Albanian j. agric. sci. 2018;17 (1): 84-90 *Agricultural University of Tirana*

RESEARCH ARTICLE **(Open Access)**

Assessments of Mitigation Techniques on Ammonia Emissions from Animal Slurries and Digestate during Storage

ALDA BICOKU[1*], GIORGO PROVOLO[2], ELISABETTA RIVA[2], SEIT SHALLARI[1] AND TATJANA DISHNICA[1]

[1]Department of Agroenvironment and Ecology, Agricultural University of Tirana, Tirana, Albania
[2]Department of Agricultural nd Environmental Sciences, University of Milan, Via Celoria 2 20133 Milano, Italy

Abstract

One of the environmental concerns relates to ammonia emissions from animal manure. Their effect include acidification, eutrophication and secondary particle ($PM_{2.5}$) formation. Ammonia volatilize from manure in housing, during storage and during spreading. To reduce ammonia emissions from manure suitable techniques should be identified. The purpose of this study is to carry out the potential measurement of ammonia emissions from animal manure and evaluate its reduction using various mitigation techniques. The experiment was carried out at a controlled temperature of 20^0C using six different slurries of three different types: pig, cow and digestate. The slurries were analyzed for total Kjeldhal nitrogen, ammoniacal nitrogen (TAN) and pH, at the beginning of the experiment, according to standard methods (APHA, 2005). Each slurry was tested in duplicate measuring ammonia emission from a 1 L container with acid traps and comparing the emissions of the raw slurries and with the following mitigation techniques: oil, clay, sawdust, straw and concentrated sulfuric acid of 98%. The results demonstrated that the more effective techniques are the acidification at a pH lower than 5.5 and addition of oil to create a barrier to volatilization. The reduction obtained with these techniques compared to the raw slurries were higher than 80% reaching in some case, values over 95%. The mitigations effect for cow slurries was lower than for pig slurries and digestates.

Keywords: Ammonia, environment, manure, digestate, emission mitigation.

1. Introduction

The emissions of ammonia (NH_3) are considered as a big political question and as well as of the scientific research because constitute a threat to health and the environment [14] [16]. Ammonia (NH_3) which is emitted by the agricultural sector, has the highest contribution of the nitrogen in the atmosphere [28]. The agriculture contributes significantly to the creation of greenhouse gases (GHG) and in the creation of the ammoniac (NH_3). In the Europe and the USA about 75% of NH_3 emissions are derived from livestock products (Webb et al., 2005). Also in the Europe, the NH_3 emissions from livestock manure account for up to 80% of total emission [31]. The organic fertilizer management can also affect the atmospheric emissions of the ammonia. The major anthropogenic sources identified include excreta from domestic animals (50%) and use of synthetic nitrogen (N) fertilizers (25%) Manure from farm animals is the principial source [13]. The spread of ammonia in the air from the livestock sector poses a risk to animal and human health [12] and the emission of NH_3 through air ventilation can damage the surrounding nature as a result of acidification and eutrophication [7] [20]. NH_3 contributes not only to soil eutrophication and acidification, but also indirectly contributes to N_2O emissions, including N cycles in natural ecosystem [24]. The additional NH_3 losses can occur during storage [18] and application in the ground [36] reducing the values of livestock manure as a N fertilizer for plant production. In addition they represent a loss of valuable fertilizer N. The most important factors influencing ammonia emission are the concentration of urea in urine and total ammoniacal nitrogen (TAN) in the slurry, the emitting surface, pH of the slurry, the air velocity and the slurry temperature [37]. In animal house, NH_3 is a health risk to animal and man, because long term exposure to NH_3 combined with dust can cause severe

*Corresponding author: Alda Bicoku; E-mail: alda_bicoku@yahoo.com
(Accepted for publication Mars 20, 2018)
***ISSN**: 2218-2020, © Agricultural University of Tirana*

