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Review

Methane and nitrous oxide emission from livestock manure

Sonali Prusty*, U. B. Sontakke and S. S. Kundu

Dairy Cattle Nutrition Division, National Dairy Research Institute, Karnal, Haryana, India-132001.

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Methane (CH_4) is a greenhouse gas which contributes significantly to global warming and a significant proportion of atmospheric methane is produced by livestock. Livestock contribute 18% of global greenhouse gas (GHG) emissions. Apart from enteric emission, decomposition of livestock manure under anaerobic conditions is also a source of methane. The later condition arises in confined management system. There is difficulty in disposing off the excreta and wastes produced on a large scale; they are stored in large pits which provide suitable environment for CH_4 production. Another green house gas is nitrous oxide (N_2O), released during the nitrification-denitrification of nitrogen contained in livestock waste. Cattle and feedlots are responsible for 26% of N_2O emissions from anthropogenic sources. Being greenhouse gases, their large scale emission is detrimental to the environmental safety. So, different strategies are emerging to either subside their emission from faeces and animal wastes or to use them effectively for energy saving purposes.

Key words: Global warming, manure, methane, nitrous oxide.

INTRODUCTION

Livestock contribute to climate change through the emissions of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) which cause global warming. The global warming potential of N_2O and CH_4 are 310 times and 23 times the global warming potential of CO_2, respectively. They together contribute 18% of global greenhouse gas (GHG) emissions (Steinfeld et al., 2006). Apart from enteric emission, decomposition of livestock manure under anaerobic conditions is another important source of methane. Normally the organic matter in manure is hydrolyzed and converted to volatile fatty acids. Only when the manure is stored for a long time especially in confined management system without fast disposing off, does the multiplication of the methane producers result in substantial release of methane. Nitrous oxide emission is associated with manure management and the application and disposition of manure as fertilizer. Considering the detrimental effect of the above gases to environmental safety, different strategies are emerging to either subside their emission from faeces and animal wastes or to use them effectively for energy production purposes.

LIVESTOCK MANURE DISPOSAL

The manure disposal systems vary with variation in the

*Corresponding author. E-mail: world.sonalindri@gmail.com.

Table 1. Methane emissions (MT) in terms of CO_2 equivalent from manure management (Source; Environment Protection Agency, USA).

Country	Year			
	1990	2000	2005	2020
India	18.83	80.52	23.20	27.48
China	15.70	19.76	80.91	28.32
France	13.79	13.30	13.25	13.29
Germany	27.10	23.27	19.63	16.65
USA	31.19	38.08	39.18	43.83
World total	222.52	225.38	234.57	269.47

species of livestock, size of herd, climate, type of animal management system, storage period of manure. Manure management systems can be classified into dry and liquid/slurry manure management systems. Dry systems include solid storage, dry feedlots, deep pit stacks and daily spreading of manures. Liquid systems use water to facilitate manure handling and manure is stored in concrete tanks and lagoons. The cattle manure is generally categorized into liquid stable manure, solid stable manure and meadow manure. The stable manure is produced by animals in confinement rearing system. Stable manure is also produced in grazing system at the night time in shelters and also by the dairy animals during milking. The liquid stable manure is stored in the manure tanks outside the animal houses which provide an anaerobic environment. Mostly aerobic condition occurs in meadow manure, produced by the animals in grazing. Sheep are grazing animals and spend the cold winter months inside animal houses only, where they produce solid manure. Goats also produce solid manure. Pig manure is generally of liquid or semi solid type. Poultry birds are generally kept in cage system and produce solid manure except laying hens.

Liquid systems create the ideal anaerobic environment for methane production whereas warm climate make the condition more conducive. In solid system methane production is very less though an increased production has been noticed with rainfall. N_2O production from manure is an initial aerobic and then an anaerobic process. Dry, aerobic management systems may provide an environment more conducive for N_2O production though the relationship between degree of aeration and N_2O production form manure has not been established (Jun et al., 2000).

