# Reduction of Methane Emissions from Manure

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ABSTRACT: Slurry is the most common manure system in Dutch animal husbandry. Cost effective options to reduce methane emissions, without increasing emissions of ammonia and nitrous oxide, are covering the outdoor slurry storage, shortening the indoor storage time, frequent and complete removal of the slurry from the building, lowering the slurry temperature and filtration of the air from the livestock house and storage facility. Other, from a cost and management point of view less favorable, options are aeration, acidification, feed adjustments and controlled anaerobic digestion. In The Netherlands the average temperature of outdoor storage is less than 10.2°C, but the indoor storage for pig manure is around 17°C. Quick removal of slurry from the animal housing can reduce methane emissions by 66%. In addition, measurements showed a reduction of more than 50% of methane emissions for well covered outdoor storages with slurry at rest. Since most of the methane is produced in the livestock house it is evident that filtering the methane from the ventilation air can be an effective mitigation option. Air filters, which are still under development, can result in a reduction of up to 50% of the total methane emissions from livestock. Implementation of reduction options in agriculture are only possible if farmers are willing to co-operate. Additional income from emissions trading might be a stimulating option.

#### **1 INTRODUCTION**

Abatement of carbon dioxide (CO<sub>2</sub>) emissions from the combustion of fossil fuels is not successful. The emission of CO<sub>2</sub> is still increasing compared with the emission levels of the reference year 1990. According to the Kyoto protocol, CO<sub>2</sub> emissions in the Netherlands should be reduced by 6% (-13 Mton) in 2010, but these emissions are expected to increase by 17% (37 Mton) if there are no changes in policy (VROM, 2000). Next to CO<sub>2</sub>, methane (CH<sub>4</sub>) is the most important non-CO<sub>2</sub> greenhouse gas. In this paper we will focus on manure related CH<sub>4</sub> emissions from pigs and ruminants. The Dutch CH<sub>4</sub> emission is 25 Mton CO<sub>2</sub>-eq of which agriculture is responsible for 40% (European Environment Agency, 1999) of which 32 % (7.9 Mton CO<sub>2</sub>-eq) originates from enteric fermentation and 8 % (2.1 Mton CO<sub>2</sub>-eq) from animal manure.

An investigation will be made of potential  $CH_4$  emission reduction options evaluated in the context of  $NH_3$  and  $N_2O$  emissions.

# 2 OPTIONS TO REDUCE METHANE EMISSIONS FROM MANURE

## 2.1 Temperature

Below 20°C the production of  $CH_4$  is positively affected by the growth rate of different type of methanogenic bacteria (Sharpe & Harper, 1999), which is a long term effect, and by the speed of  $CH_4$  formation in a liquid, which is a thermodynamic process. It is not easy to predict the net effect of low temperature on the bacterial population and from this the gas production. However, for a

given population thermodynamic processes determine the actual speed of  $CH_4$  formation. So cooling of the slurry can be a strong abatement option for  $CH_4$  emissions.

The average temperature on a yearly basis in The Netherlands was  $10.2^{\circ}$ C between 1990 and 2000 (KNMI, 2000). The average temperature of indoor stored pig slurry is around 17°C (Novem, 1991). The emission reduction associated with this temperature difference can be about 66% (Hilhorst et al., 2001; Zeeman, 1994, Chynoweth *et al.*, 1999). For cattle slurry the difference is about 1-2°C resulting in a reduction of about 5-10%. Thus, transferring the slurry as soon as possible to an outdoor storage facility is a cost effective abatement option for CH<sub>4</sub> emissions.

Active cooling of the slurry surface of an indoor storage is a feasible abatement technique. An effective way of cooling is using groundwater, which is possible in the Netherlands. At an experiment on a Dutch pig farm it was possible to cool the slurry surface to about 14°C with groundwater of about 10°C. The commercially available cooling system consisted of cooling elements floating on the slurry surface. During a year the cooling system was switched on and of with a 2 weekly interval to find a reference. The measured emission reduction for  $CH_4$  as well as for  $NH_3$  was between 30 to 50% (Groenestein & Huis in 't Veld, 1996.

#### 2.2 Slurry in rest in a covered outdoor storage

As long as pig slurry is at rest,  $CH_4$  emissions will be less than from agitated slurry. This is the case for slurry in an outdoor storage. The slurry in indoor storages will experience some agitation because of the regular dropping of faeces and urine and during filling or emptying the storage. Hence, emissions from slurry storage will be higher than for slurry in rest but lower than for thoroughly mixed slurry. From measurements it was concluded that the emissions of pig slurry in rest is at least half that of thoroughly mixed slurry. For practical applications, the  $CH_4$  emissions of slurry at rest can be estimated at about 75% of that of thoroughly mixed slurry.