lung diseases [29]. High concentration of NH_3 may reduce animal performance. The seasons of the year affect the concentration of ammonia in the air. During the spring seasons there is an increase in ammonia concentration. Meanwhile, the ammonia emissions from the livestock sector relate to the management of manure and have a higher percentage (> 80%) of emissions in autumn and winter. This finding is confirmed by Hristov's results (2011). Over the last decades, livestock production has intensified in many parts of the world, rising emissions of NH_3 [15] and CH_4 [34]. Ideally, manure management should aim at reducing the potential for NH_3 and CH_4 emissions. The agricultural activity has had a strong evolution and intensification, coupled with an increased impact on the environment and pollution, widespread and partial, which have adversely affected the quality of the water and of the ground. In most European countries, ammonia levels are exceeded and as a result in these countries the criticisms are maximum. ECE-UN negotiations aim to control NH_3 emissions [3]. Many scenarios have been drawn up for future emission limitations of NH_3. There are several ways to manage nitrogen cascades that have been implemented by the EU and some are under discussion (EC, 2001, EC, 2005; EC, 2008). However, despite the political goals and European directives it has been possible to achieve a relatively small reduction of NH_3 emissions from agriculture [39] and spending on additional measures is higher in this sector [1]. In the thematic Strategy on Air Pollution (TSAP), the European Commission has set itself objectives for the protection of human health and the environment (EC, 2005). To improve the knowledge on ammonia emissions, the mitigation strategies that need to be taken and their impact on the formation of particles in human and ecological systems [5] [30], many recent studies have been able to apply to evaluate the effectiveness and efficiency of various mitigation measures by providing the best suggestions for them [22] [40]. To mitigate the effect of these emissions on the environment, many guidelines and regulations have been created by governments in different countries. Most of these regulations encourage the recycling of manure and their more efficient use by promoting the introduction of specific strategies for softening and introducing technologies at the farm level. Among these, reducing emissions from storage is a relevant issue. Mitigation options during storage (eg, coverage, acidification) are proposed, but they are not always easy to implement and apply in some areas. There are three basic ways to reduce ammonia volatilisation during storage: (1) by manipulating animal feeding strategies [27]; (2) by using additives ; [19] [2] (3) by covering stores [26]. A cover can reduce ammonia emission by increasing the surface's resistance to ammonia volatilisation or by reducing the emitting surface. Additionally, some cover materials serve as ammonia adsorbents. Concurrently, the cover retains the odorous materials within the liquid, decreasing the amount of gas escape, and thus reducing the concentration of odorous gases in the surrounding area. Different materials for covering liquid manure storage facilities to reduce gaseous emission have been investigated and are in use for odor and ammonia [32], [21], [41]. Manipulating the balance between ammonia and ammonium by lowering the pH value of a slurry is another measure to reduce emissions [35], [11], [23], [8], [17], [6], [25]. For farmers, the loss of NH_4^+ via NH_3 emission from animal houses, manure stores and applied manure will reduce the fertilizer value of animal manure [33]. Technologies that have the ability to reduce NH_3 emission while still maintaining a high predictability of N fertilizer value of manure may contribute to reducing the oversupply of N to crops. Acidification of manure is an obvious treatment for the purpose of reducing NH_3 emission from livestock production. Until now developments of the technology have failed due to the risk of foaming and because of the potential hazards associated with the use of acids [9]. Reducing the pH of slurry by adding easily fermented biomass to slurry stores has been shown to reduce NH_3 emissions from stored slurry and following land application [38], [10]. Use of inorganic straw coatings can reduce ammonia emissions effectively but do not affect methane emissions . It has been proven that a solid coverage reduces NH_3 emissions and greenhouse gases, respectively, 30 and 50%. It has also been found that emissions were less in the period under conditions of cold climate compared with stock in hot weather conditions [4]. Given these concerns caused by the NH_3 high level of environmental pollution in the air, scientific research has focused and continues to research new mitigation techniques such as covering the surface of manure with different materials. The aim of this work was to assess the mitigation potential of different covers (straw, sawdust and oil) and acidification on NH_3 on ammonia volatilization during storage on a laboratory scale of different types of slurries: pig, cow and digestate.

2. Material and Methods

2.1. Slurries used in the experiment

In order to evaluate the effect of different mitigation techniques six different slurries were collected in commercial farms in Lombardy, two for each of the following types: pig, cow and digestated.

Each slurry before the experiment was analysed to determine the content of total kjeldahl nitrogen (Ntot), ammoniacal nitrogen (N-NH4), Total and Volatile solids, pH with standard methods (APHA, 2005).

The initial characteristics of the slurries are reported in Table 1.

Table 1. Chemical characteristics of the slurries used in the experiment.

