Evaluation of Simplified Covering Systems to Reduce Gaseous Emissions from Livestock Manure Storage

M. Guarino, C. Fabbri, M. Brambilla, L. Valli, P. Navarotto

Abstract. *Ammonia, methane, and carbon dioxide are the primary atmospheric emissions from cattle and pig farms. A significant part of these emissions is produced by the decomposition of slurry organic matter during manure storage and treatment phases. Present solutions to contain emissions from storage lagoons generally involve reducing the free surface of the slurry by covering it either with permanent fixed structures or temporary floating ones. This study investigated the effectiveness of five simple floating covers in reducing emissions from pig and cattle slurry. The coverings included vegetable oil (a mixture of rapeseed and soybean oil), expanded clay, chopped maize stalks, chopped wheat straw, and chopped wood chips. All were tested at two different thicknesses: 70 and 140 mm for solid coverings, and 3 and 9 mm for liquid. Slurry samples covered with the above-mentioned materials were placed in nine stainless steel airtight cylinders measuring 190 dm^3. Gaseous and odor concentrations in the headspace were monitored using a Bruel & Kjaer 1302 multi-gas monitor and a T07 olfactometer. The flotation aptitude of the different coverings was also tested. Results revealed substantial differences in ammonia emission reduction efficiency (1% to 100%) and odor abatement (0% to 90%), and high levels of reduction efficiency were achieved by all the tested covers at the higher thickness. However, equally valid results were not obtained for methane emissions reduction. In regard to flotation aptitude and cover deterioration on slurry, expanded clay and wood chips demonstrated long-term resistance to both deterioration and sinking.*

Keywords. *Ammonia, Emission, Floating cover, Odor, Slurry.*

Estimations of atmospheric emissions from Italian cattle and pig farms are primarily concerned with ammonia (97% of the total national ammonia emissions), methane (52%), and nitrous oxide (48%) production. It has been demonstrated that a significant part of these emissions is produced during manure storage and treatment due to the decomposition of slurry organic matter and prolonged contact with the atmosphere (Valli et al., 2000).

A key role is played by nitrogen, in all its different biochemical forms, which together with carbohydrates is an essential element in the life cycle of organisms and fundamental for ensuring good livestock productions. Nevertheless, animals are unable to metabolize all the nitrogen supplied in their diet (e.g., through tissue preservation, growth, and/or milk production). According to literature, dairy cows tend to excrete an average 79% of the supplied nitrogen, while pigs excrete 65% (Tamminga, 1992; CRPA, 2001).

The forms and amounts of nitrogen excreted in slurry vary according to diet and animal species. An average of 60% to 90% of nitrogen excreted in urine is represented by urea in dairy cows (Bristow et al., 1992), while the percentage is about 70% to 90% for pigs (Bristow et al., 1992; Petersen, 1998). Most of the nitrogen excreted in feces is in organic form (namely partially or totally undigested proteins). Nitrogenous components, present in both urine and the feces, have a strong influence on ammonia emission into the atmosphere, although this importance varies with the emitting stage under consideration.

Nitrogen excretion as urea is extremely important in livestock housing because of enzymatic hydrolysis. Organic nitrogen, mainly present in the feces, is highly unstable and reacts with the urease enzyme (Kastelaar and Rap, 1994), but it can only be considered an important source of emission in the event of mineralization caused by long-term storage. In fact, with reference to urease reaction, it should be stressed that under farm conditions, with relatively high temperatures and extensive paved surfaces, urea excreted by animals is transformed into ammoniac nitrogen (eq. 1) in just a few hours (Elzing and Monteny, 1997a):

$$NH_3 + H_2O \xrightarrow[\text{pH, T}]{} NH_4{}^+ + OH^- \quad (1)$$

Even though this balance largely depends on slurry temperature and the ammonia acid dissociation constant (K_a), with a value that ranges from 0.8×10^{-10} (Hashimoto and Ludington, 1971) for concentrated slurries to 3.982×10^{-10} (Weast et al., 1986) for the more diluted ones, it has been shown that pH plays the most important role (Elzing and

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The authors are **Marcella Guarino, ASABE Member,** Researcher, Department of Science and Veterinary Technology for Food Safety, University of Milan, Italy; **Claudio Fabbri,** Researcher, Animal Production Research Center (CRPA SpA), Reggio Emilia, Italy; **Massimo Brambilla,** Laboratory Technician, Department of Science and Veterinary Technology for Food Safety, University of Milan, Italy; **Laura Valli,** Researcher, Animal Production Research Center (CRPA SpA), Reggio Emilia, Italy; and **Pieriuigi Navarotto,** Professor, Department of Science and Veterinary Technology for Food Safety, University of Milan, Italy. **Corresponding author:** Marcella Guarino, Department of Science and Veterinary Technology for Food Safety, University of Milan, Via Celoria 10, 20133 Milan, Italy; phone: +39-02-503-17927; fax: +39-02-503-17909; e-mail: marcella.guarino@unimi.it.

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Table 1. Brief description of the tested covering materials.

Material	Description
Vegetable oil	Mixture of rapeseed (50%) and soybean (50%) oil.
Chopped wheat straw	Individual straws measuring from 7 to 100 mm long.
Chopped maize stalks	Individual stalks measuring 100 mm long, with a structure very similar to that of chopped wheat straw.
Wood chips	Produced by mechanical chopping of wood: chips measure 20 to 30 mm long and may be dried to prevent deterioration.
Expanded clay	Very light and resistant granules with a diameter of 8 to 12 mm.

Monteny, 1997b; Groot Koerkamp and Elzig, 1996; Monteny et al., 2000):

- 6 < pH < 7: almost all the ammoniac nitrogen tends to be in solubilized form (NH_4^+).
- pH > 7: the balance is shifted toward the non-ionized and volatile form (NH_3).
- pH $\geq$ 11: all the nitrogen is present as NH_3.

According to Haslam et al. (1924), airspeed is another factor that can physically affect ammonia emission from slurry storage. A drop in wind speed results in higher levels of NH_3 in the gaseous layer above the free surface of the slurry, leading to a significant reduction in ammonia emission. The animal stocking density must also be taken into account. In particular, greater volumes of slurry per live weight unit lead to higher emissions from manure storage due to the very long extended storage time laid down in regulations.

At present, the main solutions adopted to reduce emissions from slurry storages involve reducing the free surface of the slurry by either constructing rooftops or covering the surface with different materials. Extensive bibliographical documentation from the early 1990s onward attests to a growing interest in the latter, with the development of both rigid and floating covers (Mannebeck, 1985) made from different materials and designed to resist the action of atmospheric agents. Rigid covers are either attached to the tank structure and supported by various types of frames, or are self-supporting and created to form a fixed cover (with roof, sealed, with floor) that is not in contact with the slurry. As an alternative, floating covers are allowed to float freely on the entire slurry surface.

