Reduction of Odor and Odorant Emissions from Slurry Stores by Means of Straw Covers

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Swine (*Sus scrofa*) slurry stored in open storages is a source of airborne contaminants. A customary practice for ammonia and odor control consists of covering the surface of the slurry with floating materials, such as straw. Although straw covers have been proven to generally reduce gaseous emissions, more knowledge is needed regarding how age, moisture content, and microbiological development of the straw cover affect the emissions of odor and odorants to develop recommendations for the practical use of straw covers. This study compiles data on odor concentration and odorants above swine slurry covered by straw of different ages and moisture contents, during a 9 wk laboratory scale study. The results showed that aged straw covers significantly reduced emissions of ammonia (by 99%), dimethyl sulfide (by 81%), phenol (by 92%), p-cresol (by 95%), skatole (by 98%), and benzaldehyde (by 97%), while no significant differences were found between uncovered and covered slurry for emission of odor, hydrogen sulfide, volatile fatty acids, dimethyl disulfide, and indole. The moisture content of the straw cover neither affected emissions of odor nor odorants. This study suggests that the main mechanism for odor and odorants emission reduction from straw covered slurry is as a physical barrier and not as a biofilter. However, the reduction in emissions of specific gases (such as ammonia, dimethyl sulfide, p-cresol, and benzal alcohol) appears to be also caused by the straw cover acting as a biofilter.

Animal production is a source of airborne contaminants including gases, odors, dust, microbes, and insects. With the emergence of large livestock operations, the concentration of odors in the areas surrounding the animal production facilities and their impacts on neighbors have increased (Bullers, 2005; Donham et al., 2007). Odor complaints related to animal production have also increased during the past decade (Bazen and Fleming, 2004; Schiffman and Williams, 2005). Consequently, governments have promulgated odor regulations, and odor emission has become a major problem faced by livestock producers (NRC, 2003).

More than 168 volatile compounds have been identified in swine farms (O’Neill and Phillips, 1992; Schiffman et al., 2001), of which some are responsible for unpleasant odors. Previous literature has identified three main groups of compounds that are responsible for swine odors: sulfurous compounds (e.g., hydrogen sulfide, dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide); phenols and indoles (e.g., p-cresol, indole, skatole); and, volatile fatty acids (VFA, e.g., acetic acid, propanoic acid) (Hobbs et al., 2000; Zahn et al., 2001; Wright et al., 2005; Blanes-Vidal et al., 2009a). The odor components p-cresol, skatole, 4-ethylphenol, and acetic acid have been identified as the most important odorants regarding odor intensity (Zahn et al., 2001; Wright et al., 2005), while phenols, indoles, and sulfur-containing compounds have been identified as the most abundant odorants (Hobbs et al., 2000; Blanes-Vidal et al., 2009a).

Livestock production is recognized as a major source of ammonia (NH₃) emitted to the atmosphere (ECETOC, 1994; Hutchings et al., 2001). Ammonia is also an odorous gas, although its contribution to the overall swine odor has been proven to be low (Hobbs et al., 1999, 2000; Le et al., 2005; Blanes-Vidal et al., 2009b). Ammonia emission is mainly of concern because deposition of ammonia or particulates containing ammonium (NH₄⁺) to soil, water, or vegetation may cause acidification and eutrophication of natural ecosystems (Roeloffs and Houdijk, 1991; Porteous et al., 2002).

Covering of open slurry storage facilities is the most widely used ammonia and odor control method in Europe. Covers are

**Abbreviations:** GC/MS, gas chromatography/mass spectrometry; OC, odor concentration; SD, slurry added straw dry; SH, slurry added straw and high moisture content; SM, slurry added straw and moderate moisture content; TD, thermal desorption; U, uncovered slurry; VFA, volatile fatty acids; VOC, volatile organic compounds.
usually classified depending on the materials used, into degradable (e.g., straw, silage, oil) or nondegradable (e.g., concrete, plastic). Floating covers are flexible covers made up of degradable or nondegradable materials (e.g., straw, geotextile materials); that float on the surface of the slurry. Although organic solid materials originally present in the swine slurry can float on the top of the stored swine slurry, forming a natural crust that lowers gas escape, the formation of an effective layer of floating materials on swine slurry often requires the addition of materials (e.g., straw) on the slurry surface to abate gas emissions (Misselbrook et al., 2005; Blanes-Vidal et al., 2008). Addition of straw is a low cost covering method in comparison to rigid slurry covering systems of concrete or plastic, as straw is a cheap and readily available agricultural material.

It has not been completely determined whether the gas emission reduction caused by the covers is mainly the result of physical, chemical, or biological processes (Hudson et al., 2008). Straw covers may serve to physically obstruct gas transport from the slurry surface to the atmosphere, decrease wind speed over the slurry, and increase the concentrations of gases below the cover and above the surface of the slurry, which lowers the gas escape from the slurry surface. If straw is placed on the slurry surface and is not actively mixed with slurry, the reduction of odor and odorants emission by means of the physical mechanism begins from the moment the straw cover is applied to the odor source.