Slurry	*Total nitrogen*	*Ammoniacal nitrose*	*pH*
Pig n.1	2.95	2.55	7.49
Pig n.2	5.13	3.60	8.03
Dairy cow n.1	3.34	1.64	6.70
Dairy cows n.2	2.43	0.99	7.24
Digestate n.1	6.01	4.13	8.13
Digestate n. 2	4.11	2.44	8.00

2.2. Experimental conditions

To assess ammonia emissions from the different slurries we used 2 L bottles filled with 1 L of slurry and acid traps. The bottles were placed in a controlled temperature case set at 20°C in order to avoid effect of temperature variation during the experiment. The lids of the bottles were connected to two Teflon tubes (6 mm inner diameter). One of the tube was open to suck the room air while the second tube was connected to two drechsel bottles filled with containing 200 ml of 1% boric acid solution to capture the ammonia contained in the air. The second drechsel bottle was connected to a gas measuring indicator and an analog flow meter to regulate and monitor the flow of air obtained from the pipe system. The air was sucked from the piping system by a pump (EVO30 series, Oead), connected to the analogue flow, regulated to a continuous flow of 1 l/min. We used four acid traps for each run as shown in Figure 1. An additional acid trap was used as reference to measure the ammonia concentration of the room air. Before each run, the flows were calibrated using a digital flow meter (PFM710S-C4-A, SMC). At the end of each run, the content of the drechsel bottles were titrated with sulphuric acid 0.1N to determine the amount of ammonia trapped.

Figure 1. Setup of the Emission Measurement System

For each slurry we measured the ammonia emissions for 24 hours in duplicate using raw slurry as refence and the following mitigation techniques:
Straw: a layer of approximately 1 cm of barley straw was carefully placed on top of the bottle;
Sawdust: a fixed amount of sawdust was used for each bottle in order to create a layer of about 1 cm in the bottle;
Clay: a complete coverage of the slurry was obtained with commercial clay granules;
Oil: a layer of about 3 mm of oil has been gently poured into the bottle;
Acidification: sulfuric acid was added the slurry in the bottled with 98% and gently mixed till the pH was below 5.5
Each technique was applied soon after filling the bottles with raw slurry and just before the start of the run.
The amount of ammonia obtained by titration for each condition, after subtracting the room emissions value has been referred to the amount of slurry in the bottle and expressed as grams of ammonia emitted per chilogram of slurry and per day.
The standard deviation for each duplicates has been used to show the variability of the test.

3. Results and Discussion

The results obtained have been organized in three graphs to compare the effect of the mitigation techniques on each type of slurry.
The ammonia emitted by the pig slurries are reported in figure 2. It can be noticed that the best results in reducing ammonia emissions have been obtained with oil and acidification.
The two slurries had significantly different emissions due to their different initial concentration of nitrogen and to the higher pH of pig n.2.
In the case of pig slurry n. 1 the best technique which reduces 94.5% ammonia nitrogen in the air is the addition of oil. The results show that straw coverage reduces the amount of ammonia nitrogen by 15.8%, sawdust coverage reduces by 9.6%, clay coverage reduces by 29.7% and sulfuric acid coverage reduces by 89.8%.
In the case of pig slurry n. 2, the best mitigation technique which reduce the amount of ammonia nitrogen in the air of 97.5% is the addition of concentrated sulfuric acid. The use of other techniques results in lower reductions. The straw coverage reduces the amount of ammonia nitrogen in the air by 32,2%, sawdust coverage reduces by 13,9%, clay coverage reduces by 51.0% and oil coverage reduces by 83.0%.

