Photocatalytic TiO₂ coating-to reduce ammonia and greenhouse gases concentration and emission from animal husbandries

Marcella Guarino *, Annamaria Costa, Marco Porro

Department of Veterinary and Technological Sciences for Food Safety, Faculty of Veterinary Medicine, via Celoria 10, Università Degli Studi, 20133 Milan, Italy

Received 29 September 2006; received in revised form 5 April 2007; accepted 11 April 2007

Abstract

Animal production is a main source of NH₃ emission into the environment and a significant producer of other polluting gases. Most of the best available techniques (BAT) that could be used today are not very widely applied in the field because of costs, especially in existing livestock buildings. Industrial applications show that TiO₂ catalytic paint can be used to transform NH₃ into N₂, N₂O or NO and water. Field experiments aimed at determining effects on indoor air quality and NH₃ and polluting gas emissions into the environment of coating pig house walls with TiO₂ catalytic paint and to assess the potential efficiency of this simple painting technique as a low cost BAT technique for animal farmers.

The trial was performed in two identical mechanical ventilated farrowing rooms in a swine farm in Northern Italy. Environmental parameters, ventilation rate and gas concentrations were continuously monitored in the two units throughout a 28 day production cycle. NH₃, N₂O, CO₂, CH₄ average concentrations of 5.41, 1.18, 6.28 and 2109.38 mg m⁻³ (reference unit without treatment) and 3.76, 1.13, 5.32 and 1881.64 mg m⁻³ (experimental unit) were, respectively, recorded during a full farrowing cycle. Pollutant emissions, expressed on a Livestock Unit (LU, i.e., 500 kg live weight) basis, were 16.33, 3.57, 18.96 and 6365.01 kg y⁻¹ LU⁻¹ (reference unit) and 11.37, 3.43, 16.11 and 5695.58 kg y⁻¹ LU⁻¹ (experimental unit), respectively. Significantly higher pollutant concentrations and emissions were found in the untreated reference unit, under similar environmental conditions and with identical numbers of sows and piglets per unit.

Keywords: TiO₂; Piggery; Ammonia; Emissions; BAT solution

1. Introduction

The EU 96/61/EC Directive, also known as IPPC (Integrated Prevention Pollution Control, 1994), adopted by Italy (Decree no. 372 of 04/09/99) for existing installations including intensive animal housings, aims at regulating all forms of emission into the atmosphere, water and soil, and obliges producers to declare the final destination of any waste.

The directive is based on the concept of best available technique (BAT) according to which farmers choose and adopt market technologies which not only prevent or limit emissions but are also sustainable and economically affordable.

More than 90% of ammonia emissions into the environment originate from agriculture (Buijsman et al., 1987) and about 97% of agricultural emissions originate from livestock and related activities. Fifty percent of these livestock emissions are discharged from livestock houses and manure storage (Leneman et al., 1998; Wathes et al., 1997).

A lot of air quality studies have shown that the gases released from swine manure are likely to lower the quality of indoor air with consequent decreases in swine performance and environmental air quality (Osada et al., 1998).

Titanium dioxide (TiO₂) is used in industrial applications to abate pollutant emission into the atmosphere.
Widespread research has been made into the photo catalytic properties of TiO₂ because of its potential use in sterilisation, sanitation, and anti-pollution applications.

Researchers have shown that photo catalytic oxidation can be used to break down and destroy many types of inorganic and organic pollutants in both the environment (Li et al., 2004) and aqueous solutions (Wold, 1993). Ammonia, in particular, is degraded by TiO₂ in water solutions (Murgia et al., 2005) and in the atmosphere (Levine and Calvert, 1977; Il’Chenko and Golodets, 1975) leading to the production of N₂, or N₂O or NO and water along one of the three following main paths (Il’Chenko and Golodets, 1975):

1. 2NH₃ + 1.5O₂ = N₂ + 3H₂O
2. 2NH₃ + 2O₂ = N₂O + 3H₂O
3. 2NH₃ + 2.5O₂ = 2NO + 3H₂O

In a more recent experimental study, Lee et al. (2002) report that the photo catalytic oxidation of NH₃ to NOₓ/NO is the only pathway for NH₃ decomposition on naked TiO₂.