Following addition of straw to a slurry surface, the straw cover is colonized by microorganisms. The microbial population growing in the straw cover may convert the gases emitted from the slurry (including odorous compounds) into biomass, nonodorous compounds, carbon dioxide, and water (Miner and Pan, 1995; Xue et al., 1999; Bicudo et al., 2002; Hudson et al., 2008). Unlike the physical barrier effect, the biofiltration effect is not immediate, as the development of a microbial population takes time, and so, its impact is expected to be associated with the age of the cover. The degradation of the straw in a manure storage tank can modify the chemical properties of the slurry (e.g., pH), which can indirectly affect the emission of gases. Therefore, in some cases the reduction of odor and odorant emissions by straw covers can be partly attributed to chemical mechanisms (Xue et al., 1999; Hudson et al., 2006).

Management techniques that can be used to abate the emission of odor and odorants from slurry storages such as straw covers are currently being evaluated for their effectiveness. The performance of straw covers depends, first, on keeping the straw cover over the slurry surface (Hudson et al., 2008), that is, the straw cover should not drift due to wind, nor sink. Second, the performance of the straw cover may depend on environmental conditions inside the cover. In this respect, slurry storages not protected by a water tight solid cover are exposed to rainfall which may result in periodic fluctuations in the moisture content of the straw cover. The moisture content may affect the physical barrier effect of the straw cover, but is expected to particularly impact the microbial filtration effects of the cover.

Although straw covers have been proven to reduce emissions of odorants, more knowledge is needed regarding how moisture content, caused by rainfall, and microbiological development in the straw cover affects the odor reduction efficacy of straw covers to develop recommendations for the practical use of straw covers. The objectives of this paper were to evaluate the effect of the moisture content of straw covers (rainfall) on the reduction of emissions of odor and odorants from stored swine slurry, and to evaluate the contribution of the biological mechanism on the odor reduction effect of straw covers.

### Materials and Methods

#### Experimental Setup

The study was conducted at the Research Centre Bygholm in Eastern Jutland, Denmark. Slurry was collected from a local finishing pig farm, whose slurry handling system consisted of collection in underfloor pits and storage in an outside prestorage unit. Every 2 to 3 wk the slurry was pumped to an outside storage unit where it was stored for up to 9 mo before being land applied between March and May.

The experimental set-up consisted of 15 dynamic flux chambers in which the slurry was incubated at constant temperature (15°C ± 4°C) during a 9 wk period. The flux chambers were 0.049 m³ with a diameter of 0.36 m. Before starting the study, 15 43-kg samples of homogenized slurry were taken from the prestorage unit. The slurry samples were filled into 15 63-L experimental plastic barrels (dynamic flux chambers) and placed inside an experimental slurry laboratory (Fig. 1). One day after collection, a fixed amount of chopped straw (350 g chamber⁻¹) was mixed into 12 of the slurry samples. All samples were subsequently thoroughly mixed, subsampled for slurry characterization, and then left undisturbed for 3 d before a 9 wk storage period. The chambers were left open and undisturbed during the storage period except during sampling for odor and odorants determination.

The evaluation of the influence of the moisture content of the straw covers (caused by rainfall) on the emission of odor and odorants, involved the following four treatments (Fig. 1): (1) uncovered slurry (U); (2) slurry added straw dry (SD), that is, no rainfall; (3) slurry added straw and moderate moisture content (SM), that is, moderate rainfall; (4) slurry added straw and high moisture content (SH), that is, high rainfall. Rainfall was simulated by adding water to the slurry crust by a vessel with perforated nozzles, at specific rates during the 9 wk storage period (Fig. 2). Moderate moisture content in straw covers was simulated by adding the amount and pattern of rain that fell in an average year during the dry season (April–May) in Eastern Jutland, Denmark (i.e., 50 mm month⁻¹), while high moisture content was simulated as the rainfall during rainy season (October–November) at the same location (i.e., 100 mm month⁻¹). The pattern of rain (mm day⁻¹) and final amount of added water (L chamber⁻¹) for both treatments are shown in Fig. 2. Uncovered slurry and SD cover were not watered. Each treatment was stored in triplicate, resulting in 12 chambers (Fig. 1).

To determine the effect of the age of the straw cover on the emission of odor and odorants, an additional set of three more chambers (SDnew) containing slurry added straw (Fig. 1) was stored under the same conditions and simultaneously as the SD treatment previously
mentioned (i.e., no water was added to the three extra chambers during the 9 wk storage period). One day before finalizing the 9 wk experimental period, the aged dry straw cover was removed from the three extra chambers and new straw (0.35 kg chamber⁻¹) was added on the surface (with no active mixing with the slurry). Therefore, at the end of the 9 wk storage period, the three additional chambers (SDnew) contained aged slurry (same storage time as all other 12 chambers) covered by new dry straw.

Measurements

Measurements of concentrations of odor and volatile organic compounds (VOCs), and slurry characterizations were performed at the beginning of the experiment (Week 0), and at the end of the experiment (Week 9) (Table 1). Concentrations of NH₃ and H₂S in the headspace air were measured six times in the course of the experiment: at Week 0, Week 2, Week 4, Week 6, Week 8, and Week 9. All measurements taken at the beginning of the experiment (Week 0) were performed in six chambers corresponding to two treatments: Uncovered slurry (Uweek₀) and slurry covered with dry straw (SDweek₀). Since no water was added, at the beginning of the experiment all barrels added straw (SDweek₀, SMweek₀, and SHweek₀, hereafter represented by SD-SM-SHweek₀) were assumed to be similar. All measurements taken after Week 0 were performed in all five treatments (i.e., 15 chambers).

