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NITROUS OXIDE PRODUCTION FROM SOIL AND MANURE APPLICATION: A REVIEW

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ABSTRACT

The aim of this review is to summarize the current knowledge about the nitrous oxide (N_2O) production by soils and highlighting future research needs for emission abatement. The article investigates a scientific literature regarding N_2O emissions from the soil according to different factors, such as condition and soil type. Temporal variations can also be explained by the soil temperature and water content. The main review part is focused on solid manure and effluent application to soil. Nitrous oxide gas is formed in soils through the microbiological processes of nitrification and denitrification, and emissions are mainly released after land spreading. Emissions of N_2O are strongly affected by the timing of manure application, reflecting the effects of weather conditions. Key factors for N_2O emissions are the soil moisture, redox potential, available carbon and microbial processes. Recent studies on the effects of seasonal environmental temperature are discussed. Finally, emission factors from land application of solid or effluent manure are listed in table.

Key words: nitrous oxide; soil; manure; slurry; field application

INTRODUCTION

Agriculture is a major contributor of nitrous oxide (N_2O) emissions to the atmosphere, one of the more powerful greenhouse gases (Paustian *et al*., 2004). According to Crosson *et al.* (2011) the main components of agricultural emissions are N_2O released from soils related to application of nitrogen (N) fertilizers (38 %), N_2O from manure management (38 %), N_2O from burning of savannah, forest and agricultural residues (13 %). Animal production systems are a significant contributor to N_2O emissions from soil, it represents 30 % of agricultural emissions (Kelly *et al*., 2008; Adler *et al.*, 2015). However, the N_2O output from the agriculture is underestimated.

N_2O emissions occur both directly on agricultural lands and from N transported to non-agricultural lands. Nitrogen is used inefficiently in most cropping systems: only half of N inputs are captured in crop biomass and the remainder is lost from the system through leaching and/or through gaseous losses of N_2, N_2O, NO_x, or NH_3 from agricultural soils. A portion of the N that is subjected to microbial transformations, including oxidative pathways (nitrification) and reductive pathways (denitrification), involving mineral N compounds, both of which can form N_2O as a by-product (Paustian *et al.*, 2004). In livestock farming, N_2O production takes place in soils and manures. Typically, 70 % to 90 % of the N ingested by herbivores is excreted, either during grazing or via application of manure collected outside grazing periods (Schils *et al*., 2013). Castillo *et al*. (2001) showed that about 72 % of consumed nitrogen is excreted with faeces and urine in dairy cows. N_2O emissions can be direct emissions from organic manures or inorganic fertilizers applied to soil or direct N deposition by grazing animals (Crosson *et al*., 2011).

Microbial N_2O production and consumption processes depend on several interacting environmental controls such as N supply, soil temperature, soil moisture, oxidative reduction potential, the availability of labile organic compounds, soil type, soil pH and climate (Monaghan and Barraclough, 1993; Bouwman

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et al., 2013; Butterbach-Bahl *et al*., 2013; Marsden *et al*., 2016). No significant correlations were observed between N_2O fluxes and environmental factors, such as rainfall and soil mineral-N (Yamulki *et al*., 1998). However, in the study of Bell *et al*. (2015a), emissions were related to fertiliser N rate; although the trend was non-linear. N_2O emissions increased linearly with increasing fertilizer N rates and NO_3 concentration and amounted to 1.0 to 1.6 % of fertilizer N applied (MacKenzie *et al*., 1997; Bhandral *et al.* (2003a). According to Whalen (2000), N_2O emission from fertilization was directly related to the level of fertilization to 150 kg $N.ha^{-1}$. Emission rates of up to 1590 µg N_2O-$N.h^{-1}m^{-2}$ occurred in the field, while small rates of deposition to the soil were occasionally observed (Allen *et al*., 1996). Nitrous oxide emission increased with increased NO_3 concentration and fertilizer N rates (MacKenzie *et al*., 1997).

N_2O is produced as a result of two microbial processes operating in the soil profile, whereby it is a by-product of the reduction of nitrate to nitrogen gas (N_2) (denitrification), the ammonification of nitrate and the oxidation of ammonium (NH_4^+) to NO_3^- (nitrification) (Casey *et al*., 2006; Klein and Eckard, 2008; Saggar *et al*., 2013; Boon *et al*., 2014). These processes are affected by a number of soil factors, such as soil oxygen and moisture contents, temperature, mineral N content, available soil carbon and pH. Weather conditions, such as rainfall, can affect soil moisture and oxygen contents, and consequently affect N_2O production (Luo *et al*., 2008).