TiO₂ is used to produce self-cleaning ceramic tiles for hospitals, public restrooms and other settings where cleanliness is vitally important (Malloy, 1999; Watanabe et al., 1995). It destroys bacteria and viruses (Maness et al., 1999) purifies water and air (Bahnemann and Cassano, 2002) and also removes ethylene from air in fruit, vegetable, and cut flower storage areas to prevent deterioration and increase product shelf life.

Several field experiments in urban areas have demonstrated the capacity of TiO₂ compounds to reduce nitrous oxides (NOₓ) produced by vehicle emission (Allen et al., 2005).

In air treatments or application, TiO₂ must be placed on a surface so that the gas can pass over it and react. UV light is usually shone on some sort of matrix with a high surface area.

According to literature, when a TiO₂ treated surface is irradiated with UV light, then oxygen is created which oxidizes the NOₓ in air into nitric acid ions (Allen et al., 2005). These ions can then be washed away by rainfall or neutralised by the alkaline composition of concrete.

Many studies have been published on the use of TiO₂ as a photo catalyst. Photo catalysis is basically defined as an accelerated photoreaction produced by a catalyst. In catalysis, a catalytic entity participates to accelerate the chemical transformation of a substrate, without, however, undergoing any transformation itself. Photo catalysis does not lead to energy storage; it merely speeds up a slow event undergoing any transformation itself. Photo catalysis does not lead to energy storage; it merely speeds up a slow event via a photon-assisted process.

The reaction starts with the exposure of TiO₂ to sunlight; TiO₂ absorbs sunlight to generate two types of carriers; electrons (e⁻) and holes (h⁺). One of the notable characteristics of TiO₂ is that the oxidizing power of holes is greater than the reducing power of the excited electrons (Fujishima et al., 1999).

Due to the wide range of applications and the expectations in many fields, this study was aimed at measuring the effects of TiO₂ catalytic painted walls on air quality inside swine houses, on emissions of NH₃ and greenhouse gases into the environment, and on assessing its potential as a simple, low cost BAT procedure for livestock houses.

For this preliminary study conducted to test the TiO₂ effects on pollutants in piggeries, the farrowing room was chosen for its characteristics of highly controlled microclimate conditions, mainly due to the mechanically controlled incoming airflow.

2. Methods

2.1. Experimental facility

The experimental field test was conducted in two identical farrowing rooms (one control and one treated) of a swine farm located 25 km West of Milan, in Northern Italy. The ground surface of both rooms measured 10.95 × 17.30 m, the height was 2.40 m. The rooms, identical for structure and management (see Fig. 1), were mechanically ventilated: air entered the room from the roof through a perforated ceiling made of a PVC sheet. The incoming air was provided by a tunnel under the building corridor such that the fresh and clean air was spread first in the corridor and then entered the room (see Fig. 1). The 6 windows (100 × 80 cm wide), placed on the external wall in both rooms, are always hermetically closed to avoid direct air changes with the external environment.

The selected piggery had a ventilation control system (FANCOM) based on a free running impeller type Fancom FMS with a 70 cm diameter for continuous, real-time monitoring of the ventilation rate. In each farrowing room there were 2 chimneys, the first chimney had a maximum ventilation rate of 7666 m³ h⁻¹ and the second one a maximum ventilation rate of 7566 m³ h⁻¹.

The measurement error varied between + and – 45 m³ h⁻¹ (Berckmans et al., 1991). This type of ventilation sensor has an accuracy of 3% between 200 and 20,000 m³ h⁻¹ and a pressure difference of 0–120 Pa.

Indoor and outdoor temperatures were also monitored every 15 min by the same climate control system.

Thirty sows were housed from 3 to 5 days before farrowing to 21 days after delivery. Each sow was assigned 10 piglets after parturition. All the sows of the farm were administered the same liquid feed three times a day (at 9.00, 15.00 and at 21.00). Diet formulation is reported in Table 1, the feed was mixed with water according the ratio 1:3.