To sample odors and odorants above the slurry surface, a lid was fastened on top of each barrel with a steel tension belt to make the lid/barrel interface airtight. Each lid was supplied with four ports which were used for air inflow and outflow, and for sampling the headspace air. The outflow orifice was located 0.245 m from the inflow orifice and 0.087 m from the sampling ports. Air drawn from outside the laboratory and filtered through an activated charcoal filter was continuously pulled through the barrels at a constant airflow, which was secured by critical orifices inserted inside the outflow tube of each barrel. Headspace air was homogenized by an air-mixing fan installed inside the chamber. So that the emissions of odor and odorants were not hindered by enhanced headspace gas concentrations, the airflow rate ventilating the chambers was chosen to be 1.85 L min⁻¹, which ensured that the headspace air of the chambers was replaced more than five times h⁻¹ (5.5 times h⁻¹).

Air samples for olfactometric evaluation were collected in 30-L Tedlar bags using a vacuum box. All samples were analyzed by eight trained odor panellists within 24 h, to determine the odor concentration (OC), expressed as odor units m⁻³ (OU m⁻³), in accordance with the European standard for the measurement of odors EN13725 (European Committee for Standardisation, 2003). In parallel with the collection of air samples for olfactometric analyses, VOC’s from the headspace of the flux chambers were absorbed onto thermal desorption (TD) tubes. The TD tubes (Air Toxics adsorbent tubes, PerkinElmer, Waltham, MA; packed with Supelco adsorbents, Sigma-Aldrich, Bellefonte, PA) were inserted between the headspace and an air pump that sucked air with a sampling rate of 0.5 L min⁻¹. The VOC’s in 10 L of air were preconcentrated in the TD tubes. The absorbed VOC’s were subsequently thermally desorbed and quantified by gas chromatography/mass spectrometry (GC/MS) (Varian CP-3800, Varian Inc., Palo Alto, CA).

Ammonia concentrations in the headspace air were measured by means of precision gas detector tubes (Kitagawa, Japan; ranges 3.6 × 10⁻⁴ to 5.6 × 10⁻² mg L⁻¹ and 3.6 × 10⁻³ 1.9 × 10⁻¹ mg L⁻¹). The H₂S concentrations were measured using a H₂S analyzer (Jerome 631-X, Arizona Instruments LLC, Chandler, AZ), with averaged values consisting of five readings. Dry matter was determined after drying samples at 105°C for 24 h. Volatile solids were measured in accordance with standard methods (APHA,
Table 1. Measurements and samplings carried out during the 9 wk storage period.

<table>
<thead>
<tr>
<th>Week</th>
<th>Measurements</th>
<th>Treatments</th>
<th>N chambers</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Odor concentration in headspace air</td>
<td>U and SD-SM-SH†</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Concentration of VOC's† in headspace air</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Concentration of NH₃ and H₂S in headspace air</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thickness of the straw cover</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Physicochemical characteristics of the slurry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2, 4, 6, 8</td>
<td>Concentration of NH₃ and H₂S</td>
<td>U, SD, SM, SH and SD new §</td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>Odor concentration in headspace air</td>
<td>U, SD, SM, SH and SD new §</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Concentration of VOC's in headspace air</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Concentration of NH₃ and H₂S in headspace air</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thickness of the straw cover</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Physicochemical characteristics of the slurry</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Measurements were taken in slurry added straw dry (SD) treatment and assumed to be similar for slurry added straw and moderate moisture content (SM) and slurry added straw and high moisture content (SH) treatments.

‡ VOC, volatile organic compounds.

§ Chambers corresponding to SD new at Weeks 2, 4, 6, and 8 did not contain new straw, as the removal of the aged straw cover and the addition of new straw, in SD new treatment was performed at Week 9.

1995). Slurry total N was determined using the Kjeldahl method (APHA, 1995), and the ammonium nitrogen (NH₃-N) content of slurry samples was analyzed using the ISO 7150–1 NH₃ test. Concentrations of VFA (i.e., acetic acid, propanoic acid, 2-methyl propanoic acid, 3-methyl butanoic acid, and pentanoic acid) in the slurry were determined by gas chromatographic analyses (HP 6850 series, Agilent Technologies, Santa Clara, CA). Slurry pH and temperature (T) were measured with a standard electrode (Metrohm, Herisau, Switzerland). The thickness of the straw cover was measured by an articulated T-square.

**Statistical Analysis**

Before the statistical analysis, data on OC and concentrations of odorants in the air (VOC's, NH₃, and H₂S) were normalized by natural logarithmic transformations (log_e). Data on slurry characteristics and concentration of odor and odorants were analyzed by analysis of variance. Samples from the different treatments and times were determined to be statistically different at the 0.05 significance level using PROC GLM in SAS software (SAS, 2002). When a significant difference was found, pair wise comparisons between treatments and times were done in a least square means test using the PDIFF option adjusted for multiple comparisons by the Tukey test.