Most of the N_2O originates from microbiological transformations of N in the animal excrements, urine and dung during storage and management and following application or deposition to land (Paustian *et al*., 2004; Oenema *et al*., 2005; Ross *et al*., 2014). The major contributor is normally the denitrification process under anaerobic conditions, but nitrification under aerobic conditions may also contribute (Crosson *et al*., 2011; Saggar *et al*., 2013; Li *et al*., 2015). Denitrification rates in agricultural grassland systems are variable, mainly due to the soil type, management and weather conditions (Klein and van Logtestijn, 1996). Results of Boon *et al.* (2014) indicate that denitrification is the key driver for N_2O release in peatlands. The results of Ball *et al.* (1997) suggested that denitrification was the main N_2O production process at the grassland site, but nitrification may have been equally important at the drier site.

However, according to Koops *et al.* (1997), nitrification is the main N_2O producing process. Nitrous oxide production through denitrification was only of significance when denitrification activity was high. In another field study, the amount of N lost as N_2O through denitrification was negligible, and all N_2O produced must have thus originated from nitrification (Saggar *et* al., 2004b).

Soil

Soils contribute to about 65 % of the total N_2O produced by terrestrial ecosystems (Saggar *et al*., 2004a; Borhan *et al*., 2012). Although, it is well established that soils are the dominating source for atmospheric nitrous oxide (N_2O), we are still struggling to fully understand the complexity of the underlying microbial production and consumption processes.

Microbial production in soils is the dominant nitrous oxide source; the emissions are increased with use of nitrogen fertilizers (Davidson, 2009; Butterbach-Bahl *et al*., 2013), from manure and urine excreta applied and aerobic and anaerobic degradation of livestock waste in the lagoons and dry manure piles (Crosson *et al*., 2011; Borhan *et al*., 2012; Regaert *et al*., 2015).

The rate of formation and emission of N_2O varies through time with changes in the soil conditions, denitrification rates, type of crop, porosity, moisture content, temperature, redox potential, available carbon, microbial processes, N content of the soil, nitrogen fertilizer type, crop management and soil texture (Carran *et al*., 1995; Bouwman, 1996; Klein and van Logtestijn, 1996; MacKenzie *et al*., 1997; Saggar *et al*., 2004b; Chianese *et al*., 2009). Also, soils are key sites for denitrification and are much more important than groundwater (Bouwman *et al*., 2013).

While rates of emissions from soil vary considerably due to a number of factors, many studies show a rough proportionality between the total N entering the soil from anthropogenic inputs and the amount lost as N_2O. Bouwman (1996) analyzed measurements of N_2O emission from fertilized and unfertilized fields. N_2O losses from anhydrous ammonia and organic N fertilizers or combinations of organic and synthetic N fertilizers were higher than those for other types of N fertilizer. The excreta from grazing animals adds high amount of substrate in soil for N_2O to be produced by the microorganisms (Bhandral *et al*., 2010). Most of the N_2O resulting from manure is produced in manure-amended soils through microbial nitrification under aerobic conditions and partial denitrification under anaerobic conditions, with denitrification generally producing the larger quantity of N_2O (Montes *et al*., 2013).

Soil moisture and temperature

The availability of N and the factors that alter the redox potential of the soil, such as changes in soil moisture conditions have major effects on the production of N_2O in soils (Bhandral *et al*., 2003a; Saggar *et al*., 2004a). MacKenzie *et al*. (1997) and Borhan *et al*. (2011b) reported that N_2O emissions increased when soil moisture increased. Authors noted that rainfall prompted anaerobic denitrification of oxidized nitrogen species in the soil environment. The heavy rainfall increased N_2O emissions (Sun *et al*., 2016). Results of Boon *et al.*

(2014) indicate that N_2O production is strongly related to rainfall events, water content movements and irrigation. According to Regaert *et al.* (2015), the high emission peaks occur due to denitrification in times of anaerobiosis, especially after a rainfall. Whalen (2000) found that simulated rainfall gave pulsed N_2O emission from denitrification of accumulated NO_3-N, indicating that further emissions will occur with an increase in soil moisture. Also, high residual soil NO_3-N can result in additional episodic N_2O efflux in response to rainfall (Whalen, 2000).