Rigid covers require longer assembly times and are more expensive to set up (MAFF, 1999) but are guaranteed to last longer. The alternative floating covers can be cheaply constructed from both organic and inorganic materials such as straw, expanded clay granules, vegetable oil, wood chips, rice husks, and corn stalks (Clanton et al., 2001). Therefore, apart from natural crusts (basically formed by undigested emerging fiber), floating covers can be created by mixing slurry with vegetal material. However, there are some practical limitations to their use:

- The risk of chemical and biological degradation through contact with the slurry.
- Drift effect caused by wind action.
- The risk of mixing with the slurry.
- The possible risk of sinking and consequently blocking the drainage systems.

Despite the above disadvantages, several studies have shown that floating covers can provide a valid emission abatement system. For example, a reduction efficiency of 70% to 90% has been recorded for ammonia emissions (De Bode 1991; Bundy et al., 1997; Miner and Suh, 1997; Hashimoto and Ludington, 1971).

Materials and Methods

The study was aimed at evaluating the efficiency of five simplified floating covers (table 1) in reducing ammonia, methane, carbon dioxide, and odor emissions from slurry storage facilities, as well as their respective flotation aptitude and capacity.

Table 2. Main chemical and physical features of the pig and cattle slurries used to test the emission reduction effectiveness of the covering materials.

Analytical Features[a]	Maize Stalks	Wood Chips	Vegetable Oil	Expanded Clay	Wheat Straw	Mean ± SD
Pig slurry						
pH	7.4	7.5	7.5	7.2	7.3	7.38 ± 0.13
TS (10^{-3} kg kg^{-1})	22.6	22.6	18.8	28.2	24.4	23.32 ± 3.41
TS (% RW)	2.3	2.3	1.9	2.8	2.4	2.34 ± 0.32
VS (10^{-3} kg kg^{-1})	14.1	14.7	11.3	19.5	15.1	14.94 ± 2.95
VS (% TS)	62.4	65.0	60.1	69.1	61.9	63.7 ± 3.5
TKN (10^{-6} kg kg^{-1})	2904	2487	2127	2522	2675	2543 ± 284
TKN (% TS)	12.8	11.0	11.3	8.9	11.0	11.01 ± 1.39
N-NH_4 (10^{-6} kg kg^{-1})	1943	1850	1594	1459	1741	1717 ± 194
N-NH_4 (% TKN)	66.9	74.4	74.9	57.9	65.1	67.8 ± 7.1
Cattle slurry						
pH	7.1	7.2	7.1	7.4	7.1	7.18 ± 0.13
TS (10^{-3} kg kg^{-1})	55.6	73.7	61.4	60.3	56.1	61.42 ± 7.32
TS (% RW)	5.6	7.4	6.1	6.0	5.6	6.14 ± 0.74
VS (10^{-3} kg kg^{-1})	37.6	52.6	41.3	39.9	37.6	41.8 ± 6.24
VS (% TS)	67.6	71.4	67.3	66.2	67.0	67.9 ± 2.0
TKN (10^{-6} kg kg^{-1})	3056	3528	3544	3409	3311	3369 ± 199
TKN (% TS)	5.5	4.8	5.8	5.7	5.9	5.52 ± 0.44
N-NH_4 (10^{-6} kg kg^{-1})	1430	1818	1733	1711	1469	1632 ± 172
N-NH_4 (% TKN)	47.0	52.0	49.0	50.0	44.0	48.4 ± 3.0

[a] TS = total solids, RW = raw weight, VS = volatile solids, and TKN = total Kjeldahl nitrogen.

Testing of Emission Reduction

Two thicknesses of each floating cover were tested: 70 and 140 mm for solid covers, and 3 and 9 mm for liquid covers (vegetable oil). The effective reduction of gas emission on two kinds of manure was tested for each covering material: one from a full-cycle swine farm, and the other from a dairy cattle farm. The main chemical and physical features of the two slurries are reported in table 2.

The TS concentration in pig slurry is quite low (table 2) due to the common practice of flushing out farrowing barns. The VS/TS percentage, on average 63.7% ± 3.5%, is characteristic of slurries subjected to aerobic/anaerobic transformations during storage, while fresh slurries have an average VS/TS percentage of 75% to 78% (*ASAE Standards*, 2005). The same information can be deduced from ammoniac nitrogen expressed as a percentage of total nitrogen: an average of 50% to 55% in fresh slurries, which tends to increase as a result of urease action.

The cattle slurry was taken from a free-stall cubicle dairy cow house equipped with one scraper. The VS/TS percentage is 67.9% ± 2.0% (77% in fresh slurry according to *ASAE Standards*, 2005), and the ammoniac/total nitrogen ratio is 48.4% ± 3.0% (17% in fresh slurries according to *ASAE Standards*, 2005), caused by an absence of straw and a minimum farm tank storage of three months.

We encountered considerable practical difficulties in measuring gases (ammonia, methane, and carbon dioxide) and odor emissions from the surface of the stored slurry, basically caused by container dimensions, load variability, gas diffusion from the internal mass to the surface, and climatic conditions, which can all effect the emissive flux.

Accurate and repeated measurements were carried out using nine stainless steel airtight cylinders with a volume of 190 dm^3 (1.5 m high and 0.4 m diameter), used to simulate the average storage conditions of farm tanks (fig. 1, left).

Nine batch reactors were used for each covering material: three were set up with the lower covering thickness, three with the higher thickness, and the remaining three were set up without any covering, as controls. Each batch reactor was partially filled with about 150 dm^3 of slurry. A special rotational homogenization and distribution system was constructed to ensure that each reactor was filled with the same type of pig slurry. The mixed slurry was fed to the reactors via nine flexible pipes (fig. 1, right). Another special tank was also fitted with a mixing device for similarly preparing cattle slurry, which has a higher density than pig slurry. The mixer was kept switched on during filling operations to ensure that the same type of cattle slurry was delivered to each reactor.

Figure 1. The batch reactors (left) and the rotational homogenization and distribution device (right) used in the pig slurry distribution experiment.

All the covering materials, with the exception of vegetable oil, were conditioned before the trial to accurately reproduce the real conditions of the farm tanks. In fact, covering materials, in real situations, are subjected to a variety of phenomena (water/slurry imbibition and drying, volatile suspended solid and nitrogenous compound enrichment, compacting) that transform the surface layer. Such transformations affect covering permeability and, consequently, gas diffusion into the atmosphere.