The reduction efficiencies (%) in odor and odorants emission rates of the different straw covers (SD Week 9*, SM Week 9*, SH Week 9*, and SD new*) were calculated according to Eq. [1]:

Reduction efficiency = 100 – Relative concentration [1]

where the relative concentration (%) was defined as (Eq. [2]):

Relative concentration (%) = (Concentration above covered slurry/Concentration above uncovered slurry) × 100 [2]

**Results and Discussion**

**Effect of Moisture Content and Slurry Storage Time**

**Physicochemical Characteristics**

The thickness of the straw cover at the beginning of the experiment was 0.10 m, and after the 9 wk storage period it ranged between 0.07 and 0.10 m. A visual evaluation of the slurry surface in all 15 chambers was performed. Chambers containing slurry with no added straw (U Week 9) did not develop a natural crust (Fig. 3). In all chambers containing slurry added straw, the straw was afloat after the 9 wk storage period and it covered the entire surface area.

Previous studies have indicated that dry straw, kept free of rain, will float on slurry, but when wetted by rain, it may sink (Clanton et al., 1999; Guarino et al., 2006). In this respect, it should be mentioned that the ratio between perimeter and surface area in the present laboratory study was substantially higher than in commercial storage units, and the edge effects (i.e., friction and cohesion between the straw and the chambers walls) probably affected the performance of the straw cover and prevented it sinking. Therefore, no final conclusions regarding the flotation ability of the straw covers under normal conditions in livestock facilities can be made from the present study.

No differences between the physicochemical characteristics of uncovered slurry and slurry added straw at Week 0 (U Week 0 and SD-SM-SH Week 0*) were found (Table 2). The comparison between the physicochemical characteristics of the uncovered slurry at Week 0 and Week 9 (U Week 0 and U Week 9) indicated that VFA's concentrations, total N and NH₃-N contents, dry matter, and volatile solids of the slurry significantly decreased during the storage period, while the pH significantly increased from 7.1 to 8.1 during that period. The change in pH is particularly important, as it strongly affects the emissions of odorants, especially VFA's, NH₃, and H₂S (Shurson et al., 1998; Blanes-Vidal et al., 2009b). Increases in pH after 9 wk of storage have been found in previous studies under equivalent experimental conditions (Hobbs et al., 1999; Berg et al., 2006).

At Week 9, pH, total N content, and concentration of propanoic acid were found to be significantly different across slurry cover treatment. The presence of the straw covers, regardless of the moisture content, always lowered the pH of the slurry relative to uncovered slurry, but this reduction was more pronounced the higher the moisture content. Reductions in pH in dry straw covered slurry relative to uncovered slurry have been reported by Xue et al. (1999); Hudson et al. (2006) and Blanes-Vidal et al. (2008), in laboratory and pilot scale studies with diary and swine liquid manures.
Concentration of Odor, Volatile Organic Compounds, H$_2$S, and NH$_3$ in the Headspace Air

At the start of the experiment, concentrations of odor, NH$_3$, and most of VOCs were higher in the headspace of slurry with straw cover chambers than in the uncovered slurry chambers, although not significantly at 0.05 level (Table 3). From Week 0 to Week 9, significant increases were observed in concentration of NH$_3$, H$_2$S, dimethylsulfide, carbon disulfide, acetic acid, and phenols above the uncovered slurry; whereas indoles and VFA’s (except acetic acid) were found to decrease above the uncovered slurry.

The highest OCs were found in the air sampled above slurry covered by straw with high moisture content (SH$_{\text{Week 9}}$), and the lowest OCs were found in the air sampled above slurry covered by dry straw (SD$_{\text{Week 9}}$). However, these differences were not statistically significant.

Concentrations of NH$_3$, dimethylsulfide, phenol, p-cresol, skatole and benzylalcohol, were significantly higher above uncovered slurry (U$_{\text{Week 9}}$) than above covered slurry (SD$_{\text{Week 9}}$, SM$_{\text{Week 9}}$, and SH$_{\text{Week 9}}$). The straw cover may have influenced the emissions of these gases by means of physical mechanisms (acting as a physical barrier), chemical mechanisms (altering the chemical properties of the slurry), or biological mechanisms (acting as a biofilter). No differences between uncovered (U$_{\text{Week 9}}$) and covered slurry (SD$_{\text{Week 9}}$, SM$_{\text{Week 9}}$, and SH$_{\text{Week 9}}$) were found for concentration of H$_2$S, and the remaining VOCs indicated in Table 3.

Concentration of total N and propanoic acid in the slurry samples were significantly modified by the addition of straw.

![Image: Visual evaluation of the slurry surface in flux chambers at the end of the experiment (Week 9) for uncovered slurry (U$_{\text{Week 9}}$), slurry added dry straw (SD$_{\text{Week 9}}$), slurry added straw and moderate moisture content (SM$_{\text{Week 9}}$), and slurry added straw and high moisture content (SH$_{\text{Week 9}}$).]