In the study of Allen *et al*. (1996), emissions were related to other factors including soil moisture, rate of plant growth and carbon availability. The corresponding data for poorly-drained soil were 0.2 mg N_2O-N.kg^{-1} of deposited dung and 148 mg N_2O-N.kg^{-1} of deposited urine (Allen *et al*., 1996). The largest N_2O fluxes occurred when water-filled pore space values were very high (70-90 %), indicating that denitrification was the major process responsible (Dobbie *et al.*, 1999). Greater fluxes were obtained from grassland soil than from arable soil at equal water-filled pore space values (Dobbie and Smith, 2001). Nett *et al.* (2015) concluded that substantial N_2O emissions can occur after high input of available organic carbon (C) and N even in a coarse-textured soil with low waterholding capacity. N_2O is produced during several microbial processes in the N cycle of terrestrial and aquatic systems (Schils *et al.*, 2013).

Also Luo *et al*. (2015) found that the greatest N_2O fluxes recorded were generally associated with rainfall events and high water-filled pore space. An increase in the water-filled pore space of the soil creates anaerobic conditions that together with high levels of N and C availability in the soil owing to the presence of the excreta would have led to a greater opportunity for N_2O production and emission (Luo *et al*., 2015). The smaller N-emissions from the grassland were attributed to its relatively dry siting on a slope of 20 % (Mogge *et al.*, 1999).

Soil temperature (15 - 20 °C) is the most significant driver of N_2O production with a 1 °C rise in the soil temperature increasing emissions in grassland fields grazed with dairy cows and with young stock (Hargreaves *et al*., 2015). With an increase in temperature from 10 to 20 °C, the denitrification rate increased about 10-fold in non-irrigated plots and three-fold in irrigated plots (Saggar *et al*., 2004b). The positive effect of temperature on denitrification rate was much more pronounced under non-irrigated than under irrigated conditions (Klein and van Logtestijn, 1996; Saggar *et al*., 2004b). Soil temperature in the field was found to limit denitrification rate in all seasons relatively to the denitrification rate measured at 25 °C in the laboratory. This temperature effect was greatest in the cool-wet season (Luo *et al*., 1999). Denitrification losses increased with temperature in pastures treated with cattle slurry, while N-losses from pastures treated with farmyard manure remained unaffected by temperature (Saggar *et al*., 2004b).

Soil condition and type

Several soil-management practices such as soil compaction, tillage and drainage affect the production and transport of N_2O. Emission release is influencing also by the soil's physical conditions, i.e. aeration and soil water content (Saggar *et al*., 2004b). Eckard *et al.* (2010) noted that high N_2O emission rates generally coincide with soil conditions that are conducive to denitrification; nitrification is often an essential prerequisite for the conversion of N fertilizer inputs into soil NO_3^-.

Compaction caused a seven-fold increase in N_2O emission. From the compacted soil, about 10 % of the total N applied as nitrate was emitted, whereas the emission was 0.5 % from the uncompacted soil (Bhandral *et al*., 2003a). In grazed pastures, animal treading is an important cause of soil compaction (Saggar *et al*., 2004). There were no significant differences in emissions among the other three sources (urine, ammonium and urea), which were about one-tenth and one-third of those from nitrate in the compacted and uncompacted soils, respectively (Bhandral *et al*., 2003a).

Porosity has substantial effects on the production of N_2O in soils (Bhandral *et al*., 2003a; Saggar *et al*., 2004a). Exponential increases in flux were occurred with increasing soil water-filled pore space and temperature; increases in soil mineral N content due to fertilizer application also stimulated emissions (Dobbie *et al*., 1999).

Emission of N_2O was higher with no till than with conventional tillage, and with corn than with soybean or alfalfa (Bhandral *et al*., 2003a). A corn system using conventional tillage, legumes in rotation and reduced N fertilizer would decrease N_2O emission from agricultural fields (MacKenzie *et al.*, 1998).

Nitrous oxide emissions from soils are highest when soil aeration is limited (e.g. under wet or compacted soil conditions) and the availability of soil mineral N is high (Klein, 2004). In intensive animal agriculture, high N_2O emission rates generally coincide with anaerobic soil conditions and high soil NO_3^-, primarily from animal urine patches (Klein and Eckard, 2008). However, no effect on N_2O was observed under the aerobic experimental conditions (Leiber-Sauheitl *et al*., 2015). Animal grazing and the use of machinery can also reduce soil aeration due to compaction and pugging, particularly under wet conditions (Klein and Eckard, 2008). Emissions continued over much longer periods (to 60 days) from sandy and stony loams than from a silty clay loam (to 30 days) (Allen *et al*., 1996). The results of Leiber-Sauheitl *et al*. (2015) indicate that sheep excreta do not significantly increase emissions from degraded peat soils. Fluxes of N_2O between grassland and the atmosphere were measured over 1 year using three plots which have been maintained at a constant pH of 3.9, 5.9 and 7.6 over many years (Yamulki *et al*., 1997). The emissions (3 yrs) from winter wheat and spring barley were lower (0.2-0.7 kg N_2O-N.100 kg^{-1} N applied) than from cut grassland (0.3-5.8 kg N_2O-N.100 kg^{-1} N) (Dobbie *et al*., 1999).