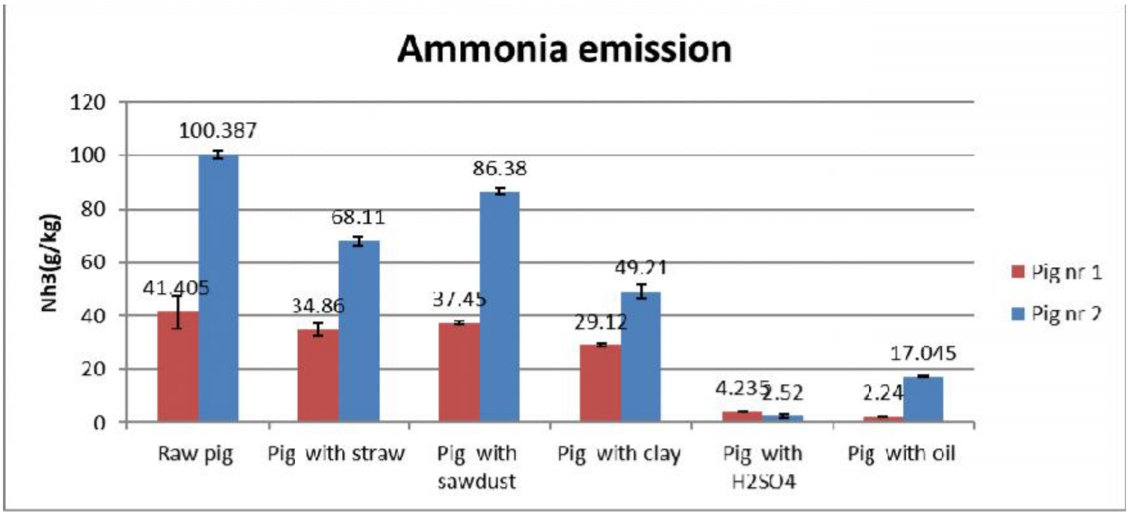

Figure 2. Ammonia emissions from two pig slurries with different mitigations techniques

Figure 3 shows the results of the ammonia nitrogen released from digestates. For both slurries the best solutions are addition of oil and acidification. The two digestates have similar emissions although the digestate n.2 has a lower nitrogen content.

In the case of digestate n.1, the best coverage technique is the oil coverage technique which reduce the amount of ammonia nitrogen in the air by 97.8%. Acidification as a similar value, 96.7%, Other techniques have more limited effect on reduction. The straw coverage reduces it by 47.4%, the sawdust coverage reduces it by 56.5%, clay coverage by 53.7%.

In the case of digestate n.2, the best coverage technique is the sulfuric acid coverage technique which reduce the amount of ammonia nitrogen in the air by 97.7%. The straw coverage reduces it by 43.1% , the sawdust coverage reduces by 56.9% , the clay coverage by 62.1% and the oil coverage by 95.8%.

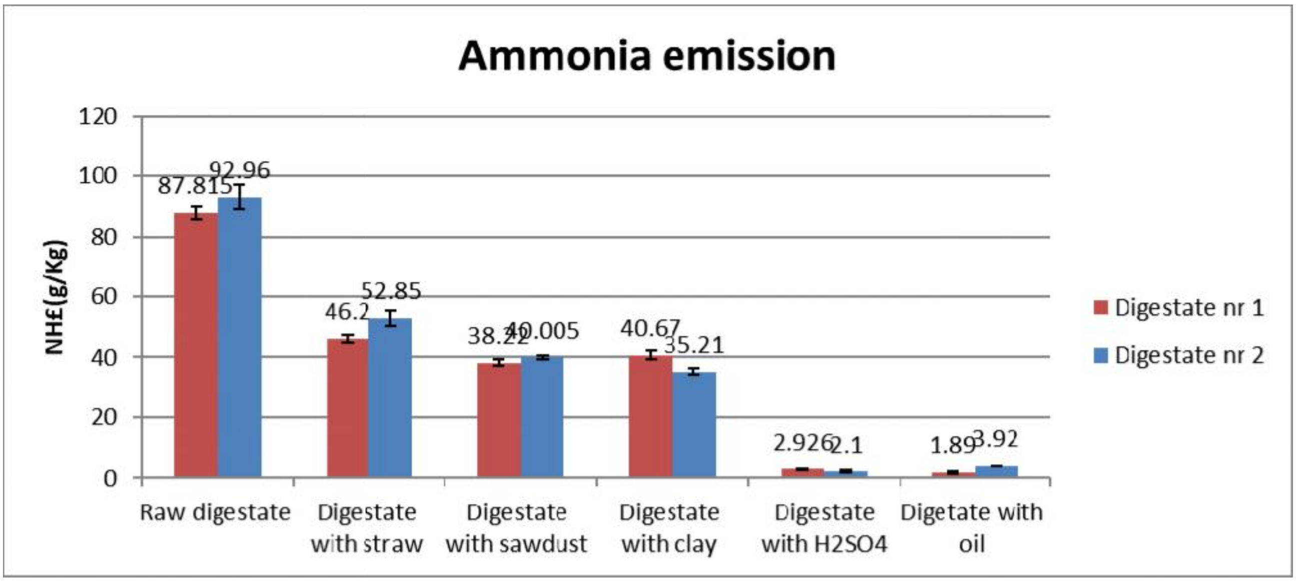

Figure 3. Ammonia emissions from two digestates with different mitigations techniques

The results of the ammonia nitrogen released from cow slurries are reported in figure 4. In the case of cow slurry n. 1 the best coverage technique is acidification which reduce the amount of ammonia nitrogen in the air by 95.4 %. Other techniques have more limited effect on reduction compared to the acid sulfuric coverage technique. The straw coverage reduces it by 56.9 %, the sawdust coverage reduces it by 95.1 % , clay coverage by 76.2 % and the oil coverage reduces the amount of ammonia nitrogen in the air by 79.6 %.