### Table 2. Thicknesses of straw covers and physicochemical characteristics of slurries†‡.

<table>
<thead>
<tr>
<th></th>
<th>Start of experiment</th>
<th>End of experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U$_{\text{Week 0}}$</td>
<td>SD-SM-SH$_{\text{Week 0}}$</td>
</tr>
<tr>
<td>Thickness, cm</td>
<td>0a</td>
<td>10b</td>
</tr>
<tr>
<td>pH</td>
<td>7.10a</td>
<td>7.08a</td>
</tr>
<tr>
<td>T, °C</td>
<td>16.0a</td>
<td>15.8a</td>
</tr>
<tr>
<td>Dry matter, g kg$^{-1}$</td>
<td>40a</td>
<td>42a</td>
</tr>
<tr>
<td>Volatile solids, g kg$^{-1}$</td>
<td>27a</td>
<td>31a</td>
</tr>
<tr>
<td>Total N, g L$^{-1}$</td>
<td>5.2a</td>
<td>4.4ab</td>
</tr>
<tr>
<td>Ammonium N, g L$^{-1}$</td>
<td>3.0a</td>
<td>3.0a</td>
</tr>
<tr>
<td>Acetic acid, g m$^{-3}$</td>
<td>5878a</td>
<td>4601a</td>
</tr>
<tr>
<td>Propanoic acid, g m$^{-3}$</td>
<td>2957a</td>
<td>2738a</td>
</tr>
<tr>
<td>2-Methyl propanoic acid, g m$^{-3}$</td>
<td>499a</td>
<td>497a</td>
</tr>
<tr>
<td>3-Methyl butanoic acid, g m$^{-3}$</td>
<td>701a</td>
<td>699a</td>
</tr>
<tr>
<td>Pentanoic acid, g m$^{-3}$</td>
<td>136a</td>
<td>134a</td>
</tr>
</tbody>
</table>

† Values are arithmetic means from three repetitions per treatment.
‡ Same letters (a, b, c, d) within rows indicate no significant differences ($P > 0.05$) between U$_{\text{Week 0}}$, SD-SM-SH$_{\text{Week 0}}$, U$_{\text{Week 9}}$, SD$_{\text{Week 9}}$, SM$_{\text{Week 9}}$, and SH$_{\text{Week 9}}$.
Same letters (u, v, w) within rows indicate no significant differences ($P > 0.05$) between U$_{\text{Week 9}}$, SD$_{\text{Week 9}}$, and SD$_{\text{new}}$. 

Concentration of Odor, Volatile Organic Compounds, H$_2$S, and NH$_3$ in the Headspace Air

At the start of the experiment, concentrations of odor, NH$_3$, and most of VOCs were higher in the headspace of slurry with straw cover chambers than in the uncovered slurry chambers, although not significantly at 0.05 level (Table 3). From Week 0 to Week 9, significant increases were observed in concentration of NH$_3$, H$_2$S, dimethylsulfide, carbon disulfide, acetic acid, and phenols above the uncovered slurry; whereas indoles and VFA’s (except acetic acid) were found to decrease above the uncovered slurry.
Table 3. Concentration of odor and odorants in air sampled above uncovered and straw covered slurries†‡.

<table>
<thead>
<tr>
<th>Odor concentration (OC), OU m⁻³</th>
<th>Start of experiment</th>
<th>End of experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UWeek 9</td>
<td>SD-SM-SHWeek 0</td>
</tr>
<tr>
<td>Odor concentration (OC), OU m⁻³</td>
<td>760 (7a)</td>
<td>1027 (6a)</td>
</tr>
<tr>
<td>NH₃, mg m⁻³</td>
<td>55 (4a)</td>
<td>155 (3fa)</td>
</tr>
<tr>
<td>H₂S, mg m⁻³</td>
<td>0.1 (a)</td>
<td>0.1 (a)</td>
</tr>
<tr>
<td>1-Butanol, μg m⁻³</td>
<td>77 (47a)</td>
<td>506 (17a)</td>
</tr>
<tr>
<td>Trimethylamine, μg m⁻³</td>
<td>81 (20a)</td>
<td>657 (31b)</td>
</tr>
<tr>
<td>Acetic acid, μg m⁻³</td>
<td>64 (25a)</td>
<td>142 (41a)</td>
</tr>
<tr>
<td>Propionic acid, μg m⁻³</td>
<td>66 (12a)</td>
<td>55 (5a)</td>
</tr>
<tr>
<td>2-Methyl propanoic acid, μg m⁻³</td>
<td>9.0 (21a)</td>
<td>12 (24a)</td>
</tr>
<tr>
<td>Butanoic acid, μg m⁻³</td>
<td>3.1 (97a)</td>
<td>1.8 (76a)</td>
</tr>
<tr>
<td>3-Methyl butanoic acid, μg m⁻³</td>
<td>9.0 (2)</td>
<td>29.5 (2)</td>
</tr>
<tr>
<td>Pentanoic acid, μg m⁻³</td>
<td>0.4 (87a)</td>
<td>0.1 (173a)</td>
</tr>
<tr>
<td>Dimethyl sulfide, μg m⁻³</td>
<td>6.2 (32a)</td>
<td>2.1 (30a)</td>
</tr>
<tr>
<td>Dimethyl disulfide, μg m⁻³</td>
<td>9.4 (51a)</td>
<td>2.4 (137a)</td>
</tr>
<tr>
<td>Carbon disulfide, μg m⁻³</td>
<td>0.1 (90a)</td>
<td>0.0 (173a)</td>
</tr>
<tr>
<td>Phenol, μg m⁻³</td>
<td>1.0 (73a)</td>
<td>0.8 (32a)</td>
</tr>
<tr>
<td>p-cresol, μg m⁻³</td>
<td>1.1 (115ab)</td>
<td>0.2 (165a)</td>
</tr>
<tr>
<td>Indole, μg m⁻³</td>
<td>1.6 (87a)</td>
<td>1.7 (28a)</td>
</tr>
<tr>
<td>Skatole, μg m⁻³</td>
<td>18.4 (43a)</td>
<td>0.3 (152a)</td>
</tr>
<tr>
<td>Benzy alcohol, μg m⁻³</td>
<td>0.09 (0)</td>
<td>0.1 (73a)</td>
</tr>
<tr>
<td>Benzaldehyde, μg m⁻³</td>
<td>12.2 (20a)</td>
<td>1.8 (90a)</td>
</tr>
</tbody>
</table>