METHANE AND NITROUS OXIDE EMISSIONS FROM LIVESTOCK

The contribution of GHG emission from enteric fermentation and manure management is almost in the ratio of 9:1. In the industrial model of livestock production under which a large number of animals are housed in confinement, the faeces and animal wastes are stored in massive lagoons that create a suitable anaerobic pool for CH_4 production. Methane contributes to 15% of enhanced greenhouse effect whereas agriculture and associated sectors are responsible for 50% of the anthropogenic methane emissions (Bhatia et al., 2004). The annual global emission of CH_4 was reported to be 535 MT (Houghton et al., 1996). In India the methane's share in total GHG emissions was 30% in 1985 which declined to 27% in 2008 due to relatively higher CO_2 emissions from the fossil fuels. But there was a rise in the absolute value from 18.85 Tg in 1985 to 20.56 Tg in 2008 (Garg et al., 2011). The methane emission figures from manure management in several countries and world total have been suggested by Environmental protection agency of USA (Table 1).

Nitrous oxide contributed to 5% of enhanced greenhouse effect. Agriculture and associated sectors were responsible for 70% of the anthropogenic emissions of N_2O (Bhatia et al., 2004) whereas cattle and feedlots were responsible for 26% of N_2O emissions from anthropogenic sources (IPCC, 2001). Kroeze et al. (1999) reported annual global emissions of 17.7 MT of N_2O. The reports of Mirzaei and Hari Venkatesh (2012) suggested 75% contribution of livestock sector to agricultural N_2O emissions that equates to 2.2 billion tonnes of CO_2 equivalent. IPCC (1996) has reported the global N excretion in the range of 60-100 kg year^{-1} for dairy cattle, 40-70kg year^{-1} for non-dairy cattle, 12-20 kg year^{-1} for sheep and 16-20 kg year^{-1} for swine, respectively. As per the report of INDITE (1994) in UK the $NH^+{}_4$-N stored in livestock wastes is 250 kt and when applied to lands accounted for more than 12% of the total N_2O-N emissions from all terrestrial sources. Sneath et al. (1997) reported N_2O emissions of 800 mg from UK livestock buildings. MAFF (1989) estimated a total flux of 2 kt of N_2O-N year^{-1} from excreta (dung and urine) by grazing animals on 5 Mha grazing land in the UK. The uncertainty in livestock methane emission data is due to the lack of information about emission factors for the various sources. Singhal and Mohini (2004) estimated total methane emission on the basis of 'methane per kg feed intake' from different categories of animals in different agro-climatic conditions fed on different types of feeds. Prusty et al. (2014) reported that methane production by buffalo per day could be predicted most reliably (R^2 = 0.82) from the NDF, NFC and CP intake through fodders. Methane emission factors of 45 kg $hd^{-1}year^{-1}$ for dairy cattle manure and 3 kg CH_4 hd^{-1} $year^{-1}$ for beef cattle manure has been recommended by Pattey et al. (2005) in the North-America under cool conditions.

Global warming potential of methane and nitrous oxide

The contribution of methane is less than 2% of all the factors leading to global warming. The global warming potential is 21-23 times (UNFCC, 1995; IPCC, 2001) more than carbon dioxide. N_2O emissions contribute to depletion of ozone in the stratosphere, as in stratosphere nitrous oxide is converted to nitric oxide gas which is hazardous at sea-level. A significant increase of atmospheric N_2O concentration at a rate of 0.22 ± 0.02% per year has been reported (Battle et al., 1996). High atmospheric life of N_2O (166 ± 16 years) along with its 310 times (Tomlinson et al., 2013) global warming potential raised huge concern for the emission of N_2O.

Methane generation from livestock manure

Manure from livestock consists of a proportion of organic volatile solids which are fats, carbohydrates, proteins and other nutrients that act as source of food and energy for the growth and reproduction of anaerobic bacteria. The acid formers group of bacteria break down the volatile solid in manures to a series of fatty acids in the acid forming stage and in the next stage highly specialized methane formers convert the acids to methane gas and carbon dioxide. The methane formers are pH (6.8-7.4) sensitive, strict anaerobes and functions best at 95°F (Monteny et al., 2001). These conditions often occur when large numbers of animals are managed in a confined area (for example, dairy farms, beef feedlots and swine and poultry farms) where manure is stored in large piles or disposed of in lagoons. The main factors affecting methane emission from livestock manure are the amount of manure that is produced and the portion of the manure that decomposes anaerobically. The methane production is represented as methane conversion factor (MCF) in which the actual methane production is expressed as the ratio between the actual and the ultimate methane production, the later occurs with very long storage time.