In the case of organic fertilizer from cow no.$_{2,}$ as the best coverage technique is the sulfuric acid coverage technique which reduce the amount of ammonia nitrogen in the air by 88.9%. The straw coverage reduces it by 67.4 % , the sawdust coverage reduces by 78.1 % , the clay coverage by 43.3 % and the oil coverage by 74.6 %.

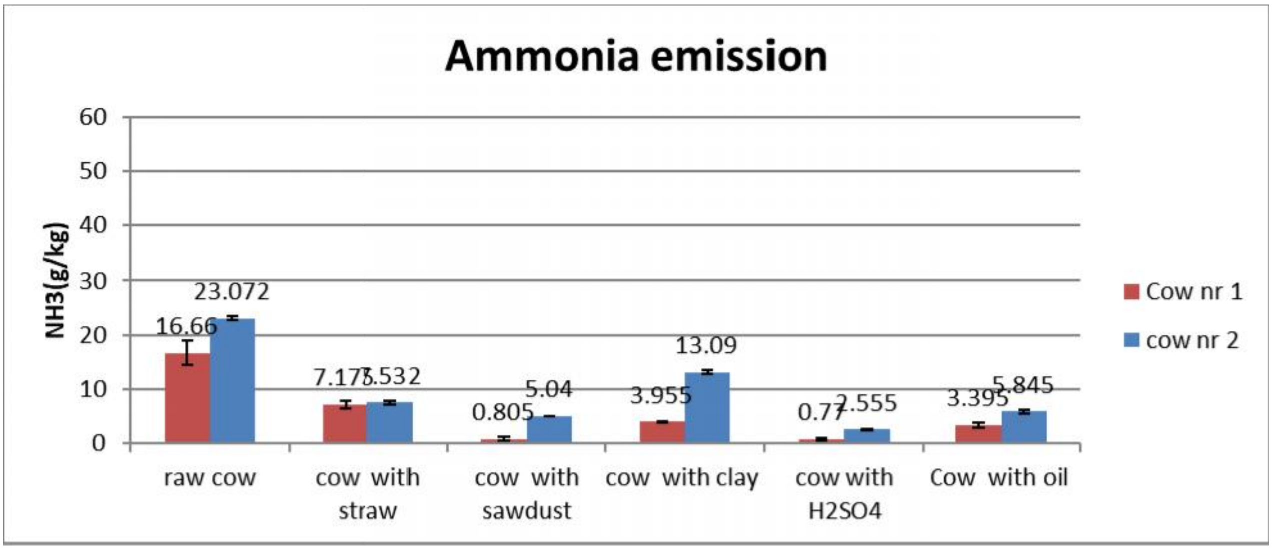

Figure 4. Ammonia emissions from two cow slurries with different mitigations techniques

4. Conclusions

The results of this study confirm the possibility to reduce significantly the ammonia emissions from slurry stores covering slurry stores or reducing the pH of the slurry.

A surface layer of oil reduced ammonia emissions creating a barrier to volatilization because TAN is not soluble in oil.

Lowering the pH value of slurry can reduce effectively ammonia emissions.

The type of slurry has a great influence in the mitigation effect of the different techniques

Pig slurries and digestates have much hogher emission potential than cow slurries.

This study showed that the best mitigtion technique that smoothes the amount of ammonia nitrogen in the air from organic livestock manure results to be acidification at a pH lower than 5.5 but also with the addition of oil good results were obtained.

The other covering materials (straw, sawdust, clay granules) were less effective reducing the emissions by 40-70%.

The results obtained highlight the difficulties to obtain a value of the reduction of emissions with a mitigation technique that can be considers generally valid. The type of slurry but also the specific characteristics of the slurry can greatly affect the mitigation effect.