To achieve this partial transformation, all the covering materials (with the exception of vegetable oil, which is naturally impermeable and has a lower density than slurry) were placed in steel baskets (the same size as the batch reactor) and immersed in a farm tank for about 30 days with the same slurry used for the trials (fig. 2). The different coverings were then removed and immediately placed on the slurry surface inside the batch reactors. Ammonia, methane, carbon dioxide and odor emissions were measured for every kind of slurry for each variation of the covering system.

Determination of Ammonia, Methane, and Carbon Dioxide Emissions

Each material was tested for a period of one week. Three measurements were taken at three different times during the trial: the day after filling (t_0), and three (t_3) and seven (t_7) days after filling. After sealing the cylinders, the gaseous composition of the headspace was monitored online for each reactor using a Bruel & Kjaer 1302 multi-gas monitor (Innova Air Tech Instruments A/S, Ballerup, Denmark). This device measured any increase in gas concentration due to slurry emission. The sampled air was reintroduced into the headspace after being measured (fig. 3, left).

Gas emissions were measured according to the "chamber method" (Mosier, 1989; IAEA, 1992; Smith and Arah, 1992; Brewer and Costello, 1999; Hornig et al., 1999; Pedersen et al., 2001), which monitors gas accumulation in an enclosed headspace over time using a gas analyzer. A variety of chambers have been designed and labeled as closed, open, mega, and vented (Berges and Crutzen, 1996; Sibbesen and Lind, 1993; Smith et al., 1994; Velthof et al., 1997). These methods have the advantage of being cheap and can detect even very low fluxes, making them most suitable for short-term studies.

Because the cylinder is airtight, gas concentration in the headspace tends to initially increase in a linear manner until it reaches a constant asymptotic value, where the partial

Figure 2. Preparation of the covering material showing the baskets used for confining the layers of floating material on the surface of the lagoon.

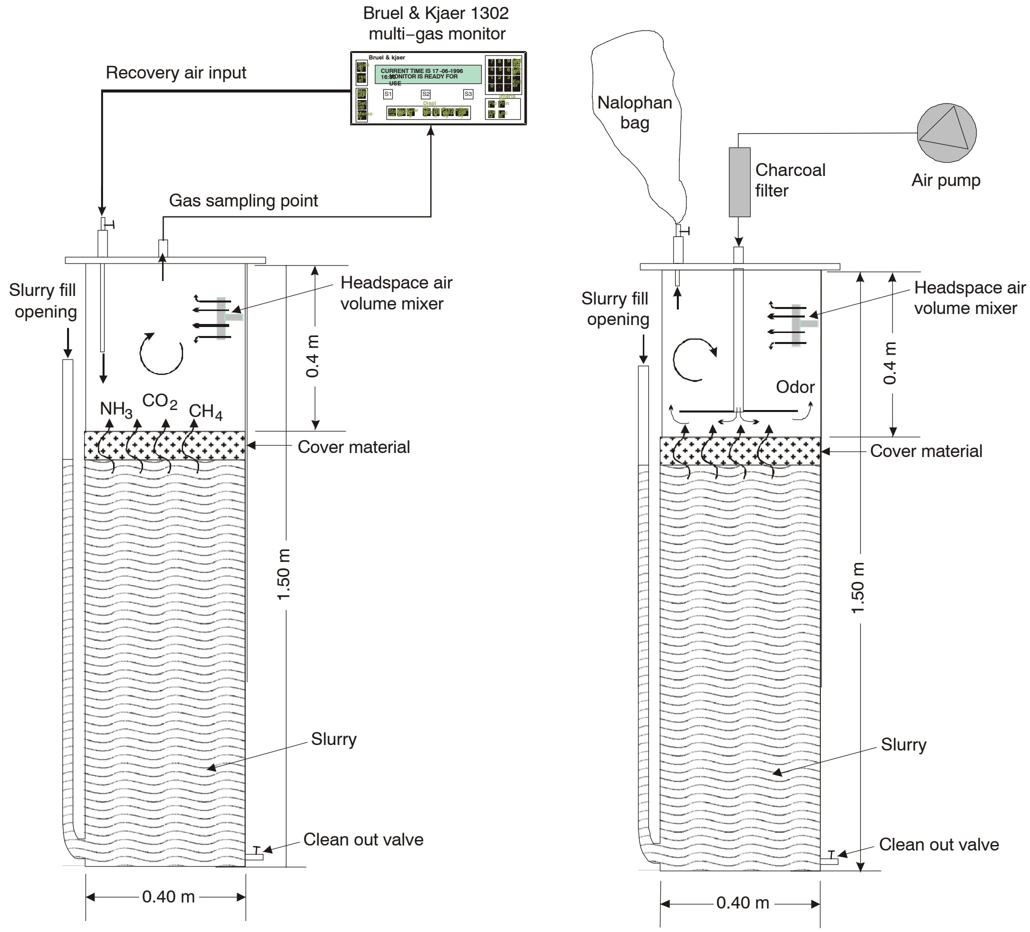

Figure 3. Diagram illustrating the flow of air withdrawn from the headspace of the reactor and conveyed to the Bruel & Kjaer 1302 monitor (left) or to the nalophan bag for olfactometric analysis (right).

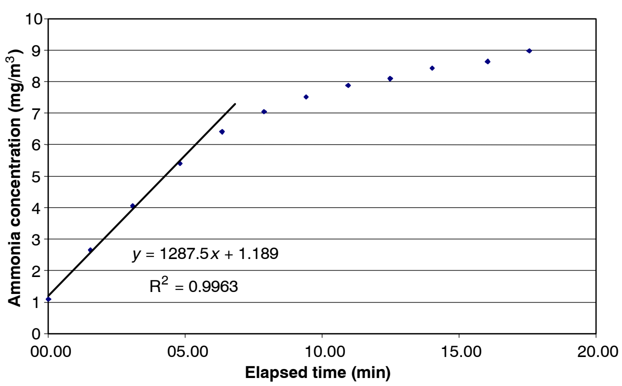

Figure 4. Example of a saturation function with related regression line.

pressure of the gases in the headspace equals the vapor pressure of their dissolved fraction in slurry. Therefore, the angular coefficient of the regression line, calculated in the initial linear part of the gas saturation function (fig. 4), represents slurry emitting potential, as the vapor pressure of the dissolved ammonia is not influenced by its partial pressure in the initial gaseous phase. Consequently, the concentration gradient can be assumed as the emissive flow in calm atmospheric conditions. A fan was used to mix the headspace volume to prevent any errors during sampling. Regression linearity was verified by means of the Fisher test of interference.