Soil pH plays a critical role in determining the overall rate of several important processes in the agricultural nitrogen cycle. During denitrification, the activity of nitrous oxide reductase (N_2O-R) is reduced at low pH. Liming decreased N_2O production under some conditions with the greatest proportional reductions occurring in the urine amended fluvial soil (McMillan *et al*., 2016). It was concluded that the microbial community of the soil had adjusted to the low pH and was responsible for the entire production of N_2O. Chemodenitrification is also responsible for some NO_x production, especially at low pH (Yamulki *et al*., 1997). Under laboratory conditions, similar treatments produced large emissions from loam soils having pH of 4.5–6.5 and zero emissions from a peat soil with pH of 3.8 (Allen *et al*., 1996). Mean fluxes of N_2O decreased appreciably with increasing acidity (Yamulki *et al*., 1997). Sterilization of soil cores by autoclaving reduced N_2O emissions almost to zero at all pH values, but residual production of NO_x was found even at low pH. Increasing the pH of unsterilized soil cores from pH 3.9 to 6.5 led to a reduction in NO_x and especially N_2O fluxes (Yamulki *et al*., 1997).

The study of Whalen *et al.* (2000) indicate that most of the microbial potential for nitrification and denitrification (> 90 %) was located in the upper soil horizons, in the 0- to 20cm soil zone depth. Comparisons of the ^{15}N enrichments in the soil mineral N pools and the evolved N_2O suggested that most of the N_2O was produced in the 5–8 cm zone of the soil (Monaghan and Barraclough, 1993).

Field application

N_2O emissions from soil application of animal wastes are a major contributor to total GHG emissions from agriculture (Mihina *et al*., 2012). N_2O emissions from fertilizer use, manure application and deposition by grazing livestock were estimated at 2,482 Mt CO_2.yr^{-1} in 2010 with an expected 18 % increase by 2020 (Montes *et al*., 2013). The fundamental problem may be that most animal excrements are being applied to small land areas close to animal confinements, resulting in environmental degradation (Sherlock *et al*., 2002).

Although land application can supply nutrients for crop production, it leads to gaseous emissions of N_2O, which can be detrimental to the environment (Sharpe, Harper, 1997). Yamulki *et al.* (1998) noticed that the use of livestock excreta increased N_2O emissions significantly above those from the control plots. Field application is considered to be the main source of agricultural N_2O since all manure types significantly increase microbial production of N_2O from soils (Jungbluth *et al.*, 2001; Crosson *et al*., 2011).

Sources of N_2O emissions are indirect - from wastes storage and direct, associated with volatilisation of land applied manures (Ross *et al*., 2014). The fluxes of N_2O emissions vary with waste, time after application, type of application, supplemental water additions and soil type (Sommer *et al*., 1996; Saggar *et al*., 2004b). The variation in the extent of emissions from different types of manure demonstrates the effect of manure properties such as moisture content, total N and available N content on emission generation (Bell *et al*., 2016). N_2O fluxes were enhanced by the fresh dung but not by urine (Hargreaves *et al*., 2015).

Solid manure

The potential for N_2O emission after manure applications to agricultural soil is dependent on a combination of manure properties and environmental conditions (Bell *et al*., 2016). The results of Allen *et al.* (1996) and Mogge *et al*. (1999) clearly showed that the long-term application of farmyard manure enhanced distinct C-pools in soils available for mineralization and consequently gaseous N-emissions. There were lower nitrous oxide emissions directly from mineral N-fertilizers compared to organic manures.

Mogge *et al*. (1999) measured denitrification N-losses and nitrous oxide emissions from sandy soils. They compared a field fertilized mainly with farmyard manure for 30 years (93 kg N $ha^{-1}yr^{-1}$) with a field fertilized with cattle slurry for 30 years (333 kg N ha^{-1} yr^{-1}) and with grassland (92 kg N ha^{-1} yr^{-1}). Annual gaseous N-losses from field with farmyard manure were twice of those obtained from the other sites (denitrification 4.9 kg N_2O-N. $ha^{-1}yr^{-1}$; nitrous oxide 5.3 kg N_2O-N.$ha^{-1}yr^{-1}$). The smaller N-emissions from the grassland were attributed to its relatively dry siting on a slope of 20 % (Mogge *et al.*, 1999).