Nitrous oxide generation from livestock manure

Nitrous oxide is produced during the nitrification-denitrification of nitrogen contained in livestock waste (Monteny et al., 2001). Initial nitrification step is important to provide the essential substrate ($NO^-{}_3$) for the microbial denitrification processes. There are several other ways of producing N_2O, as nitrifier-denitrification coupled chemical paths are also important. Its production requires an initial aerobic reaction and then an anaerobic process. Nitrous oxide is formed from N compounds of feeds or excreta during processes where oxygen is consumed. Dry, aerobic management systems may provide an environment more conducive for N_2O production. The majority of nitrogen in manure is in ammonia (NH_3) form. Nitrification occurs aerobically and converts this ammonia into nitrate. Denitrification occurs anaerobically, and nitrous oxide is one of the intermediate reaction products. Biochemical oxygen demand (BOD) and nitrogen concentration affect N_2O generation. Pereira et al (2012) observed a significant increase in the NH_3, CO_2 and CH_4 production from dairy cattle excreta with a change in storage temperature from 5 to 35°C.

$$NH_4^+ \xrightarrow{\text{Nitrosomonas spp}} NO_2^- \xrightarrow{\text{Nitrobacter spp}} NO_3^-$$
$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

IPCC (1996) guidelines for measurement of methane and nitrous oxide emission from manure

The methane emission is expressed as kg CH_4 $year^{-1}$. The annual emission factor multiplied with total population from animal category, gives the assumed total methane emissions from the animal population. The annual emission factor is decided from the daily volatile solids (kg) excreted, maximum methane producing capacity (m^3 kg^{-1}) of volatile solid (VS) for manure, methane conversion factor for manure management system in particular climate region, fraction of manure handled using manure system of a particular animal population. The climate categories for emission factor as per IPCC recommendations are ‘cool’, ‘temperate’ and ‘warm’. Methane conversion factor for cool climate is 1% for solid waste system and 39% for liquid/ slurry waste system and deep litter (cattle, sheep) system. The volatile solids from manure of an animal category will vary with composition of diet and other factors such as straw addition. In conventional solid and slurry system the volatile solid produced is 87.3 and 84.3% of the cattle manure DM whereas it is 79.6 and 80.7% of the pig manure DM, respectively (Steineck et al., 1999). Below is given the composition of VS as suggested by Sommer et al. (2002) (Table 2).

The most important parameters for estimation of nitrous oxide are derivation of nitrogen excretion that is generally expressed as kg N $year^{-1}$. According to the guidelines, cattle, pigs and poultry only account for the nitrous oxide emissions and other animals like sheep, goat, camels, which do not account for manure management under wet

Table 2. Composition of volatile solids from animal slurry.

Parameter	Nutrient	Cattle slurry (%)	Pig slurry (%)
Degradable VS	Fat	9	10
	Protein	8	30
	Carbohydrate	21	25
Degradation resistant VS	Carbohydrate	52	35

VS, Volatile solids.

system are eliminated from the category of animals producing N_2O. Population data is same as used for estimation of methane from enteric fermentation and manure management. Nitrogen excretion values those are used for estimating nitrogen excretion animal^{-1} are as follows, dairy cattle - 60, non-dairy cattle - 40, pigs - 16 and poultry - 60 kg animal^{-1} year^{-1}. Nitrogen excretion (anaerobic lagoon/ liquid system and any other system) is derived as percentage of N_2 excretion from total N_2 excretion from animals. According to IPCC (1996) guidelines the percentage of N_2 excretion in anaerobic lagoon from non-dairy cattle manure is zero and for dairy cattle is 6 whereas in liquid system it is 4 for dairy cattle manure. In anaerobic lagoon, liquid system and other systems of storage the percentage of N_2 excretion were 1, 2 and 52 for poultry manure and 1, 38 and 0 for pig manure, respectively. Nitrous oxide emission per animal is determined by multiplying the nitrogen excretion using emission factors, which is the N_2O- N per kg excreted N. IPCC default emission factor for Asia is as follows: anaerobic lagoons and liquid systems-0.001 and others systems-0.005. Total emission is determined by multiplying the number of animals in each category with the emission factor. Emissions from all categories are aggregated and total emission expressed as Gg nitrous oxide year^{-1}.