To account for the different headspace volumes and to compare the various samples, calculations included:

- The concentration gradient over time of the linear tract of gaseous concentration function (Δ_c / Δ_t).
- The volume of the headspace above the emitting surface (V_{HS}).
- The emitting surface (A).

The emissive flow (E, kg m^{-2} s^{-1}) of the various reactors was accordingly calculated as:

$$E = \frac{(\Delta c \cdot V_{HS})}{(\Delta t \cdot A)} \tag{2}$$

The various covering and control samples were compared by applying Student's t-test to the emissive flow values (E). The typical trend of one monitoring of the headspace saturation function is shown in figure 4. The duration and intensity of the concentration gradient depend on the slurry emissive potential (which is affected by NH_4^+ concentration, pH, volatile and suspended solids), the headspace volume, and the temperature of the two phases (slurry and air). As the latter variable was the same for all repetitions, it was not considered in the calculations.

Determination of Odor Emissions

A sample of air was taken from each reactor at t_7 and submitted for olfactometric analysis (fig. 3, right, for measurement device details) in order to determine the odor

Table 3. Main features (total solids content and density) of pig slurry used for the flotation aptitude testing.

Slurry Features	High (4%) TS Contents				Low (1.5%) TS Contents		
	Bin 1 Expanded Clay	Bin 2 Wood Chips	Bin 3 Wheat Straw	Bin 4 Maize Stalks	Bin 5 Wood Chips	Bin 6 Wheat Straw	Bin 7 Maize Stalks
TS (g kg^{-1} as collected)[a]	45.52	46.69	43.67	37.6	15.41	15.2	14.31
Density (kg m^{-3})[b]	1.023	1.024	1.022	1.020	1.010	1.010	1.009

[a] TS = total solids.
[b] Density calculated according to the following equation: density = (TS + 221.6) / 221 (Piccinini and Bortone, 1991).

abatement efficiency of each tested cover. Each batch reactor was equipped with a pump and a charcoal filter to blow purified air onto the slurry surface using a diffusion disk slightly smaller than the reactor diameter. It was thus possible to simulate wind action on farm tanks. Before sampling, the headspace was fluxed with an airflow of 5 dm^3 min^{-1} to sufficiently change the filtered air. The volume of fluxed air was at least three times higher than that of the headspace. Further purified air was fluxed into the headspace, and thanks to the airtight sealing, any odorous air from the headspace could be collected in nalophan bags (Clanton et al., 2001) and subsequently analyzed using the olfactometer (CEN, 2003), within 24 h of sampling, to determine the odor concentration expressed as odor unit per cubic meter (OU m^{-3}).

Testing of Flotation Aptitude

The flotation aptitude of all the solid covering materials on pig slurry was also tested at two different total solids concentrations (about 14.9 g kg^{-1} and 43.3 g kg^{-1}). Flotation aptitude and resistance to sinking are fundamental for guaranteeing the correct choice of covering and storage lagoon management, as sinking coverings not only affect emission reduction but also increase lagoon deposits, leading to complications during the emptying phase, not to mention higher management costs.

Seven plastic bins (90 cm height and 50 cm diameter) were filled with 60 dm^3 of pig slurry at two different total solids (TS) concentration to test the long-term flotation aptitude of the coverings. Three of the bins were filled with pig slurry at about 1.5% TS concentration, while the remaining four contained pig slurry at about 4% TS concentration (table 3). This trial was aimed at checking the influence of slurry density on covering flotation aptitude. These two TS pig slurry concentrations were chosen as representative of the two main kinds of swine farms: full-cycle farms, where frequent flushing in the farrowing compartment leads to high TS dilutions, and fattening barns, where slurry is usually more concentrated due to its removal by scrapers and vacuum systems.

Such tests were carried out on all the tested materials, with the exception of vegetable oil. The covering flotation aptitude was tested with both the TS concentrations; only the expanded clay was tested with one TS concentration. Photographs of the coverings were taken every 2 to 4 weeks to record the flotation conditions of the materials. These conditions were then related to daily recorded meteorological data (temperature, rainfall, relative humidity).

Results

Evaluation on Ammonia, Methane, and Carbon Dioxide Emission

The slurry temperatures, recorded during the gas emission tests, are reported in table 4. The trials involving pig slurry were carried out in the spring (11.7°C average temperature), while those involving cattle slurry were carried out in the summer (18.5°C average temperature). In some tests, we recorded average temperatures that were significantly different from the seasonal average temperature (e.g., the temperature of 5.2°C during the vegetable oil test with pig slurry). Table 4 also shows the temperature range recorded during the tests. Very high maximum temperatures were recorded in both the summer and winter, which might have affected the results.

All the tested covers for pig slurry showed good ammonia reduction efficiencies (over 75%), with statistically significant values exclusively at greater thickness (9 mm for oil and 140 mm for all the other materials), as shown in table 5. These are comparable to those reported by Hornig et al. (1999), who found reduction efficiencies of 79.9% for chopped straw coverings (5 to 15 cm of depth) and reduction efficiencies of 91% for granules of expanded clay.

Vegetable oil was the most effective material: 100% for the thicker layer (9 mm), and 79% for the thinner layer (3 mm). These high efficiencies are comparable to those found by Portejoie et al. (2003), who reported an ammonia reduction emission of 93% for 10 mm thick oils. This efficacy may be due to the fact that total ammoniac nitrogen is not soluble in oil, which therefore forms an impermeable and continuous barrier on the slurry surface.

The thinner coverings did not show significant emission reduction efficiencies, presumably because they are materials that tend to get easily soaked, thus enhancing the exposure of the ammoniac nitrogen to air. Reference reactors (those set

Table 4. Temperature range during slurry emission tests.

Covering	Temperature of Pig Slurry (°C)			Temperature of Cattle Slurry (°C)		
	Minimum	Maximum	Average[a]	Minimum	Maximum	Average[a]
Maize stalks	10.3	26.2	16.5	15.3	39.3	20.3
Wood chips	NA[b]	NA[b]	9.3	6.7	24.7	19.5
Vegetable oil	4.3	7.5	5.2	11.5	26.5	13.3
Expanded clay	7.8	15.8	12.7	15.0	33.0	21.0
Wheat straw	6.0	27.0	15.0	10.7	28.3	18.2

[a] Average = average temperature during measurements.
[b] NA = not available.

Table 5. Emission and reduction effectiveness of the tested coverings for ammonia, methane, and carbon dioxide emissions from pig slurry.