Measurements were taken in the two rooms for 27 days, i.e., for the complete farm farrowing cycle. That is from when the sow entered the room 1 week before delivering to when the piglets were 21 days old.
2.2. Gas measurement

NH₃, CH₄, CO₂, and N₂O concentrations were continuously measured in the exhaust ducts (see Fig. 1) using an infrared photoacoustic detector IPD (Bruel and Kjaer, Multi-gas Monitor Type 1302, Multipoint Sampler and Doser Type 1303) collecting data every 15 min, for the two rooms during the 27 days of experiment.

2.3. Treated room

One room was used as a control room while the other room was treated with TiO₂ to test the effect. A transparent and odourless TiO₂ liquid solution was sprinkled on the inside walls (see Fig. 1) of the treated room. A coating amount of 70 g m⁻² was used for a total surface of 150 m².

The liquid solution, Activa – PPS® (Proactive Photocatalytic System Technology) is produced by Global Engineering S.p.A (via Camperio, 9, Milano). In the Safety Data Sheet (S5-300B, October 13, 2003) available from the producer it is reported that this product has no negative effects on animal and operator health. Twelve solar spectrum lamps (36 W, 230 V, 50 Hz, G13, Poker by Plexiform, Italy; 122 cm long) were installed to simulate sunlight radiation in the room in two rows transversely positioned to the inspection corridor.

The lamps were placed 2 m above the floor. They emitted UV-A radiation within a range of 315–400 nm with a power consumption of 36 W per lamp.

Table 1
Formulation of sows diet

<table>
<thead>
<tr>
<th>DIET</th>
<th>% of total diet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>75.00</td>
</tr>
<tr>
<td>Wheat mill</td>
<td>5.63</td>
</tr>
<tr>
<td>Wheat flour middlings</td>
<td>3.25</td>
</tr>
<tr>
<td>Peas meal</td>
<td>3.00</td>
</tr>
<tr>
<td>Soybean meal</td>
<td>2.65</td>
</tr>
<tr>
<td>Wheat bran</td>
<td>2.50</td>
</tr>
<tr>
<td>Beet pulp meal</td>
<td>1.75</td>
</tr>
<tr>
<td>Rice flour milling</td>
<td>1.25</td>
</tr>
<tr>
<td>Corn meal</td>
<td>1.14</td>
</tr>
<tr>
<td>Linseed</td>
<td>0.75</td>
</tr>
<tr>
<td>Animal fat</td>
<td>0.75</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>0.38</td>
</tr>
<tr>
<td>Soybean oil</td>
<td>0.38</td>
</tr>
<tr>
<td>Fish meal</td>
<td>0.30</td>
</tr>
<tr>
<td>Salts, aminoacids etc.</td>
<td>1.27</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>
A lighting regime with darkness versus lightness period (Wood lamps were continuously switched on, night and day except for the 16th, the 17th, the 23rd and the 24th days of the cycle) was chosen to test the effect of these lamps.

2.4. Statistical analysis

Variance analysis (ANOVA) was performed on the collected data using SAS statistical package (2004) to investigate the effects of environmental parameters and TiO$_2$ coating on indoor pollutant concentrations and emissions from the piggy.

Data were also subjected to correlation analysis using the correlation procedure (Pearson) of SAS, to estimate the relationship between TiO$_2$ treatment and ammonia and greenhouse gases concentration.

3. Results and discussion

3.1. Environmental parameters

The measured environmental conditions in the pig units are shown in Table 2. The experimental conditions, average, minimal and maximal values and the standard deviations can be considered identical in both test rooms, except for a small difference of 1.6 °C in room temperature at the beginning of the cycle, when sows were lodged in the cages of the room. This difference in temperature disappeared after 7 h. In Fig. 2, the ventilation rate for the two rooms during the experimental period is reported.

Variance analysis supports this statement, showing that environmental parameters, with no significant difference between the two rooms, had no effect on pollutants concentrations, whilst coating reduced them significantly.

Since the experimental units were farrowing rooms, the environmental temperature was quite high at the beginning of the cycle (28.90 °C and 27.30 °C) with a more or less linear decrease to 19.50 °C and 18.90 °C at the cycle end.