FACTORS AFFECTING NITROUS OXIDE AND METHANE EMISSION

Housing system

Housing plays a more important role on GHG emissions in non-ruminants production systems since most of the emission in those systems comes from the manure. As described by the International Atomic Energy Agency (IAEA, 2008), the types of housing systems in Asia needs different strategies for manure treatment. Greater CH_4 emissions were reported from farmyard manure followed by liquid slurry and deep litter manure (Külling et al., 2003). Hristov et al. (2012) investigated the effect of manure management on barn floor on NH_3, CH_4, N_2O, and CO_2 emissions and found that CH_4 emissions were considerably lower for the flush manure systems (37 mg m^{-2} h^{-1}) than gravity-flow system (1,216 mg m^{-2} h^{-1}) on barn floor. Methane emissions from manure were much greater from dairy barns where manure is stored for prolonged periods of time compared with barns where manure is removed daily. Philippe et al. (2007) reported that fattening swine reared on deep litter released nearly 20% more GHG than those on slatted floors (0.54 Vs 1.11 g pig^{-1} day^{-1} for N_2O, and 16.3 Vs 16.0 g pig^{-1}day^{-1}for CH_4, respectively).

Deep litter system of pig housing had a great potential for N_2O production, mainly caused by poor O_2 availability in the compacted deep litter (Groenestein and Van Faasse,1996). Amon et al. (2001) observed similar N_2O emissions from the tying stall with manure managed in slurry based (609.6 mg N_2O livestock unit^{-1} day$^{-1)}$ or straw based system (619.2 mg N_2O livestock unit^{-1} day^{-1}).

Species and individual variation

Cattle slurry produced less N_2O than pig slurry and poultry manure whereas methane production depends on the organic matter content. The rate of organic matter production was highest from poultry manure followed by pig slurry and cattle manure (Corre et al., 1997). The Department of Animal Husbandry, Dairying and Fisheries (2010) of India estimated the amount of excreta year^{-1} in million tonnes to be 22.93 by sheep and goat, 8.26 by pig, 14.18 by poultry and 427.12 by cattle and buffalo. Methane production increased with the organic matter (volatile solids) content of the excreta. Poultry manure, pig slurry and cattle manure produced methane in decreasing order per kg of manure. But the large figure for CH_4 production from cattle is due their more volume of faeces excretion. Similar observations of higher methane production from pig (356 L kg^{-1} VS) and sow (275 L kg^{-1} VS) manure compared to dairy cattle manure (148 L kg^{-1} VS) has been reported by Moller et al. (2004). Bala (2013) reported non linearity in the methane emissions in relation to the manure mass in case of horses. He observed an emission of 1.40 and 9.31 g methane day^{-1} from 10 and 20 kg manure, respectively using fermentation chamber. Sharma (2014) suggested that selection of individual animals based on residual feed intake (RFI) would be helpful to reduce enteric methane emissions. Animals with low RFI produced less methane while maintaining the productivity and thus contributing less GHG to the environment. Further research need to be done regarding relation of RFI with emission of gases from livestock manure.

Feed

Lodman et al. (1993) observed higher ($p < 0.05$) methane production from the manure of cattle fed a high grain diet compared to that of the cattle fed a forage det. Jarvis et al. (1995) observed an increased methane emission from grass and clover fed dairy cows and heifers. Hindrichsen et al. (2005) observed effect of feeding different concentrate diets based on oat hull, soybean hull, apple pulp, *Jerusalem artichoke*, molasses and wheat on the methane emissions from slurries of their origin. The slurry originating from molasses diet showed maximum methane emission at 14 weeks of storage though the proportion of methane produced from slurry compared to total emission (enteric and slurry) did not vary with treatments. Hindrichsen et al. (2006) observed 6.6% manure methane emission of the total methane in dairy cattle, fed on forages only, compared to 13% when fed on forage and concentrate in 1: 1 ratio. But Aguerre et al (2010) and Yohaness (2010) observed that increasing the grass and concentrate ration from 47: 53 to 68: 32 had no effect on manure methane emission. Doreau et al. (2011) observed higher manure methane production in hay and corn silage based diet compared to corn grain diet whereas the reverse was observed for N_2O and CO_2 emissions.