Application of cattle dung increased N_2O emissions significantly in comparison to untreated field (fluxes up to 290 μg N.m^{-2} h^{-1}) for period of 15 months (Yamulki *et al.*, 1998). The emission for dung from sheep fed ryegrass during the 3 M measurement (0.13 kg N_2O-N.ha^{-1}) was lower than that from those fed forage rape (0.71 kg N_2O-N.ha^{-1}) (Luo *et al*., 2015).

Urine

According to Di and Cameron (2006), N returns to the soil in animal urine as a major source of N_2O emissions in the intensive animal agriculture. Peak emissions were observed 24-48 h after urea application, high emissions were observed immediately after the urine application with rates reaching a peak of 89 mg N.m^{-2}.d^{-1} within 6 h, with 7 % of the applied urine-N lost as N_2O over 42 days (Saggar *et al*., 2004b). Large emissions were detected immediately following cow urine application to pasture. These coincided with a rapid and large increase in water-soluble C levels in the soil, some of this increase being attributed to the solubilization of soil organic matter by high pH and ammonia concentrations (Monaghan and Barraclough, 1993). Overall, urine significantly increased N_2O emissions up to 14 days after application, with rates amounting to 6 kg N ha^{-1} d^{-1} (Saggar *et al*., 2004b). Application of urine to the soil (at a rate equivalent to 930 kg N.ha^{-1}) increased the amount of mineral and microbial N in the soil. This was followed by increases in emissions of N_2O (from 15 mg N_2O-N.m^{-2}.d^{-1} to 330 mg N_2O-N.m^{-2}.d^{-1}) (Williams *et al*., 1998). The initial rate of N_2O release from the urine treatment was significantly higher than that of the other treatments. The average releases were 9.1, 6.9, 2.6 and 2.1 mg.N_2O-N for the urine, urea, ammonium sulphate and control treatments, respectively (Sherlock and Goh, 1983). A detailed study was carried out to investigate the effects of applying animal urine, fertilizer (ammonium nitrate) and fertilizer+urine on emission of NO and N_2O from soil (Williams *et al*., 1998). The fertilizer was applied at a lower rate than the urine. Nevertheless, the fertilizer still increased NO and N_2O emission with denitrification the dominant process (Williams *et al*., 1998).

Denitrification and N_2O emission rates were measured following two applications of artificial urine (40 g urine N.m^{-2}) to a perennial rye-grass sward on sandy soil (Klein and van Logtestijn, 1994). Urine application significantly increased denitrification and N_2O emission rates up to 14 days after application, with rates amounting to 0.9 and 0.6 g N.m^{-2}.d^{-1} (9 and 6 kg N.ha^{-1} day^{-1}), respectively. Total denitrification losses during the 14 day periods were 7 g N.m^{-2}, or 18 % of the urine-N applied. Total N_2O emission losses were 6.5 and 3 g N.m^{-2}, or 16 % and 8 % of the urine-N applied for the two periods. The minimum estimations of denitrification and N_2O emission losses from urine-affected soil were 45 to 55 kg N.ha^{-1}yr^{-1}, and 20 to 50 kg N.ha^{-1}yr^{-1}, respectively (Klein and van Logtestijn, 1994). The total emission for urine from sheep fed ryegrass during the 3-month measurement was higher (1.19 kg N_2O-N.ha^{-1}) than that from those fed forage rape (0.17 kg N_2O-N.ha^{-1}) (Luo *et al*., 2015).

Klein and van Logtestijn (1994) and Koops *et al*. (1997) proposed that the initial stimulation of N_2O emission on urine application could be explained by either chemodenitrification or by anaerobiosis in microsites, as a result of CO_2 generated from rapid hydrolysis of urinary urea. The reason for the stimulated N_2O release caused by urine is unclear. One possibility is a chemical reaction (chemodenitrification) between minor urine components, especially amino acids and soil constituents.