† Values are geometric means (calculated by back transformations of loge arithmetic means) and values in parenthesis are coefficients of variation on loge basis (calculated as the ratio of the standard deviation to the arithmetic mean of loge statistics).
‡ The GLM analysis was carried out on loge basis. Same letters (a, b, c, d) within rows indicate no significant differences (P > 0.05) between UWeek 9, SD-SM-SHWeek 0, UWeek 9, SDWeek 9, SMWeek 9, SHWeek 9, and SDnew. Same letters (u, v, w) within rows indicate no significant differences (P > 0.05) between UWeek 9, SDWeek 9, and SDnew.

(Table 2). The decrease in the NH₃ emissions from covered slurry can be partly attributed to the change in the slurry chemical properties. The addition of materials with a high carbon/nitrogen ratio (C/N) (e.g., straw) increases the amount of degradable C which promotes immobilization of inorganic N from the slurry into the microbial biomass (Sommer et al., 2006). This modification in the chemical equilibrium in the slurry can lead to reduced NH₃ emissions. Besides, the addition of straw significantly decreased the pH of the slurry. A decrease in pH of the slurry shifts the NH₃/NH₄⁺ equilibrium toward a higher NH₄⁺ concentration in the slurry and lowers the free NH₃ concentration, which leads to lower NH₃ emissions from the slurry.

Controlling the emissions of H₂S from stored slurry is especially important, as H₂S has been identified as one of the main odors responsible for high OCs measured above slurry storages (Hobbs et al., 2000; Blanes-Vidal et al., 2009a). Some authors have reported a negative correlation between pH and emission of H₂S (Arogo et al., 2000; Blunden and Aneja, 2008). When the pH of slurry is basic (pH > 8) most reduced sulfur exists as HS⁻ and S²⁻ ions, and emission of H₂S is consequently low (Shurson et al., 1998). In our study, pH at Week 9 for the four different treatments decreased in the following order: pHUWeek 9 > pHSMWeek 9 > pHSDWeek 9 > pHSHWeek 9, which may explain the pattern of the observed emission of H₂S (Table 3). On the other hand, according to Xue et al. (1999), when NH₃ and H₂S contact a moist surface in the straw layer, they tend to be captured in the layer and held there, until saturation is reached. Therefore, lower emissions should be expected from watered straw covers (i.e., SHWeek 9 and SMWeek 9) than from dry covers (SDWeek 9). As a consequence, the effects of pH and moisture content of the straw cover may have counteracted each other, leading to nonsignificant differences in H₂S concentrations at the end of the experiment.

As was previously mentioned, the NH₃ concentration at Week 0 was significantly higher above the covered slurry in comparison to the uncovered slurry. The concentration of NH₃ above the uncovered slurry significantly increased during the first 4 wk of the storage period and the concentration above the covered slurry (SD, SM, and SH) dropped significantly during the same period. Regarding the increase in NH₃ concentration above uncovered slurry over time, Hobbs et al. (1999) found that the emission rates of NH₃ from uncovered finishing swine slurry increased over a 112 d storage period. The increase in NH₃ concentration is expected to be due to the observed increase in pH during the storage period.

At Week 2, no significant differences in NH₃ concentrations were found among the four treatments (U, SD, SM, and SH). Previous authors have demonstrated that a straw cover significantly reduces the emission of NH₃ in comparison to uncovered slurry (Sommer et al., 1993; Xue et al., 1999). In the present study, all straw covers (regardless of their moisture content) were only effective in reducing NH₃ emissions 4 wk after the straw cover was established (Fig. 4). The difference in results is expected to be caused by the fact that the straw cover in this study was mixed into the slurry according to the Danish recommendations for slurry cover establishment.

The reduction of the concentration of NH₃ above the covered slurries over time can be related to various factors: (i) the development of a microbial population (which will be addressed separately in the current paper), (ii) lower pH and higher C to N ratio in the
slurry caused by straw degradation, and (iii) a lowered contribution of the slurry-drenched straw to the total emissions of gases. As time passed, fewer straw fragments were wetted by slurry, because of drying (in SD treatment) or watering (in SM and SH treatments). At Week 9, a considerable higher proportion of the surface area was observed to be dry (Fig. 3). On the other hand, the comparison between SM and SH in Fig. 4 shows that, at Week 2 and Week 4, NH₃ emissions were slightly lower in SH in comparison to SM, probably due to the higher amount of added water and the increased washing effect of the slurry drenched straw.