Covering	Thickness	Temp. (°C)	Ammonia ($mg\ m^{-2}\ s^{-1}$) Average ± SD	Ammonia Reduction[a]	Methane ($mg\ m^{-2}\ s^{-1}$) Average ± SD	Methane Reduction[a]	Carbon Dioxide ($mg\ m^{-2}\ s^{-1}$) Average ± SD	Carbon Dioxide Reduction[a]
Maize stalks	Control	16.5	1.240 ± 0.228		10.96 ± 6.63		60.26 ± 7.76	
	70 mm		1.064 ± 0.528	14.2% (–)	17.55 ± 13.93	NA (–)	61.39 ± 18.61	NA (–)
	140 mm		0.198 ± 0.063	84.0% (**)	11.88 ± 14.88	NA (–)	51.19 ± 7.44	15.0% (–)
Wood chips	Control	9.3	0.430 ± 0.355		1.61 ± 1.20		27.36 ± 6.25	
	70 mm		0.428 ± 0.208	0.5% (–)	1.48 ± 1.23	8.5% (–)	19.80 ± 8.14	27.6% (*)
	140 mm		0.086 ± 0.047	80.0% (**)	1.2 ± 0.85	25.6% (–)	17.12 ± 4.11	37.4% (**)
Vegetable oil	Control	5.2	0.309 ± 0.163		9.04 ± 5.91		--[b]	
	3 mm		0.063 ± 0.079	79.5% (**)	7.91 ± 6.68	12.4% (–)	--[b]	--[b]
	9 mm		0.000 ± 0.000	100% (**)	8.13 ± 4.57	10.0% (–)	--[b]	--[b]
Expanded clay	Control	12.7	0.323 ± 0.117		8.23 ± 7.40		42.17 ± 13.78	
	70 mm		0.269 ± 0.194	16.81% (–)	7.48 ± 4.45	9.0% (–)	33.94 ± 13.10	19.5% (–)
	140 mm		0.080 ± 0.034	75.1% (**)	6.85 ± 4.23	16.8% (–)	27.46 ± 10.76	34.9% (*)
Wheat straw	Control	15.0	0.853 ± 0.476		4.27 ± 3.46		48.17 ± 13.95	
	70 mm		0.561 ± 0.261	34.2% (–)	4.55 ± 1.75	NA (–)	44.89 ± 28.99	6.8% (–)
	140 mm		0.120 ± 0.061	86.0% (**)	3.07 ± 1.01	28.0% (–)	38.66 ± 8.63	19.7% (*)

[a] (–) = not significant, (*) = $P < 0.05$, (**) = $P < 0.01$, and NA = not available (emission rate higher than control).
[b] Not measured.

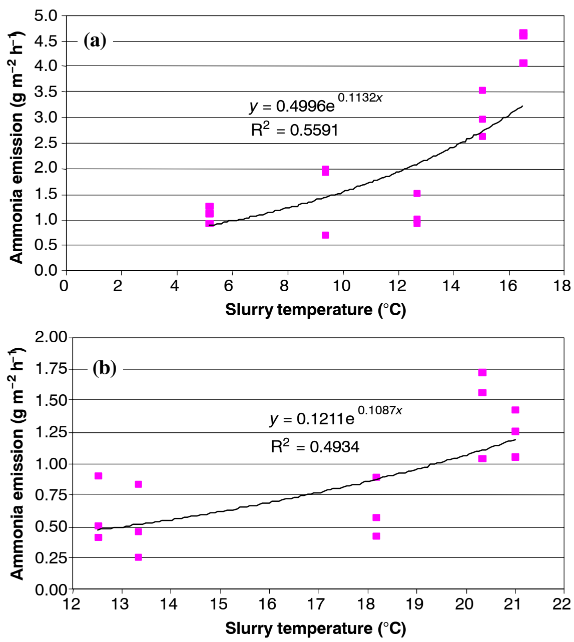

Figure 5. Ammonia emission and slurry temperature correlation in both (a) pig and (b) cattle tests.

up without any covering system on the slurry surface) showed emissions ranging from 1.11 g $m^2\ h^{-1}$ (recorded during the coldest times with the slurry temperature at 5.2°C) to 4.46 g $m^2\ h^{-1}$ (with a slurry temperature of 16.5°C), with average emissions of 2.27 g $m^2\ h^{-1}$. These values can be compared to the results of Sommer (1997), who reported NH_3 volatilization from uncovered slurry ranging from 0.23 to 1.41 g $m^{-2}\ h^{-1}$ in a 5°C to 20°C air temperature range. The total nitrogen concentration and the ammoniac/total nitrogen ratio, as reported by Ni (1999), might also have affected the resulting emission factors.

The higher temperatures recorded in the test carried out on expanded clay (12.7°C) caused emissions to be lower than those measured on wood chips (9.3°C) because of the lower percentage of ammoniac nitrogen in slurry (57.9% vs. 74.4%). Figure 5a shows the relationship between ammonia emission and pig slurry temperature.

Figure 5 illustrates the correlation between ammonia emission and slurry temperature in both pig and cattle tests. According to Ni (1999) and Monteny et al. (1998), the NH_3 release flux is essentially a function of the convective mass transfer coefficient, NH_3 concentration in the gaseous phase at the slurry surface, NH_3 concentration in the free air stream, and slurry and air temperatures.High levels of ammonia emission reduction efficiency were achieved by all the thicker tested coverings for cattle slurry (table 6).

Straw and stalks also proved to be effective in thinner layers, with emission reduction values comparable to those of vegetable oil, while expanded clay particles and wood chips efficiencies were not significantly different from that of the control. The high performance of wheat straw probably derives from the emergence of suspended solids (very common in cattle slurry), which fill in the interspaces of the wattle. The layer is then compacted by a subsequent alternation of wetting and drying processes. The reduction efficiency is higher than that obtained with pig slurry because of the higher suspended solids content of cattle slurry (61.4 g kg^{-1} vs. 23.3 g kg^{-1}). Average ammonia emission in the reference reactors was 0.89 g $m^{-2}\ h^{-1}$, ranging from 0.26 g $m^{-2}\ h^{-1}$ (with a slurry temperature of 13.3°C) to 1.72 kg $m^{-2}\ h^{-1}$ (carried out in warmer temperatures of 20°C to 21°C). The relation between ammonia emission and cattle slurry temperature is shown in figure 5b.

Differences in ammonia emissions from cattle and pig slurry can be ascribed to variations in the ammoniac/total nitrogen ratio, which is, on average, 67.8% for pig slurry and 48% for cattle slurry. In comparing the regression functions given in figure 5, we note that at a temperature of 15°C, ammonia emission from cattle slurry is 0.61 g $m^{-2}\ h^{-1}$, while that from pig slurry is 2.72 g $m^{-2}\ h^{-1}$. Furthermore, NH_3 emission in both slurries is closely related to CO_2 emission. A reduction in CO_2 emission causes the surface pH to drop and this in turn causes a drop in NH_3 emission (Xue et al., 1999; Monteny et al., 1998).