Urine patches are considered to be important sites for N_2O production through nitrification and denitrification due to their high concentration of N. Nitrous oxide production was largest in the centre and decreased towards the edge of the patch. Maximum N_2O production was about 50 mg N.m^{-2}.d^{-1} and maximum denitrification activity was 70 mg N.m^{-2}.d^{-1}. Total N loss through nitrification and denitrification over 31 days was 4.1 g N per patch, which was 2.2 % of the total applied urine-N (Koops *et al*., 1997). Variability in N_2O emissions from urine patches can arise due to differences in the urine composition, the amount of N excreted and the volume and frequency of urine events (Dijkstra *et al*., 2013; Marsden *et al*., 2016). Emissions from the urine patches were significantly greater than from the dung. The flux pattern showed a strong diurnal variation with maximum fluxes generally occurring in the late afternoon or early morning, and generally not in phase with the soil temperature changes (Yamulki *et al*., 2000).

Klein *et al*. (2003) applied cow urine and synthetic urine to pastoral soils. The largest emission factor was found in a poorly drained soil, and the lowest emission factor was found in a well-drained stony soil. The N_2O emissions had not reached background levels 4 months after urine application. In the study of Lovell and Jarvis (1996) urine was added to intact turfs taken from long-term permanent pasture on clay loam and sandy loam soils. The emissions of nitrous oxide following urine application were high (0.36 µg N_2O-N.m^{-2} min^{-1} and 29 µg N_2O-N.m^{-2} min^{-1}) but short-living (< 40 days).

Urine-treated plots (50 g N.m^{-2}) were compared to control plots to which only water (12 mg N.m^{-2}) was applied. N_2O emission peaked at 88 mg N_2O m^{-2}.d^{-1} 12 days after application. Subsurface N_2O concentrations were higher in the urine-treated plots than the controls. Subsurface N_2O peaked at 500 ppm 12 days after and 1200 ppm 56 days after application (Boon *et al*., 2014).

Cattle urine has been shown to stimulate N_2O production to a larger extent than dung due to the dual effect of a large pool of readily available N and C and increased soil water content (Boon *et al*., 2014). Application of cattle urine increased N_2O emissions significantly over that measured from control (untreated) plots and fluxes up to 192 µg N m^{-2} hr^{-1} from urine were measured over a period of 15 months (Yamulki *et al*., 1998).

Although the total average N_2O-N emissions from the dung (9.9 mg N_2O-N patch^{-1}) were equal to those from the urine (9.5 mg N_2O-N.patch^{-1}), the average loss from the urine (0.56 %) was much higher than from the dung (0.19 %) (Yamulki *et al*., 1998; Saggar *et al*., 2004b).

Slurry manure

Nitrous oxide emission from grazed dairy pasture was increased following application of slurry (farm dairy effluent). Comfort *et al*. (1990) recorded the largest emission of N_2O occurred shortly after the injection of liquid dairy cattle manure. Maximum loss occurred 5 days after injection. Higher N_2O emission was measured, when slurry was applied immediately after a grazing event. Bhandral *et al*. (2010) found that application of slurry immediately after grazing event creates conducive conditions for denitrification and also might cause priming effect on the soil. Delaying effluent irrigation after a grazing event could reduce emissions by reducing levels of surplus mineral-N. Similarly, Sharpe and Harper (1997), Whalen *et al*. (2000) and Li *et al*. (2015) suggested that emissions decreased to pre-fertilization levels within a few days. Schils *et al*. (2013) found that N_2O loss increased immediately after slurry injection and was followed by a shift in the N_2 emissions.

Slurry injections have been shown to promote conditions leading to denitrification by denitrifying bacteria, creating an anaerobic environment abundant in an inorganic N and readily oxidisable C (Comfort *et al*., 1988). In the study of Rodhe *et al.* (2006), cattle slurry was either injected below the ground or spread out on the soil surface. The injection of slurry gave rise to a broad peak of N_2O emissions during the first three weeks after application.

Lowrance *et al*. (1998) applied liquid dairy manure at four N rates (246, 427, 643, and 802 kg N ha^{-1} yr^{-1}). Denitrification rates and soil N pools increased after manure application at all rates of application. The two highest rates of manure had highest denitrification amounts. Denitrification ranged from 11 to 37 % of total N applied in the manure. Nitrous oxide evolution from the liquid dairy-manure application was often found to be greater than total denitrification from row crops on similar soils fertilised with similar rates of inorganic fertiliser (Saggar *et al*., 2004b).