The amount of N excretion in dairy cows depends closely on the feed intake. By improving the protein quality of the diet according to the actual requirements, the gain of protein by the animal can be increased and the N excretion may be reduced. Nitrogen excretion of fattening animals increases with the live weight because the protein requirements for maintenance depend on the live weight. Dietary crude protein reduction reduced both CH_4 and N_2O emissions from stored manure (Atakora et al., 2011). Külling et al. (2001) reported decreased N_2O emissions from storage manure of dairy cows fed low-protein diets, but the total GHG emissions were not affected as there was an increased CH_4 emission from the low protein manure. Velthof et al. (2005) observed large decrease in the NH_3 and CH_4 emissions during manure storage and N_2O emission from soilby by decreasing the protein content of swine diets whereas reverse effect on N_2O emissions was reported in swine (Philippe et al., 2006) and dairy cattle (Arriaga et al., 2010) on lowering the dietary protein. Shifting N losses from urine to faeces is expected to reduce N_2O emissions from manure applied soil due to the lower concentration of NH_4^+ in manure. The N excretion of pigs can also be changed by feeding with bacterial fermentable substances such as cellulose, hemicellulose and pectin. Because these substances are degraded in the hindgut of the pigs by microbes, nitrogen is needed for bacterial growth, therefore the N excreted by the urine is reduced.

Stage of animal

N saving effect is more pronounced in producing animals than in growing animals. Milk yield of the cows and CP content of milk affected the N excretion inversely (Colmenero and Broderick, 2006). Variations in methane emissions were caused by difference in milk yield and feed intake (Amon et al., 2001).

Phase feeding

Phase feeding is an effective mitigation practice for GHGs. Reducing dietary protein concentration during the production cycle to better meet the requirements of the animal, significantly lowered the N excretion (Vasconcelos et al., 2007) and consequently losses from the pen surface. A two phase feeding reduced N excretion whereas further reduction was observed using four-phase feeding (Joachim and Heinz-Jürgen, 2001).

Management system

Dry systems include solid storage, dry feedlots, deep pit stacks, and daily spreading of the manure whereas liquid management systems often use water to facilitate manure handling. Liquid systems create the ideal anaerobic environment for methane production. The largest combined N_2O-CH_4 emissions in CO_2 equivalent were observed from the slurry storage, followed by the stockpile and lastly the passively aerated compost. This ranking was governed by CH_4 emissions in relation to the degree of aerobic conditions within the manure. The CO_2 equivalent emissions from the stockpiled manure was 1.46 times higher than from the compost for dairy and beef types of cattle manure (Pattey et al., 2005). Storage treatments with proper aeration and moisture management reduced CH_4 generation from poultry manure (Li and Xin, 2010). Ventilated belt removal of laying hen manure reduced CH_4 emissions compared to deep-pit storage (Fabbri et al., 2007). Amon et al. (2001) reported lower N_2O losses from an actively turned composting pile of solid cattle manure than from an undisturbed anaerobically stored pile.

Season of year

In practice, with substrate and microorganisms being abundantly available, temperature and storage time mainly determine the amount of CH_4 produced. In Danish cattle the methane release from fresh dung pats in the field began immediately and ceased after 10-18 days and the total methane emissions varied from 37 to 170 ml kg^{-1} dung pat during late summer and spring, respectively (Holter,1997). Husted (2004) observed a significant increase in methane emission rate for pig and cattle slurries with an increase in storage temperature, with the peak emission observed at 35-45°C from pig slurry. Similar increase of two fold methane production with increase of storage temperature from 10 to 20°C has been reported by Masse et al. (2008).