In general terms, H₂S concentrations increased from Week 0 to Weeks 4 through 6, and decreased from Weeks 4 through 6 to Week 9 (Fig. 5), and so, maximum H₂S concentrations were reached about half way through the experiment (in Weeks 4–6). In a laboratory experiment where swine slurry was stored in a chamber for 8 wk, Clanton and Schmidt (2000) determined that the emission rate of H₂S (as measured by a Jerome meter) from slurry, showed an apparent maximum at Weeks 4 and 5. In the present study, H₂S concentration above uncovered slurry was at its maximum at Week 4. No significant differences in H₂S concentrations were found among U, SD, SM, and SH treatments over the experimental period as a function of straw cover moisture content. Besides, the concentration of H₂S in U, SD, SM, and SH treatments at each specific week did not follow a clear pattern (Fig. 5).

The present study suggests that the fluctuating moisture content caused by the moderate (50 mm month⁻¹) and high (100 mm month⁻¹) rainfall patterns did not affect the odor reduction effect of straw covers, as no differences in odor or odorant concentrations were found between the SD, SM, and SH treatments at Week 9. However, it is important to note that rainfall over full-scale storage tanks may influence the performance of the cover by promoting the sinking of the straw.

Finally, we should mention that the effect of water addition to the uncovered slurry was not studied in this experiment. Emissions of odor and odorants from uncovered slurry could change if exposed to rainfall, due to agitation of the liquid-air interface and reduction in the concentration of odorants in the slurry.

**Effect of Age of the Straw Cover**

In this study we considered that the physical and chemical factors that can affect the emission of odor and odorants are thickness of the straw cover and physicochemical characteristics of the slurry; and so, that the differences in the chemical composition of the straw itself (e.g., differences in N content between aged and new straw covers) have no direct effect on the odor mitigation efficiency of the cover.

We assumed that the microbial population developed during 1 d of storage (SDnew) can be considered negligible in comparison to the microbial population established in an aged (9 wk old) straw cover (SDWeek 9). Therefore, the comparison between SDWeek 9 and SDnew treatments can be used to indirectly estimate the contribution of the biological mechanism to the overall odor mitigation efficiency of the cover, provided that the physical and chemical factors affecting the emissions of odor and odorants are similar in both treatments (Xue et al., 1999; Hudson et al., 2006).

The thickness of the straw cover and the physicochemical characteristics of the slurry (including pH, temperature, and chemical composition) in SDWeek 9 and SDnew were not statistically different (Table 2). No significant differences were detected between SDWeek 9 and SDnew regarding concentrations of odor and most of the measured odorants (e.g., H₂S, acetic acid, phenol, indole, skatole). However, concentrations of NH₃, 3-methyl butanoic acid, dimethyl sulfide, p-cresol, and benzyl alcohol measured in the headspace air were significantly higher in chambers containing slurry covered by new straw covers (SDnew) than in chambers containing aged straw covers (SDWeek 9). As the physical and chemical properties of the SDnew and SDWeek 9 slurry can be considered similar; the lower concentrations of NH₃, dimethyl sulfide, p-cresol, and benzyl alcohol measured in the SDWeek 9 treatment were attributed to the mitigation effect caused by the microbial population developed in the cover during the 9 wk storage period.

**Odor Reduction Efficiency of Straw Covers and their Mechanisms of Operation**

Previous research has found straw covers efficient in reducing the emission of odor and ammonia from slurry stores. Reductions between 35 and 85% in odor concentrations and emissions by the use of straw covers, have been reported by Hornig et al. (1999), Ciccek et al. (2004), and Hudson et al. (2006). Several studies have shown that straw covers reduced NH₃ emissions by, for example, 80% when the thickness of the cover was between 5 and 15 cm (Hornig et al., 1999), or by 34 and 86% when the thickness was of 7 and 14 cm, respectively (Guarino et al., 2006).

In our study, odor concentration at Week 9 was reduced by 30% when the slurry was covered by an aged dry straw cover (SDWeek 9) and by 48% when the straw cover was new (SDnew) (Fig. 6). Odor concentration above slurry covered by straw with moderate humidity content (SMWeek 9) was only 2% lower than in uncovered slurry, and in the case of high humidity content,
OC was 19% higher from the covered slurry (SH Week 9) than from uncovered slurry. However, as it was shown in Table 3, these reductions were neither significant (P > 0.05) nor significantly different among treatments.

As in the case of OC, differences in H2S concentrations among treatments (SD Week 9, SM Week 9, SH Week 9, and SD new) were not significant at the 0.05 level, and they were not significantly different from the H2S concentration measured above uncovered slurry (U Week 9). Although not significant, the results suggest that the control of H2S by the straw covers is mainly caused by the straw cover acting as a biofilter (microbiological mechanism), since a 43% reduction was found for slurries covered by aged straw covers (SD Week 9), compared to 5% reduction when the slurry was covered by new straw (SD new).

Ammonia concentrations above uncovered slurry (118 mg m\(^{-3}\)), slurry covered by new straw (63 mg m\(^{-3}\)) and slurry covered by aged straw (2.4 mg m\(^{-3}\)) were significantly different. The efficiency in reducing NH\(_3\) emissions was 99% when slurries were covered by aged straw covers (for all levels of humidity content, that is, SD Week 9, SM Week 9, and SH Week 9), while the reduction efficiency achieved by new straw covers was only 47% (Fig. 6). Therefore, the results of this study indicate that the biological mechanism plays an important role in the reduction of NH\(_3\) emissions by straw covers, as about 50% of the reduction efficiency corresponds to the straw cover acting as a biofilter, whereas the remaining 50% is associated to physical and chemical effects.

