all treatments between days 30 and 60 of storage. It remained low thereafter. Methane emissions were similar with all treatments during the 150 days of measurement. It is therefore difficult to explain the lower COD removal in the manure treated with the chemical neutralizer.

**Additive effect on odour**

Lower detection limits in the closed system barrels are presented in Figure 5. Results from day 211 were excluded because of problems with the olfactometer, and some error bars are missing because only one replicate was available. The lower detection limit tended to increase for all treatments during the storage period. On days 71, 148 and 281, the lower detection limit was higher in the air from the barrels treated with the chemical agent than in all other barrels, but variability was high and there was not enough replication on each day for statistical analysis.

Lower detection levels for the open-system barrels are presented on Figure 6. Less variation was observed between sampling days, but variability between treatments was again too important to detect a significant treatment effect.

Odour intensity and hedonic tone measurements for the closed system barrels are presented for two sampling days on Figure 7. Samples were diluted 50 times on day 29 and 100 times on day 92. Results were not corrected for dilution. Results from four sampling days could not be used, because of problems with dilution or with the olfactometer.

All treatments had an offensive odour. Therefore, the hedonic tone scale is negative, and the least offensive treatment (highest hedonic tone) has the smallest negative value. On both days, the barrels treated with the biological neutralizer had the lowest intensity and
highest hedonic tone (Figure 7). However, there were no consistent results or correlation between the two odour measurements for the other treatments.

Odour intensity and hedonic tone measurements for the open-system barrels are presented on Figure 8. The control barrels tended to present the lowest odour intensity on all sampling days but day 150. However, there was no correlation between the hedonic tone and the intensity for any of the treatments.

The health and safety issues associated with the manure additives used in this study have been conducted by a separate research group specializing in occupational health and safety. Analysis of air samples collected just above the manure in the storage structures indicated that the additives did not increase the emission of airborne chemicals (ammonia) and
biological contaminants (bacteria, endotoxins, moulds). Therefore the additives tested did not create new hazards for farm workers and animals. Additional data are provided in a separate paper (Lavoie et al., 2003).

Conclusions
Results indicated that the additives had no effect on the closed system barrels, while one of the additives reduced degradation and ammonia emissions in the open barrel system. However, the amount of chemical neutralizer added to the manure of both systems corresponded to 14 times the dose recommended on the package, and may be economically prohibitive for commercial operations. The results nevertheless suggested that system configuration may have an impact on the additive effect. The open system should be used when it is recommended that the additive should be applied in the animal diet or the gutters. Additionally, the surface/depth ratio of the gutter should be respected, since it will impact on the relative importance of the aerobic layer and on ammonia volatilization. On the other hand, a closed system should be used when the additive is applied to the manure storage tank, especially if the tank has a cover. Finally, none of the tested additives has changed the manure slurry physico-chemical characteristics or increased the methane and ammonia emissions. Therefore the additives did not increase the negative impact of manure slurry on the environment.

Air sample collection techniques for odour analysis also need improvement. The air sampling technique used in this study may have contributed to variation within and among treatments. Gas transfer from the manure liquid phase to the headspace is not uniform. Small gas bubbles often remain trapped in the manure and are suddenly released when they aggregate to form relatively large air pockets. In closed system barrels, entrapped gas may be forced out of the manure all at once, because of the negative pressure build-up during sample collection. Odour analysis should also be conducted in triplicate, because of the possible large experimental error due to dilution, the human factor, and also the instrumental error. Analysis of air samples collected just above the manure in the storage structures indicated that the additives did not increase the emission of airborne chemical and biological contaminants. Therefore the additives tested did not create new health hazards for farm workers and animals.

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