The chosen set-point of the internal temperature in all farm rooms is automatically controlled by the Fancom FMS type controller by using the ventilation rate throughout the compartments.

3.2. NH$_3$ concentration and emission

Fig. 3 shows the mean indoor concentration of ammonia in the two rooms.

The mean NH$_3$ concentration of the reference unit is significantly higher than that of the experimental unit ($P < 0.001$, see Fig. 3) throughout the 24 h of the day. Indoor ammonia concentration reaches a peak at 8.00 AM (5.95 mg m$^{-3}$ and 4.15 mg m$^{-3}$) coinciding with the first farm inspections by operators and the lowest values were recorded at 7.00 PM (4.87 mg m$^{-3}$ and 3.72 mg m$^{-3}$), when lights were switched off and the animals were observed to be resting or generally inactive.

The average difference of ammonia concentration between the two experimental units is 1.65 mg m$^{-3}$, it means that ammonia is reduced by the treatment for the 30.50%, keeping ammonia concentration measured in the reference room as basis.

<table>
<thead>
<tr>
<th>Items</th>
<th>Reference room</th>
<th>Treated room</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average external temperature</td>
<td>14.81</td>
<td>14.81</td>
</tr>
<tr>
<td>(°C)</td>
<td>(6.30–23.80; ±3.60)</td>
<td></td>
</tr>
<tr>
<td>Average internal temperature</td>
<td>24.70</td>
<td>24.30</td>
</tr>
<tr>
<td>(°C)</td>
<td>(19.50–28.90 ± 1.93)</td>
<td>(18.90–27.30; ±1.52)</td>
</tr>
<tr>
<td>Minimum internal temperature</td>
<td>28.90</td>
<td>27.30</td>
</tr>
<tr>
<td>(°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum internal temperature</td>
<td>19.50</td>
<td>18.90</td>
</tr>
<tr>
<td>at beginning (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Internal relative humidity (%)</td>
<td>54.50</td>
<td>53.60</td>
</tr>
<tr>
<td>Average ventilation rate (m$^3$ h$^{-1}$±SD)</td>
<td>4478 ± 1193.74</td>
<td>4492 ± 974.47</td>
</tr>
<tr>
<td>Average ventilation rate</td>
<td>778</td>
<td>780</td>
</tr>
<tr>
<td>at beginning of the cycle (m$^3$ h$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average ventilation rate at the</td>
<td>6846</td>
<td>6690</td>
</tr>
<tr>
<td>end of the cycle (m$^3$ h$^{-1}$)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
NH$_3$ concentration did not increase in either room with piglet growth throughout the trial period as, even though manure depth increased, the surface area remained unaltered (Ni et al., 1999b) and the dunging area for growing piglets consisted of a totally slatted PVC floor which promotes fast manure discharge into the pit.

Animal total weight gain, including the sow’s weight loss after parturition is estimated to be 1200 kg in 27 d, starting from a 6000 kg of live weight and reaching 7200 kg at the end of the cycle.

The lack in NH$_3$ concentration increase according to live weight increase (Ni et al., 1999b) is strictly connected to the higher ventilation rate (see Table 2) set up in the ventilation controlling system, to lower environmental temperature in accordance with the growing animal physiological needs.

NH$_3$ emissions were calculated by multiplying the values of indoor NH$_3$ concentration measured in the exhaust by the monitored ventilation rate measured both every 15 min.

Daily NH$_3$ emission values were calculated to be 581.5 g d$^{-1}$ from the reference unit and 404.9 g d$^{-1}$ for the experimental unit. By considering the live weight of the pigs with the corresponding NH$_3$ emissions, ammonia emission values can be expressed as 16.3 kg y$^{-1}$ LU$^{-1}$ (LU = Livestock Unit, i.e., 500 kg live weight) for the control room and 11.4 y$^{-1}$ LU$^{-1}$ for the treated room. The latter values must be adjusted for the effective occupation time of the room by sows in the farrowing room, subtracting the amount of days dedicated to bio security procedures of all in – all out for washing, disinfecting, etc. In this way, it was calculated that sows are lodged in the room for 64% of the year, giving effective values of 10.49 kg y$^{-1}$ LU$^{-1}$ for the reference unit and 7.31 for the experimental unit.