6. References

1. Amann et al. **Costs of Ammonia Abatement and the Climate Co-Benefits**. 2011.
2. Amon et al. **Manure Management: Treatment Strategies for Sustainable Agriculture**. 1997.
3. Amon K. A.-B. **Bioenergy from cattle manure Implications of anaerobic digestion and subsequent pyrolysis for carbon and nitrogen dynamics in soil**. 2006.
4. Amon K.F. **Investigation of the methane potential of horse manure**. 2007.
5. Aneja et al. **Ammonia Assessment from Agriculture: U.S. Status and Needs**. 2009.
6. Beck and Burton. **Research of liquid slurry processing in pig complex**. 1998.
7. Berendse et al. **Sulfur Turnover and Emissions during Storage of Cattle Slurry: Effects of Acidification and Sulfur Addition**. 1988.
8. Bleijenberg et al. **Greenhouse gas emissions from covered slurry compared with uncovered during storage**. 1994.
9. Borst. A whole**-farm assessment of the efficacy of slurry acidification in reducing ammonia emissions**. 2001.
10. Clemens et al. **Reduction of Ammonia Emission from Stored Poultry Manure Using Additives: Zeolite, Alclear, Ferix-3 and PLT**. 2002.
11. Derikx et al. **Maturity indices for composted dairy and pig manures**. 1993.
12. Donham et al. **Production rates of toxic gases from liquid swine manure: Health implications for workers and animals in swine confinement buildings**. 1977.
13. ECETOC. **Climate Change Impact on Livestock: Adaptation and Mitigation**. 1994.
14. Erisman et al. **Nitrogen & Global Change.** 2008.
15. Galloway et al. **Coastal nitrogen pollution: A review of sources and trends globally and regionally**. 2004.
16. Grinsven et al. **Innovative Methods of Soil Fertility Restoration, Carbon Sequestration and Reversing CO** 2 **Increase**. 2013.
17. Hendriks and Vrielink. **GHG Emission from Livestock Manure and Its Mitigation Strategies**. 1997.
18. Kai et al. **Animal Manure Recycling: Treatment and Management**. 2008.
19. McCrory and Hobbs. **Elements for devising a policy for abating agricultural ammonia emissions in d'ammoniac d'origine agricole en France**. 2001.
20. Metcalfe et al. **Hog Manure Management, the Environment and Human Health**. 1998.
21. Miner and Moore. **A review on alternative technologies to manage manure: Cost effective and environmentally beneficial**. 2000.
22. Moss et al. **Seismic Response of Peaty Organic Soils as a Levee Foundation Material**. 2010.
23. Oenema and Velthof. **Nitrogen release from land-applied animal manures**. 1993.

24. Olesen. **Climate Change and CO2 Effects on Productivity of Danish Agricultural Systems**. 2005.
25. Pedersen. **Direct and subsequent effect of compost and poultry manure on the bioavailability of cadmium and copper and their uptake by oat biomass**. 2003.
26. Phillips at al. **Control of gaseous emissions of ammonia and hydrogen sulphide from cow manure by use of natural materials**. 1999.
27. Portejoie et al. **Effects of separation and anaerobic digestion of slurry on odour and ammonia emission during subsequent storage and land spreading**. 2002.
28. Reis et al. **Performance and methane emissions of grazing Nellore bulls supplemented with crude glycerin.** 2009.
29. Seedorf and Hartung. **Manure Management: Treatment Strategies for Sustainable Agriculture**. 1999.
30. Shibata et al. **Methane Emission from Sheep Respiration and Sheepfolds During the Grazing Season in a Desert Grassland**. 2015.
31. Sommer et al. **Physical limitations of dissolved methane fluxes: The role of bottom-boundary layer processes**. 2006.
32. Sommer et al. **Proceedings from the seminar Manure – an agronomic and environmental challenge**. 1993.
33. Sørensen and Amato. **Remineralisation and residual effects of N after application of pig slurry to soil**. 2002.
34. Steinfeld et al. **Global Farm Animal Production and Global Warming: Impacting and Mitigating Climate Change**. 2006.
35. Stevens et el. **Reducing ammonia emissions by combining covering and acidifying liquid manure**. 1989.
36. Thorman et al. **The effect of solid manure incorporation on nitrous oxide emissions**. 2008.
37. Van der Peet-Schwering et al. **Genetic Engineering, Biofertilisation, Soil Quality and Organic Farming**. 1999.
38. Vandre and Clemens. **Reducing ammonia emissions by combining covering and acidifying liquid manure**. 1997.
39. Velthof et al. **Manure Management and Treatment: Impacts on GHG emissions**. 2014.
40. Vuuren et al. **Costs of Ammonia Abatement and the Climate Co-Benefits**. 2011.
41. Williams. **Effect of Pond Fertilization with Vermicompost and Some Other Manures on the Growth Performance of Indian Major Carps**. 2003.