No statistically significant reductions in methane emission from pig slurry were found for any of the tested materials

Table 6. Emission and reduction effectiveness of the tested coverings on ammonia, methane and carbon dioxide emissions from cattle slurry.

Covering	Thickness	Temp. (°C)	Ammonia ($mg\ m^{-2}\ s^{-1}$) Average ± SD	Ammonia Reduction[a]	Methane ($mg\ m^{-2}\ s^{-1}$) Average ± SD	Methane Reduction[a]	Carbon Dioxide ($mg\ m^{-2}\ s^{-1}$) Average ± SD	Carbon Dioxide Reduction[a]
Maize stalks	Control	20.3	0.400 ± 0.235		12.76 ± 5.80		92.2 ± 21.2	
	70 mm		0.253 ± 0.126	36.7% (*)	19.47 ± 6.54	NA (*)	204.9 ± 57.2	NA (**)
	140 mm		0.159 ± 0.163	60.4% (**)	16.77 ± 3.44	NA (*)	175.5 ± 48.2	NA (**)
Wood chips	Control	19.5	0.170 ± 0.111		8.88 ± 2.59		57.0 ± 14.2	
	70 mm		0.142 ± 0.074	16.6% (–)	8.75 ± 3.11	1.4% (–)	52.3 ± 9.9	8.2% (–)
	140 mm		0.015 ± 0.012	90.9% (**)	6.07 ± 2.16	31.7% (*)	45.1 ± 14.5	20.7% (–)
Vegetable oil	Control	13.3	0.144 ± 0.074		5.01 ± 2.68		39.2 ± 9.8	
	3 mm		0.045 ± 0.05	68.5% (**)	3.30 ± 2.12	34.0% (–)	30.9 ± 5.5	21.0% (*)
	9 mm		0.013 ± 0.02	91.2% (**)	2.86 ± 3.06	42.9% (–)	26.1 ± 5.5	33.5% (**)
Expanded clay	Control	21.0	0.345 ± 0.107		16.91 ± 2.15		74.0 ± 8.6	
	70 mm		0.339 ± 0.145	1.9% (–)	15.97 ± 3.12	5.5% (–)	74.5 ± 8.8	NA (–)
	140 mm		0.125 ± 0.077	63.9% (**)	14.18 ± 0.59	16.1% (**)	73.3 ± 15.3	0.9% (–)
Wheat straw	Control	18.2	0.175 ± 0.065		5.88 ± 2.84		59.2 ± 17.1	
	70 mm		0.072 ± 0.011	58.6% (**)	8.03 ± 2.18	NA (*)	66.3 ± 26.9	NA (–)
	140 mm		0.000 ± 0.000	100% (**)	6.07 ± 1.77	NA (–)	56.9 ± 15.8	3.9% (–)

[a] (–) = not significant, (*) = P < 0.05, (**) = P < 0.01, and NA = not available (emission rate higher than control).

(table 5), but significant carbon dioxide emission reductions were detected in the thicker layers of wood chips ($P < 0.01$), expanded clay granules and wheat straw (both with $P < 0.05$), while significant emission reductions were obtained in thinner layers of expanded clay granules ($P < 0.05$). Average methane emission was 24.55 $g\ m^{-2}\ h^{-1}$, while carbon dioxide emission was 156.6 $g\ m^{-2}\ h^{-1}$, signifying prevailing aerobic micro-organism action. The only significant reduction (31.7%, $P < 0.01$) was recorded for the 140 mm thickness of wood chips (table 6). Similar results were recorded for cattle slurry: 35.6 $g\ m^{-2}\ h^{-1}$ for methane emission, and 231.5 $g\ m^{-2}\ h^{-1}$ for carbon dioxide emission.

The lower efficiency of the tested covers in containing methane emissions is probably due to the gas's very low solubility. Methane forms bubbles in the bottom layers where the organic degradation is more intense. These bubbles tend to aggregate and then suddenly rise, breaking the surface crust or the covers (even vegetable oil covers). The emission reduction induced by thicker coverings suggests that they act as a physical barrier on the manure surface. Good correlation was also found between methane and carbon dioxide emission for pig slurry (fig. 6) and cattle slurry (fig. 7). Emission intensity is strictly dependent on slurry temperature and volatile solids concentration.