According to the review by Hartung and Phillips (1994), the ammonia emission from pigs was calculated to be between 17.5 and 39.4 kg y$^{-1}$ LU$^{-1}$, values lightly higher than those obtained in this study.

The difference in ammonia concentration between the two rooms, under similar environmental conditions and with a parity of lodged animals must be explained by the photo catalytic oxidation of NH$_3$ to NO$_2$/NO$_3$ (Lee et al., 2002), ions which is then neutralised by the alkaline composition of the concrete walls and, combined with water, removed with manure into the pit at the end of the production cycle.

Seeing that the total amount of ammonia emitted by sows in Italy is estimated to be 24,298 ton y$^{-1}$ (LG MTD Allevamenti, 2004), the application of this treatment could reduce it by 30.5%, with a reduction of ammonia of 7411 ton y$^{-1}$.

3.3. CO$_2$ concentration and emission

Fig. 4 shows the mean indoor daily CO$_2$ concentration for each unit during the 27 days experiment.

The average values of CO$_2$ concentrations were significantly lower in the experimental unit (1881.6 mg m$^{-3}$) than in the reference room, 2109.4 mg m$^{-3}$ for ($P < 0.001$, see Table 3).

We cannot, however, find a reason for the low pollutant values in the TiO$_2$ treated room, but it would be possible that CO$_2$, could react with water or air humidity, as normally happens, giving the final products of H$_3$O$^+$ and HCO$_3^-$ (Pietta, 1987).

The CO$_2$ pattern is characterised by 10 h phases with positive peaks of concentration values at 9.00 AM (2470.7 mg m$^{-3}$ for the reference room and 2120.3 mg m$^{-3}$ for the experimental room), corresponding with observed increased animal activity at feeding times (9.00, 15.00, 21.00), operator and veterinary inspections by Van Ouwerkerk and Pedersen (1994). Minimum values were registered at 6.00 PM, for the reference room, (1857.2 mg m$^{-3}$) and at 4 PM for the experimental room (1685.3 mg m$^{-3}$) in coincidence with the start in decreasing daily temperature which occurred at 4.00 PM every day of the production cycle and with decreasing animal activity (Van Ouwerkerk and Pedersen, 1994). In fact CO$_2$ concentrations increase with higher respiration rate of active animals in daytime and Ni et al. (1999a) showed that carbon dioxide concentration increase with increasing activity of the pigs.

CO$_2$ and total quantity of emissions throughout the 27 days experiment were 6365.0 kg y$^{-1}$ LU$^{-1}$ and 5695.6 kg y$^{-1}$ LU$^{-1}$, respectively, for reference and experimental room.
The CO\textsubscript{2} emission results are similar to those reported by Thorbek (1969), who recorded CO\textsubscript{2} levels, released by growing pigs under ordinary feeding conditions, of 1.0 kg d\textsuperscript{-1} at 30 kg of live weight and 2.0 kg d\textsuperscript{-1} at 85 kg of live weight.

The gas emission value observed at the peak hours was 25\% more than that observed around 6:00 PM, coinciding with the rest period after afternoon feeding. Van Ouwerkerk and Pedersen (1994) also reported a similar fluctuation of CO\textsubscript{2}. It is clear that this increased production derives from the higher respiration rate of active animals in daytime. Moreover, this phenomenon might be related to pig excretion (Osada et al., 1998). The pigs were fed at 10:00–11:00 AM daily, and according to observations, most of the animals excreted after 1 or 2 h. Pigs also discharged some gas with faeces at the time of excretion.

Considering that the piggery of this study had 7 farrowing rooms, the carbon dioxide emitted by sows could be reduced by 180 ton y\textsuperscript{-1} just on this farm alone; the pollutant reduction efficiency by TiO\textsubscript{2} coating takes on more importance at a National level, with an estimate CO\textsubscript{2} reduction of 240,000 ton y\textsuperscript{-1} calculated on 713,000 sows currently present in Italy.