In summer, the anaerobically stacked farmyard manure emitted about 4.5 times more greenhouse gasses than the aerobically composted farmyard manure. Due to the lack of oxygen supply in the winter compost, N_2O and CH_4 emissions were higher than from the summer compost (Amon et al., 2001). Ellis et al. (2001) observed that in uncovered yard N_2O emission rates were 3.3 µg N m^{-2} h^{-1} in winter and spring and 6.5µg N m^{-2} h^{-1} in summer. Pereira et al (2012) noticed that cumulative N_2O emissions were not significantly different between temperatures, although numerically slightly higher at 35°C compared to 5, 15 and 25°C.

Abatement strategy

Better manure management practice is the foremost strategy to reduce GHG emissions from manure whereas recovery techniques under which the recovered methane can be used for energy generation/ flaring is an attractive alternative. The flaring process decreases up to 95% of harmful atmospheric effect of methane. In developing countries, like in India there is rarely any provision of storing liquid manure. Instead the manure is used as fuel for households for cooking and preparation of compost to fertilize the aerable lands, otherwise they are thrown in open area. These activities give rise to very little amount of methane from the manure. If livestock manure is kept under aerobic condition by turning the manure regularly, methane emission from manure management can be reduced. The livestock excreta are spread on agricultural lands as manures which make the anaerobic condition unavailable for methanogenic bacteria to degrade the organic matter. Presence of inhibiting compounds (e.g., ammonium) also determines CH_4 production during storage and composting processes.

Abatement of N_2O should be considered as part of an integrated approach to improve the efficiency of N cycling in animal production systems. Current technologies could deliver up to 50% reduction in N_2O emissions from an animal housing system but only up to 15% from a grazing system (De Klein and Eckard, 2008). In animal housings if the air is centrally exhausted, the NH_3 may be stripped with sulfuric acid (Joachim and Heinz-Jürgen, 2001) for the production of ammonium sulfate fertilizer (efficiency up to 96%). When excreta have been applied to soil, nitrification inhibitors (for example, nitrapyrin) may conserve the applied NH_4-N as NH_4^+ and reduce N_2O emissions. Avoiding grazing at moist conditions might be helpful in mitigating N_2O emissions from urine patches in pastures (Van Groenigen et al., 2006). Increasing the hippuric acid concentration through dietary manipulation has been reported to be helpful for mitigating N_2O emissions. It is assumed that benzoic acid which is a breakdown product of hippuric acid has inhibitory effects on the denitrification pathway (Van Groenigen et al., 2006). Mechanically ventilated structures provide opportunity to treat emitted GHG through filtration and scrubbing. Another interesting mitigation technology for animal housing is use of titanium dioxide (TiO_2) paint on the interior walls. Industrial uses of TiO_2 stimulated its photocatalytic properties by UV light and lead to oxidation of NH_3 and N_2O (Allen et al., 2005).

Studies by Costa et al. (2012) in swine houses showed that GHG mitigation with TiO_2 paint hold promise for future GHG reduction strategy from manures. Capturing the gases produced using impermeable membranes, such as oil layers and sealed plastic covers, can reduce NH_3, N_2O, and CH_4 emissions. VanderZaag et al. (2008) suggested use of a vegetable oil layer as manure storage cover, which was very effective, but not practical because of degradability, generation of foul odors and difficulty in preventing the oil film from becoming mixed with the manure.

CONCLUSION

Methane and nitrous oxide are produced from livestock via two sources, enteric fermentation and manure management. There is rising concern over their increased production due to their hazardous effect on the environment. Feeding diets with balanced CP and fibre would optimize the release of N_2O and CH_4. The liquid piling of manures should be avoided. Instead aerated compost of manure would be helpful for decreasing methane emission and also increase the fertility of soil. Use of manure as fuel for households for cooking is another energy remunerating alternative. Other abatement strategies such as use of ammonium compounds during composting decrease methane emissions. When excreta have been applied to soil, nitrification inhibitors (for example, nitrapyrin) may conserve the applied NH_4-N as NH_4^+ and reduce N_2O emissions. Hippuric acid has inhibitory effects on the denitrification pathway. Mechanically ventilated structures, use of titanium dioxide (TiO_2) paint on the interior walls also decrease N_2O generation. The nutritional, management and other amendment strategies could be exploited for reducing the release of CH_4 and N_2O and simultaneously converting the released gases in to a source of useful energy.

Conflict of Interests

The author(s) have not declared any conflict of interests.

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