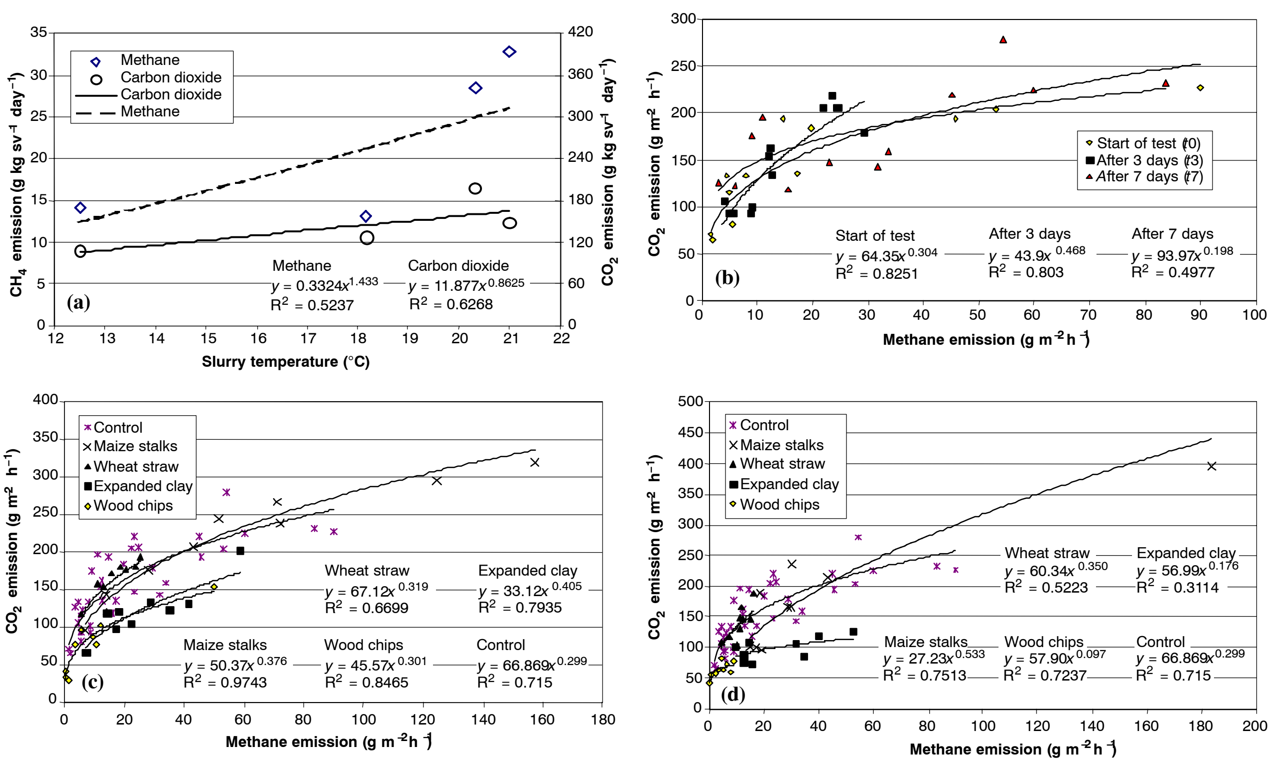

Figure 6. Methane and carbon dioxide correlation in pig slurry tests: (a) at different slurry temperatures, (b) at different times, (c) with covering at 70 mm thickness, and (d) and with covering at 140 mm thickness.

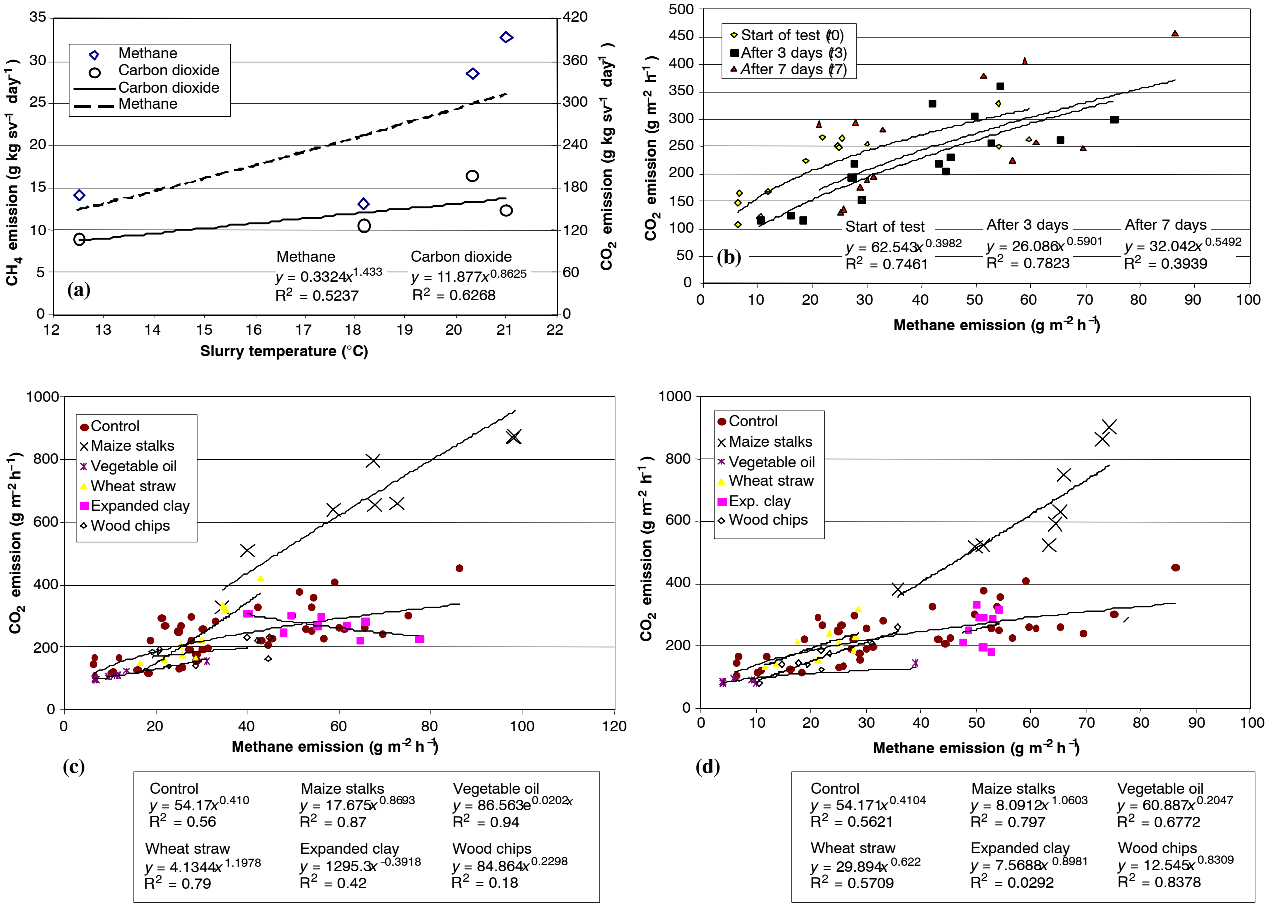

Figure 7. Methane and carbon dioxide correlation in cattle slurry tests: (a) at different slurry temperatures, (b) at different times, (c) with covering at 70 mm (3 mm for vegetable oil) thickness, and (d) with coverings at 140 mm (9 mm for vegetable oil) thickness.

Odor Reduction Efficiency of the Tested Covers

All the materials proved highly effective in reducing odors from pig slurry when used at the greater thickness (table 7), with maize stalks reducing odor by up to 90%. All the materials, except wheat straw, also proved effective in reducing odor at the lower thickness. The atypical value for wheat straw was probably caused by anomalies during the test on pig slurry, which can be shown by the good performance of straw in the case of cattle slurry (table 7). Odor emission from slurry is strongly influenced by ammonia and hydrogen sulfide (Xue et al., 1998). Xue et al. (1999) also reported that covers on slurry can lead to a decrease in the hydrogen sulfide mass transfer coefficient, while CO_2 emission reduction results in a decrease of slurry pH (tables 4 and 5).

Table 7. Emission of odor and reduction effectiveness of the tested coverings on pig and cattle slurry. Odor concentration results are expressed as average ± standard deviation.