### 3.4. N\textsubscript{2}O concentration and emission

N\textsubscript{2}O concentration was significantly higher from the reference unit than from the experimental treatment unit ($P < 0.05$, Fig. 5); the respective average values were 1.18 mg m\textsuperscript{-3} and 1.13 mg m\textsuperscript{-3}. The calculated N\textsubscript{2}O emissions values were 3.57 kg y\textsuperscript{-1} LU\textsuperscript{-1} for the reference unit and 3.43 kg y\textsuperscript{-1} LU\textsuperscript{-1} for experimental unit.

Generally speaking, N\textsubscript{2}O is generated by the denitrification process which requires oxidised nitrogen (NO\textsubscript{x}) and a sufficient amount of denitrifier. As slurry has an extremely low NO\textsubscript{x} content, it requires previous nitrification by a nitrifier. The growth rates of both micro organisms are relatively slow (Bitton, 1994). Murakami et al. (1987) reported the same phenomenon with cultivated soil.

![Fig. 4. Mean hourly indoor concentration of CO\textsubscript{2} in the two rooms during the 27 days experiment (mg m\textsuperscript{-3}).](image1.png)

![Fig. 5. Mean hourly indoor concentration of N\textsubscript{2}O in the two rooms during the 27 days experiment (mg m\textsuperscript{-3}).](image2.png)

---

**Table 3**

<table>
<thead>
<tr>
<th>Items</th>
<th>Concentration of pollutants in the two units (mg m\textsuperscript{-3})</th>
<th>$P$</th>
<th>Total emitted pollutants from the two units (kg y\textsuperscript{-1} LU\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reference room</td>
<td>Experimental room</td>
<td></td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>5.40 ± 0.80</td>
<td>3.76 ± 1.05</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>N\textsubscript{2}O</td>
<td>1.18 ± 0.07</td>
<td>1.13 ± 0.12</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>6.28 ± 1.61</td>
<td>5.32 ± 314.83</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>2109.38 ± 264.53</td>
<td>1881.64 ± 1.41</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

In our experiment, the N\textsubscript{2}O emission rate was 0.39 and 0.40 g LU\textsuperscript{-1} h\textsuperscript{-1}. Phillips et al. (1995) reported lower values, with an N\textsubscript{2}O emission rate from livestock units of 0.27 g LU\textsuperscript{-1} h\textsuperscript{-1}.

3.5. \textit{CH\textsubscript{4}} concentration and emission

The mean concentration of \textit{CH\textsubscript{4}} was significantly higher in the reference unit throughout the day with 6.28 mg m\textsuperscript{-3} vs. 5.32 mg m\textsuperscript{-3} in the experimental room, \textit{P} < 0.001. \textit{CH\textsubscript{4}} emission was higher from the reference unit (18.96 kg y\textsuperscript{-1} LU\textsuperscript{-1} vs. 16.11 kg y\textsuperscript{-1} LU\textsuperscript{-1}, \textit{P} < 0.001) and showed no increase throughout the 4 week trial. \textit{CH\textsubscript{4}} can be generated from both the pigs and the slurry (Donham and Popendorf, 1985). However, as the changes in the \textit{CH\textsubscript{4}} emission rate were not very different between the units, slurry cannot be an important factor. The unmodified values of methane concentration in the two units are the result of the reduced activity of the sows in their crates and the increased ventilation rate during the trial, from the beginning to the end of the farrowing cycle.

In this study, CO\textsubscript{2}, NH\textsubscript{3}, N\textsubscript{2}O, and \textit{CH\textsubscript{4}} emissions were measured continuously from 2 pig units in the field. Hourly emission data (Figs. 3–6) show that this type of emission varies during the day throughout the entire farrowing period.

The average hourly emissions of gas during a day over the full period of this experiment resulted independent of the sampling weeks, or increased animal live weight. All gas emissions show characteristic diurnal fluctuations depending essentially on observed increased/decreased animal activity at feeding and operator inspection times.