Emissions of N_2O from waste storages depend on whether dung and urine are collected unmanaged in corrals and paddocks, or stored anaerobically as slurry in pits and lagoons (with or without anaerobic fermentation for biogas collection, or amended with litter in deep litter stables (Oenema *et al*., 2005). Bhandral *et al*. (2003a) and Saggar *et al.* (2004b) showed that untreated dairy-farm effluent resulted in higher emissions (0.447 kg $N.ha^{-1}$) than treated dairy-farm effluent (0.382 kg $N.ha^{-1}$) over the experimental period.

Several studies with swine effluents have shown that application of these slurries increases N_2O emissions (Cabrera *et al*., 1994; Bhandral *et al*., 2003a; Saggar *et al*., 2004b). Some unidentified component of liquid swine waste may negatively impact the microbial community, as N_2O emissions were significantly less than for soils amended at a comparable level with a liquid NH_4-N fertilizer. Nitrous oxide emission from fertilization was directly related to the level of fertilization to 150 kg $N.ha^{-1}$ (Whalen, 2000). The direct effects of fertilizer application appear to be more immediate and short-lived for liquid swine waste (9200 µg N_2O-$N.m^{-2}.h^{-1}$) than for manures and slurries, which have a slower release of nitrogenous nutrients (Whalen *et al*., 2000).

Whalen *et al*. (2000) recorded 395 $mg.m^{-2}$ N_2O-N emitted after applied 29.7 $g.m^{-2}$ (297 kg $N.ha^{-1}$) of liquid lagoonal swine waste. The fractional loss of applied N to N_2O (corrected for background emission) was 1.4 %, in agreement with the mean of 1.25 % reported for mineral fertilizers (Whalen *et al*., 2000). Piggery effluent emitted the highest proportion of N_2O-N among the effluents used, with emissions of 0.585 kg $N.ha^{-1}$ or 2.17 % of the total added effluent-N (Saggar *et al*., 2004). Increased N_2O emission from a spray field fertilized with liquid swine waste was due to the interactive effects of increases in soil moisture and N (Whalen, 2000).

Application timing

Nitrous oxide emission varies with the nature of the effluent applied. Nitrous oxide emissions from land-applied effluent are highly dynamic and affected by application time, application method and rainfall or irrigation (Li *et al*., 2015). However, the dominant environmental factors influencing N_2O losses include wind speed and temperature (Li *et al*., 2015). Following field application, infiltration of liquid is influenced by manure organic matter (Petersen and Sommer, 2011).

According to Bell *et al.* (2016), the timing of application can be critical if significant losses of N from the soil are to be avoided. Conversely, loss of N via N_2O emissions is higher when manure is applied under wet conditions as N_2O production via denitrification will occur before the crop is able to utilise the available N. A proportion of N that volatilises as NH_3 is considered to be re-emitted as N_2O upon wet or dry deposition to soils from N excretion by animals (Crosson *et al*., 2011).

A number of studies have shown that soil denitrification and N_2O emission rates are highly variable throughout the season, with high rates being associated with grazing and fertiliser application in grazed pastures (Ruz-Jerez *et al*., 1994; Williams *et al*., 1998; Luo *et al.*, 1999; Saggar *et al*., 2004a,b). The highest losses by denitrification occurred in winter when soil moisture was at or above field capacity for extended periods (Ruz-Jerez *et al.*, 1994).

Manure application timing (fall vs. spring) had no effect on N_2O emissions for the annual system. Spring application has been recommended as a mean to mitigate N_2O because it avoids the high N_2O fluxes related to spring thaw and the N is supplied to a growing crop that may reduce soil mineral N availability for nitrifiers and

Table 1: N_2O emission from land application of manure and effluent or slurry

N_2O flux, spring; fertilized grassland vs. fertilized winter wheat; spread over 2 ds, closed chambers; 0 to 134 g N_2O-N ha^{-1} d^{-1} vs. 0 to 26.4 g N_2O-N ha^{-1} d^{-1} (Ball *et al.*, 1997).

Fluxes, onion (*Allium cepa* L.) field, 100 gas samples, plastic CCH, GC; 331 μg N m^{-2} h^{-1}, CV 217 % (Yanai *et al*., 2003).

Pigs SLR, during storage and after field application (permanent grassland); 5 MS, 10 m^3 slurry tanks; twice a wk, ODC, FTIR, ds 1, 2, 4, 8, 13, 20, CCH, GC; untreated 56.2 $g.m^{-3}$ (100.0 %), separated 41.3 $g.m^{-3}$ (73.5 %), anaerobically digested 77.2 $g.m^{-3}$ (137.5 %), straw covered 167.5 $g.m^{-3}$ (298.2 %), SLR aerated 558.6 $g.m^{-3}$ (994.5 %) (Amon *et al*., 2006a).