		Pig Slurry			Cattle Slurry		
Covering	Thickness	Temp. (°C)	Odor Concentration (OU_E m^{-3})	Reduction[a]	Temp. (°C)	Odor Concentration (OU_E m^{-3})	Reduction[a]
Maize stalks	Control		1500 ± 317			276 ± 39	
	70 mm	16.5	406 ± 58	73% (*)	20.3	84 ± 34	70% (**)
	140 mm		156 ± 86	90% (**)		45 ± 3	84% (**)
Wood chips	Control		769 ± 161			487 ± 95	
	70 mm	9.3	542 ± 95	30% (–)	19.5	456 ± 159	6% (–)
	140 mm		346 ± 137	55% (*)		411 ± 146	15% (–)
Vegetable oil	Control		1265 ± 56			2342 ± 728	
	3 mm	5.2	626 ± 205	51% (*)	13.3	1046 ± 423	55% (*)
	9 mm		610 ± 307	52% (*)		1061 ± 405	55% (*)
Expanded clay	Control		791 ± 245			2189 ± 924	
	70 mm	12.7	201 ± 82	75% (*)	21.0	349 ± 111	84% (*)
	140 mm		247 ± 255	69% (*)		238 ± 29	89% (*)
Wheat straw	Control		757 ± 261			624 ± 207	
	70 mm	15.0	755 ± 320	0% (–)	18.2	217 ± 82	65% (*)
	140 mm		297 ± 134	61% (*)		108 ± 19	83% (*)

[a] (–) = not significant, (*) = P < 0.05, and (**) = P < 0.01.

Table 8. Climatic condition and other parameters recorded during the flotation aptitude trial.

Time from Beginning of Trial (days)	Time between Two Measurements (days)	Air Temperature (°C)		Relative Humidity (%)		Rainfall (mm)	
		Total[a]	Partial[b]	Total[a]	Partial[b]	Total[a]	Partial[b]
0	––	6.1	6.1	83	83	0	0.0
11	11	8.0	8.0	81	81	0	0.0
18	9	8.6	10.0	81	81	7	7.8
55	38	9.9	10.8	78	77	66	58.2
59	5	10.4	15.6	79	82	75.4	9.4
73	15	11.2	14.7	79	79	86.4	11.2
98	26	12.6	17.9	80	85	158	71.6
108	11	13.2	19.7	81	85	174.8	16.8
115	8	13.9	23.5	81	82	174.8	0.0
154	40	16.1	24.2	85	85	267.8	93.0
187	34	17.1	22.8	82	84	376.3	109.5
203	17	17.3	20.7	82	84	438.5	84.6
216	14	17.2	17.0	82	80	438.9	0.4

[a] From the beginning of the trial.
[b] Between two consecutive measurements.

Testing of Flotation Aptitude

The relevant features of the pig slurry used in this test are given in table 3, while table 8 givesthe time elapsed from the beginning of the trial, the time lap between two consecutive measurements, and the temperature, relative humidity, and rainfall values calculated with reference both to the total time and time elapsed between two consecutive measurements.

The following flotation behavior was observed for the materials under consideration:

- Expanded clay (fig. 8) distributed on slurry kept the surface dry. It did not show any sinking aptitude or physical alteration over time. All the same, other authors (MAFF, 2000) noted an increase in the slurry depth inside the bin with an increase in rainfall. This occurred because expanded clay prevents rainwater from evaporating, thus leading to accumulation in the bin.
- Wood chips (fig. 9) maintained a good flotation aptitude throughout the trial. Even better results could be achieved when woods chips are applied to slurry with a higher total solids concentration.
- Wheat straw and maize stalks (fig. 10), both throughout the experiment and according to other authors (MAFF, 2000), maintained a good flotation aptitude when placed on slurry with 4% total solids during the first three months of the test. They then completely sank as a result of a significant increase in rainfall. The same materials also sank and mixed with the solid fraction when placed on slurry with 2% total solids; this had no connection with rainfall. Only straw fragments remained around the rim of the bin, probably due to friction and cohesion forces between the straw fragments and the bin wall.

Figure 8. Pictures of the expanded clay granules taken at different times during the flotation tests on pig slurry.

Figure 9. Pictures of the wood chips taken at different times during the flotation tests on pig slurry.

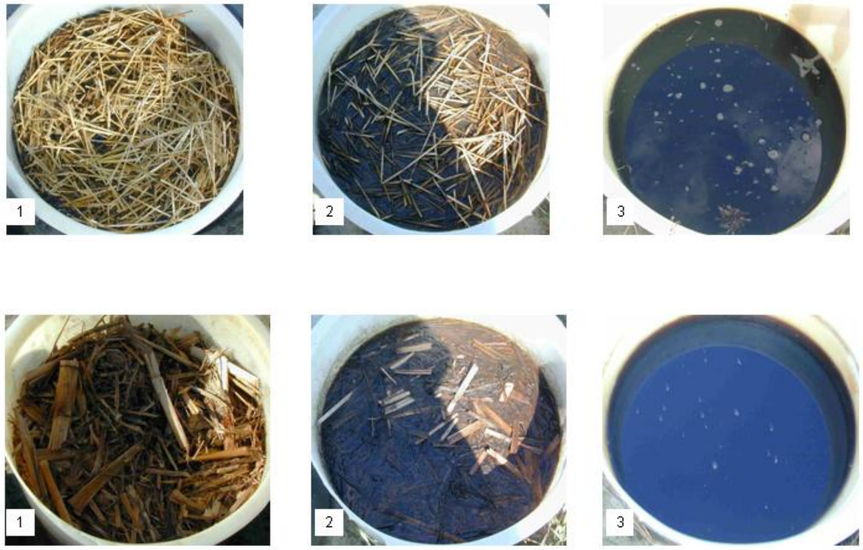

Figure 10. Pictures of the wheat straw (top) and of chopped maize stalks (bottom) taken at different times during the flotation tests on pig slurry.

Conclusions

Simplified covers offer an alternative to costly and complex rigid covers and are a practicable and effective solution for reducing ammonia and odor emissions from livestock slurry storages. The best results were achieved using thicker layers of material (140 mm for solid coverings and 9 mm for liquid coverings). Some of these materials (namely expanded clay and wood chips) also showed a good aptitude for long-term resistance to deterioration and sinking. Covering affects both ammonia and carbon dioxide gaseous exchange with free air because it modifies the slurry surface pH and acts as a physical barrier. There was a wide range of ammonia emission reductions. The best results were achieved with vegetable oil (79.5% to 100%). Thinner layers of expanded clay granules and wood chips were not efficient (70 mm). Similar results were obtained for both pig and cattle slurry. Odor emission was also significantly reduced. Only the thinner layers of wood chips on cattle slurry and wheat straw on pig slurry were ineffective.

Despite these rather encouraging results, there are some management aspects that still need to be thoroughly analyzed, such as slurry pumping and cover handling to prevent mixing cover material with the slurry, possible settling of cover material on the bottom of the storage tank, degradation of the cover caused by contact with the slurry, wind drifting, the arrangement of the cover on the surface, and possible recovery prior to seasonal emptying. Equally valid results could not be achieved with reference to methane emission reduction. At the moment, the most feasible control of methane emission is obtained by capturing it as biogas and using it as a renewable energy source.

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