Such diurnal fluctuation of CO\textsubscript{2} was reported by Van Ouwerkerk and Pedersen (1994). It is clear that this increased production derives from the higher respiration rate of active animals in daytime. Moreover, this phenomenon might be related to pig excretion (Osada et al., 1998). The sows and pigs were fed and inspected at 8:00 and 10:00 daily, and according to observations, most of the animals excreted after 1 or 2 h. Pigs also discharged some gas with faeces at the time of excretion.

The disturbance of the slurry surface caused by faeces dropping through the slatted floor may also have increased the emission of the considered gases.

According to the LG MTD Allevamenti report (2004), the methane emitted by sows in Italy was 15.491 ton y\textsuperscript{-1}, TiO\textsubscript{2} treatment could reduce this amount by 15\%, resulting in an estimate of 13,167 ton y\textsuperscript{-1} of methane emitted in Italy.

3.6. Evaluation of the relationship among concentration/emission of gases from pig units and TiO\textsubscript{2} coating treatment

The correlation analysis performed by Proc. CORR, Pearson of SAS (Statistical package) shows the clear positive effect of TiO\textsubscript{2} coating on inside pollutant concentrations as shown in the previous sections. Table 4 illustrates, as expected, that ventilation rate has a strong and positive effect on NH\textsubscript{3}, N\textsubscript{2}O, CO\textsubscript{2}, \textit{CH\textsubscript{4}} abatement (Vranken et al., 2000). Considering the similar ventilation rate values in the two units, and the almost identical environmental conditions of the rooms, the significant negative correlation found between treatment and gas concentration gains significance, indicating the strong abatement of the treatment on ammonia and greenhouse gases: NH\textsubscript{3}, N\textsubscript{2}O, CO\textsubscript{2}, \textit{CH\textsubscript{4}} concentration and emission from the piggery resulted negatively depending on the treatment, respectively, for 63\%, 20\%, 34\% and the 29\% (\textit{P} < 0.001).

N\textsubscript{2}O resulted affected negatively by room temperature (50\%, \textit{P} < 0.001).

The average measured concentrations of NH\textsubscript{3}, N\textsubscript{2}O, CO\textsubscript{2}, \textit{CH\textsubscript{4}} from the pig units were 5.41, 1.2, 6.28, 2109 mg m\textsuperscript{-3} in the reference unit and 3.76, 1.13, 5.32 and 1881.64 mg m\textsuperscript{-3} in the treated unit. During a full farrowing cycle, emissions of NH\textsubscript{3}, N\textsubscript{2}O, CO\textsubscript{2} and \textit{CH\textsubscript{4}} expressed on LU basis were 16.33, 3.6, 18.96 and 6365 kg y\textsuperscript{-1} LU\textsuperscript{-1} in the reference unit and 11.37, 3.43, 16.11 and 5695 kg y\textsuperscript{-1} LU\textsuperscript{-1} in the experimental unit.

The reference unit showed significantly higher values (\textit{P} < 0.001 for NH\textsubscript{3}, CO\textsubscript{2} and \textit{CH\textsubscript{4}} and \textit{P} < 0.05 for N\textsubscript{2}O) for all the considered pollutant concentrations and emissions. This for environmental conditions and identical number of sows and piglets for unit in the study.
Because of the low cost of the photocatalytic paint used in the trial, which costs the same as an ordinary coating, the treatment could be proposed as a low cost BAT (see Table 5 for ammonia reduction costs comparison).

4. Conclusions

The study continuously monitored NH$_3$, N$_2$O, CO$_2$, and CH$_4$ emissions from two identical farrowing units. One room was used as a control unit while the other was coated with a TiO$_2$ catalytic paint. We can draw the following main conclusions:

1. NH$_3$, N$_2$O, CO$_2$, CH$_4$ concentrations from pig units were measured to be 5.41, 1.18, 6.28, and 2109.38 mg m$^{-3}$ (reference unit) and 3.76, 1.13, 5.32 and 1881.64 mg m$^{-3}$ (experimental unit), respectively, throughout one complete farrowing cycle. NH$_3$ concentration was 30.50% lower on average over 27 measuring days in the experimental unit compared to the control room.