Covering slurry storage will reduce NH<sub>3</sub> emissions because of the thermodynamic equilibrium between the NH<sub>3</sub> and ammonium in the liquid. An unexpected side effect is that measurements showed also lower CH<sub>4</sub> emissions. Measurements are available from two independent sources. Williams & Nigro (1997) measured the CH<sub>4</sub> emission from four storage tanks: uncovered, moderately covered with a standard cover and covered with an improved cover. They performed their experiment on laboratory scale as well as on farm scale. They found a CH<sub>4</sub> reduction by about 50% for the standard cover and by about 90% for the improved cover. Uenk *et al.* (1993) measured the concentration of CH<sub>4</sub> halfway the headspace of four covered storages. The covering was of concrete, canvas, wood and corrugated board. They found similar results as William & Nigro. Both references also found an increase in emission after mixing. More basic research is needed on the effect of covering on CH4 emissions. Still it is reasonable to estimate the CH4 emission reduction of a well-covered storage at about 50% including the effect of now and then mixing.

#### 2.3 Filtration of air from housing and slurry storage facility

From the foregoing sections it can be concluded that  $CH_4$  is mainly emitted from the livestock house and to a lesser extent from the outdoor storage. Also  $CH_4$  from enteric fermentation, which is 80% of the total  $CH_4$  emission from agriculture, is emitted from the houses for about three-quarters of the year. It would be most effective to remove the  $CH_4$  from the ventilation air.

Methanotrophic bacteria can oxidize  $CH_4$  (Kightley *et al.*, 1995; Amaral *et al.*, 1995; Grant, 1999). Methanotrophic bacteria are everywhere and develop at places that have the right amount of oxygen and  $CH_4$ . With these methanotrophic bacteria a bio-filter can be operated.

Jones & Nedwell (1993) proposed a low-cost but effective method to reduce  $CH_4$  emission by covering manure with a 30-cm-thick layer of sand. In the sand a sufficient large community of methanotrophic bacteria will develop to oxidize most of the  $CH_4$  produced by the slurry.

A feasibility study was made on the use of membrane filters to clear the air from a clove box for space experiments with animals (NIVR, 1999). On one side of a membrane there was an immobilized methanotrophic culture and on the other side the ventilation air from the clove box. The air could be cleared completely. The main problem with this particular experiment was the low  $CH_4$  concentration in the air from the clove box. In livestock houses the  $CH_4$  content is higher resulting

in higher filter efficiency. For livestock houses it is expected that the high ventilation rates and possibly the  $NH_3$  concentrations will be the main problem to be solved. Filters are under development, but not yet available for practical use.

Another method is to use the principle of photo catalytic oxidization at room temperature. Methane will oxidize if it is passed over a titanium oxide surface while it is radiated by UV light with a wavelength of 385 nm. Radicals formed in the water on the titanium oxide surface will reduce the energy needed to oxidize  $CH_4$ .

#### 2.4 Biogas production

Controlled anaerobic digestion of slurry can reduce the  $CH_4$  emission from slurry. In addition the obtained energy reduces the need for fossil fuel.

In spite of all research and government incentives to promote the use of energy from biogas, only a minor part of slurry in The Netherlands and other countries is digested in biogas plants. In addition, from an energy point of view, a biogas plant is (until now) cost-effective for farms with more than about 200 cows or 2000 pigs (Van Lent & Van Doorn, 2000). No more than 10% of the farms meet this requirement. Centralized plants could be an alternative, but than the transport of manure is a drawback. Biogas plants have enjoyed much attention since mid-1970. Till now, however, even in Denmark not more than a few percent of the slurry is digested. The main reasons for success stories (Bates, 2000) are based on the income from co-fermentation, discount on electricity prices in Germany and premium price in Italy, capital grants and cheap loans in Denmark.

According to Bates (2000) a 50% reduction of  $CH_4$  emissions from manure is achievable for cooler countries like The Netherlands. The author does not agree with this estimate. Thought, an-aerobic digestion is important from an energy point of view, reduction of non-CO<sub>2</sub> emissions can not justify the investment of a biogas plant in cooler countries.

In a biogas reactor the production of biogas can be as much as 100 time higher than if the manure was stored in a conventional storage. Gas leakage of 1% equals the emissions of  $CH_4$  of a conventional manure storage. The IPCC default is 5%, but this appeared to be an underestimation (Cumby, 2000). The chance of gas leakage is larger for farm scale plants than for centralized plants probably due to the fact that operation of a biogas plant is not the farmers core business. The operator of a centralized plant will be more keen on avoiding leakage. Thus, replacing conventional manure storage by a farm scale biogas installation could result in leakage of methane which can be higher than emissions from a conventional manure storage. It is more cost-effective to promote quick removal of the slurry from the animal house to a covered outdoor storage.

# 2.5 Acidity

Growth of micro-organisms and gaseous emission rates are a function of the acidity of slurry.