Aged straw covers, regardless of their humidity content, significantly reduced concentrations of dimethyl sulfide (by 81%, on average), phenol (by 82%), p-cresol (by 95%), skatole (by 98%), and benzylalcohol (by 97%) above the slurries. In the case of phenol and skatole, a similar reduction was obtained by the new straw cover. In the case of dimethyl sulfide, p-cresol, and benzylalcohol the new cover did not significantly reduce their emissions with respect to uncovered slurry. Therefore, the microbiological mechanism does not seem to play an important role in the reduction of phenol and skatole emissions by the cover. On the contrary, the biofiltering action of the cover (microbiological mechanism) appears to be the main responsible mechanism for the reduction of dimethyl sulfide emissions, and to be responsible of about 50% and 75% of the efficiency of the straw cover in reducing the emissions of p-cresol and benzylalcohol, respectively (Fig. 6).

The interpretation of the results for odor and odorant concentrations for the different treatments is not straightforward, as the OCs perceived above slurry are the result of a complex mixture of odorants in the air; and the correlation between human response to livestock odors, and specific compounds identified by instrumental methods remains quite poor (Bunton et al., 2007). However, some studies have pointed out the important contribution of sulfur-containing compounds (mainly H2S), phenols, and indoles to the overall OC. In this study, the changes in H2S concentration for the different humidity content treatments follow a similar pattern as the OC, which suggests a positive relationship between H2S and OC. However, concentrations of all odorants above new dry straw covers were higher than concentrations above aged dry straw.

![Fig. 5. Evolution of average H2S concentration measured in the headspace of flux chambers containing uncovered slurry (U), and slurry added straw at different moisture contents (SM, SD, and SH), during the 9 wk storage period. No significant differences among treatments were found (P > 0.05). Same letters indicate no significant differences over time (P > 0.05) for all four treatments.](image)

![Fig. 6. Relative concentration of odor, hydrogen sulfide, ammonia, dimethyl sulfide, phenol, p-cresol, skatole, and benzyl alcohol above slurry covered by aged (at different moisture levels) and new straw covers. All values are shown as percent of the concentrations measured above uncovered slurry (U Week 9).](image)
covers, whereas OCs above new straw covers were lower than OCs above aged straw covers. A possible explanation of this result can be a change in the nature of the odor. Odor concentration, defined as the number of odors with neutral gas, at which 50% of the panelists can detect odor in the air sample (European Committee for Standardisation, 2003), does not include information about the nature of the odor. In a similar study, Hudson et al. (2006) observed that the nature of the odor emitted from slurry covered by permeable covers changed as time passed, being quite different from that emitted by raw swine slurry. This change was attributed to establishment of a population of bacteria and fungi on the cover material, which could produce odorous compounds that could interfere with the odor emission rates. In the present study, although the difference between OC above aged and new straw covers was not statistically significant, the higher OC above aged straw cover in comparison to new straw covers could be related to the presence of odorous compounds different from those measured here, emitted by the microorganisms present in the straw cover. These odorous compounds can contribute to an increase in the overall OC, and could be responsible for changes in the character and offensiveness of the odor emitted from straw covered slurry stores in comparison to uncovered slurry storage units.

Conclusions

Aged straw covers, regardless of their moisture content, significantly reduced emissions of ammonia (by 99%), dimethyl sulfide (by 81%), phenol (by 82%), p-cresol (by 95%), skatole (by 98%), and benzylalcohol (by 97%). No significant differences between uncovered and covered slurry were found for emission of odor, H2S, and VOCs such as VFAs, dimethyl disulfide, and indole. The different moisture contents in the straw covers caused by the moderate (50 mm month\(^{-1}\)) and high (100 mm month\(^{-1}\)) rainfall patterns did not affect the odor and odorsants reduction efficiency of straw covers after a 9 wk storage period.

Odor concentrations above slurries covered by aged straw covers were not significantly different than odor concentrations above slurries covered by new straw covers. However, concentrations of all odorsants (i.e., NH\(_3\), H\(_2\)S and VOCs) above aged straw covers were lower than concentrations above new straw covers. These differences in reduction efficiencies were significant for NH\(_3\), dimethyl sulfide, p-cresol, and benzyl alcohol.

The microbial mechanism for odorants reduction (i.e., straw cover acting as a biofilter) does not seem to play an important role in the reduction of phenol and skatole emissions by the straw cover, since a similar reduction was obtained by the new straw covers and aged straw covers. On the contrary, the microbial mechanism appears to be responsible for about 50, 100, 50, and 75% of the reduction on the emissions of NH\(_3\), dimethyl sulfide, p-cresol, and benzylalcohol, respectively, from the straw covered slurry.

The results of this study support the concept that the main mechanism for odor and odorsants emission reduction in straw covered slurry is associated with the cover acting as a physical barrier. However, the reduction in emission of specific gases (such as ammonia and p-cresol) appears to be also caused by the straw cover acting as a biofilter.

References


Hornig, G., M. Turk, and U. Wanka. 1999. Production of sulfur compounds in gases emitted by the microorganisms present in the straw cover. These odorous compounds contribute to an increase in the overall OC, and could be responsible for changes in the character and offensiveness of the odor emitted from straw covered slurry stores in comparison to uncovered slurry storage units.

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