2. NH$_3$, N$_2$O, CO$_2$, CH$_4$ as emissions, expressed on an LU basis, were calculated at 16.33, 3.57, 18.96 and 6365.01 kg y$^{-1}$ LU$^{-1}$ (reference unit) and at 11.37, 3.43, 16.11 and 5695.58 kg y$^{-1}$ LU$^{-1}$ (experimental unit), respectively.

3. The treatment decreased NH$_3$, N$_2$O, CO$_2$, CH$_4$ emissions by 30.37%, 3.92%, 10.52% and 15% (P < 0.001), respectively.

N$_2$O was negatively affected by room temperature (50%, P < 0.001).

The surfaces of the experimental room were coated with 70 g m$^{-2}$ of a TiO$_2$ paint before the beginning of the experiment, and illuminated by 12 solar spectrum lamps of 36 W each. The concentration values of NH$_3$, N$_2$O, CO$_2$, and CH$_4$ were significantly lower than in the reference unit. Pollutant emission values, calculated as the multiplication of concentration for ventilation rate showed the same difference, because of the similar volumes of air extracted from the two rooms during the trial. The cost of the TiO$_2$ treatment is 126 € (including cost of manpower) per room for

---

**Table 4**

<table>
<thead>
<tr>
<th>Housing and manure removal system type</th>
<th>Ammonia emission factor (kg pig$^{-1}$ year$^{-1}$)</th>
<th>Ammonia emission reduction (in %)</th>
<th>Cost of ammonia emission reduction (in €, kg$^{-1}$ NH$_3$ sow$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Totally slatted floor and deep pit</td>
<td>8.7</td>
<td>–</td>
<td>35-52</td>
</tr>
<tr>
<td>Partially slatted floor and scraper for manure removal in the pit</td>
<td>4.2-5.6</td>
<td>35-52</td>
<td>35-40</td>
</tr>
<tr>
<td>Totally slatted floor and re-circulating system in gutter without liquid layer</td>
<td>3.5</td>
<td>60</td>
<td>20.36</td>
</tr>
<tr>
<td>Totally slatted floor and sloping floor below for faeces and urine separation</td>
<td>5.2-6.0</td>
<td>30-40</td>
<td>10.56</td>
</tr>
<tr>
<td>In this study: TiO$_2$ coating</td>
<td>6.1</td>
<td>30</td>
<td>3.1$^a$</td>
</tr>
</tbody>
</table>

Data from “Allevamenti a basso impatto ambientale”, Bonazzi et al. (2003).

$^a$ The cost is comprehensive of manpower.

---

**Table 5**

| Percentage and costs of ammonia emission reduction and for TiO$_2$ coating in 4 different BAT housing type (farrowing rooms) |
|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Housing and manure removal system type           | Ammonia emission factor (kg pig$^{-1}$ year$^{-1}$) | Ammonia emission reduction (in %) | Cost of ammonia emission reduction (in €, kg$^{-1}$ NH$_3$ sow$^{-1}$) |
| Totally slatted floor and deep pit              | 8.7                                             | –                               | 35-52                                           |
| Partially slatted floor and scraper for manure removal in the pit | 4.2-5.6                       | 35-52                           | 35-40                                           |
| Totally slatted floor and re-circulating system in gutter without liquid layer | 3.5                           | 60                              | 20.36                                           |
| Totally slatted floor and sloping floor below for faeces and urine separation | 5.2-6.0                       | 30-40                           | 10.56                                           |
| In this study: TiO$_2$ coating                   | 6.1                                             | 30                              | 3.1$^a$                                         |

---

each year of treatment. The cost related to ammonia reduction is estimated to be 3.1 € kg$^{-1}$ NH$_3$ per sow, showing that TiO$_2$ coating is a suitable low cost BAT for gas abatement in swine husbandries.

This experiment was carried out in an in-field piggery as a preliminary study to test the effect of TiO$_2$ coating in animal husbandry on pollutant emission reduction. Since the basic chemical reaction holds for NH$_3$ it might be expected that the basic transformation of TiO$_2$ painted walls will also be successful in other livestock house types, for example dairy buildings.

References


LG MTD Allevamenti (in IPPC, Integrated Prevention Pollution Control, Decree no. 372 04/09/99).


Further Reading