From Boopathy (1996), Besson *et al.* (1985), Derikx *et al.* (1989) and Conrad & Schütz (1988) we may conclude that  $CH_4$  production has its optimum at pH 7. The  $CH_4$  emission halved at pH 6.5 and pH 8.3.

 $NH_3$  emissions are highest at pH >9 and almost stops at pH <7 (Groot Koerkamp, 1998).

Oenema *et al.* (1993) found for slurry amended with nitric acid HNO<sub>3</sub> that N<sub>2</sub>O emissions have there optimum around pH 6 and are almost zero at pH <5 or pH >8. More in general the author concludes from Oenema *et al.* that in case of N<sub>2</sub>O production from slurry, this will be sensitive to pH according to their findings.

The acidity of slurry is a dynamic parameter which is a function of time, animal type, feed etc (Monteny, 2000). The pH can range between 7.0 to 8.8 according to Hoeksma (1988) an 7.2 and 8.4 according to Sommer & Husted (1995). A reasonable generalized estimate for the pH of slurry is 7.9. Assuming the pH dependence of  $CH_4$  emissions is linear from pH 7 to pH 8.3, the pH sensitivity of the  $CH_4$  emission from slurry can be estimated at -5% per 0.1 pH unit for increasing pH.

The emissions of  $CH_4$ , N<sub>2</sub>O and NH<sub>3</sub> as function of the pH are illustrated in figure 1. As can be seen from this figure, acidifying the slurry to below pH 4.5 could be a strong option to reduce gaseous emissions. It is also clear that not knowing the slurry pH could lead to large uncertainties in  $CH_4$  emission estimates.

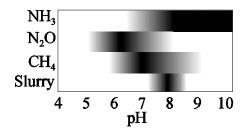


Figure 1. An illustrative overview of the effect of slurry pH on gaseous emissions.

In recent laboratory experiments at pH 6 we observed that acidification with HNO<sub>3</sub> resulted in high emissions of N<sub>2</sub>O, but emissions of CH<sub>4</sub> were eliminated. Acidification with organic acids like citric acid or lactic acid, showed higher CH<sub>4</sub> emissions at pH 6 than from untreated slurry, but no N<sub>2</sub>O emissions could be measured. Break down products from organic acids will serve as additional substrate for CH<sub>4</sub> production. Acidification below a pH of 4.5 resulted in no emissions for any of the gases. So far, acidification looks promising as an abatement technique, as can also be found from literature (Hendriks *et al.*, 1996; Lent, 1995; Hörnig *et al.*, 1998; Oenema, 1998). However, slurry is not a homogeneous substance. Because the slurry is not homogeneous the added acids can cause sudden emissions of dangerous gases causing health risks (Patni & Clarke, 1991; Van Lent *et al.*, 1995; Frénay, 1993; Hörnig *et al.*, 1997). Another problem is that of foam production which can come out of the slurry pit through the slatted floor. An anti-foam agent should solve this.

In conclusion it is not advised to use acidification as a CH<sub>4</sub> emission abatement technique. For accurate emission estimates one must take the pH of slurry in to account.

## 3 DISCUSSION AND CONCLUSIONS

Reductions by manure management. Reduction of the indoor storage time, combined with a wellcovered outdoor storage facility with the slurry in rest, is for cooler countries like The Netherlands the most cost-effective emission reduction option. This is more effective for pigs than for cattle. If the indoor storage time is reduced by a factor 2, the  $CH_4$  emission will decrease due to:

1. the lower outdoor storage temperature (cattle slurry -10% and pig slurry -40%),

2. the effect of covering (-50%), and

3. the effect of slurry at rest (-25%).

A realistic estimate for the combination of these three effects is a reduction of >50% of CH<sub>4</sub> emissions from manure.

Cooling of indoor stored pig slurry can lead to an emission reduction by more than 30%.

Filtration of the ventilation air of the animal houses is a strong option but still under development. A filter can tackle both the methane emission from slurry and enteric fermentation. The emission reduction is estimated at 50% of the total  $CH_4$  emission from livestock.

Controlled anaerobic digestion will result in avoiding  $CH_4$  emissions from a storage facility, not because of the biogas plant itself, but rather as a result of the changed manure management.

Acidification of slurry is a strong option, but at the cost of health risks. Therefore, acidification is not advised for use in livestock houses.

Emission reductions by manure management, cooling, filtration of the ventilation air and anaerobic digestion can work positively on N<sub>2</sub>O and NH<sub>3</sub> emissions as well.

The estimated emission reductions are only possible if all farmers are willing to co-operate, are able to implement these options and if these options work out as predicted. Emission trading might be an elegant instrument to implement reduction option effectively (Hilhorst *et al.*, 2002). Emissions trading could bring additional income into the agricultural sector. The income from trading can stimulate the agricultural sector to find and implement the most effective reduction options and decrease the need for government concerns and subsidies. In addition, the farmer will become keen on finding overlooked emission sources.

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