Dairy cattle SLR, during storage and after field application (grassland); 5 MS, 10 m^3 SLR tanks; twice a wk, OCH, FTIR, ds 1, 2, 4, 8, 13, 20, CCH, GC; untreated 23.9 $g.m^{-3}$ (100.0 %), separated 28.6 $g.m^{-3}$ (119.7 %), anaerobically digested 31.2 $g.m^{-3}$ (130.3 %), straw covered 52.5 $g.m^{-3}$ (219.7 %), SLR aerated 54.2 $g.m^{-3}$ (226.8 %) (Amon *et al*., 2006a).

Intensively farmed pastures, silt loam; 1 h, CCH, GC; from 0 to 100 kg $N.ha^{-1}d^{-1}$, annual emission 3-5 kg N_2O-$N.ha^{-1}$ (Carran *et al*., 1995).

Pigs and dairy SLR; 3 application, grassland, April, July, October (50 $m^3.ha^{-1}$); measured 20, 22, and 24 d after application; April, dairy SLR 1.51 kg N_2O-$N.ha^{-1}$ vs. pig SLR 0.77 kg N_2O-$N.ha^{-1}$; July, dairy SLR 0.34 kg N_2O-$N.ha^{-1}$ vs. pig SLR 0.57 kg N_2O-$N.ha^{-1}$; October, dairy SLR 0.15 kg N_2O-$N.ha^{-1}$ vs. pig SLR 0.74 kg N_2O-$N.ha^{-1}$ (Chadwick *et al*., 2000).

Pigs SLR, application, pasture, 90-d period (60 m^3 ha^{-1}, 6.1 kg total N m^3, pH of 8.14), d 25: 7.5 g $N.ha^{-1}h^{-1}$, d 67: 15.8 g $N.ha^{-1}h^{-1}$, background levels after 90 ds, total 7.6 kg N ha^{-1} (2.1 % of the N applied) (Sherlock *et al.*, 2002).

Pigs SLR, 12 ha oat field, 150,000 $plants.ha^{-1}$; sprinkler irrigation, 29,000 m^3 applied, 3 irrigations (ds 94, 101, and 108 of yr); TDL, from 19 g N_2O-N ha^{-1} d^{-1} to 0.25 to 0.38 kg N_2O-N ha^{-1} d^{-1} after first 2 irrigations, total 4.7 kg N_2O-N ha^{-1} (Sharpe, Harper, 1997).

Pigs SLR, 1,200 sows, farrow-to-finish swine farm; applied to soybean, pH 8.0, 3 irrigations (237, 242, 246 ds of yr), summer, total N in effluent 556 $\mu g.g^{-1}$, 537 $\mu g.g^{-1}$, 590 $\mu g.g^{-1}$, amount applied 144.6 kg $N.ha^{-1}$, 59.1 kg $N.ha^{-1}$, 70.8 kg $N.ha^{-1}$, total applications 274.6 $kg.ha^{-1}$ of total N; TDL; before effluent applications 0.016 g N_2O-$N.ha^{-1}$ d^{-1}, increased to 25 N_2O-$N.ha^{-1}$ d^{-1} to 38 g N_2O-$N.ha^{-1}$ d^{-1} after irrigation, total emissions 4.1 kg N_2O-$N.ha^{-1}$ (Sharpe, Harper, 2002).

3 grassland fields (dairy cows, young stock or cut for silage); 240 $N.kg.ha^{-1}$, 170 $N.kg.ha^{-1}$, 196 $N.kg.ha^{-1}$ during the 6 M prior study; CCH, 117.9 ng $N.m^{-2}.s^{-1}$, 243.5 ng $N.m^{-2}.s^{-1}$), 7.05 ng $N.m^{-2}.s^{-1}$ (Hargreaves *et al*., 2015).

Sheep urine, male Romney lambs, fed ryegrass vs. brassica rape; applied (perennial ryegrass/white clover pasture, poorly drained silt-loam soil); 3 M, CCH, GC; 1.19 kg N_2O-$N.ha^{-1}$, 0.17 kg N_2O-$N.ha^{-1}$ (Luo *et al*., 2015).

Sheep dung, male Romney lambs, fed ryegrass vs. brassica rape; applied (perennial ryegrass/white clover pasture, poorly drained silt-loam soil); 3 M, CCH, GC; 0.13 kg N_2O-$N.ha^{-1}$, 0.71 kg N_2O-$N.ha^{-1}$ (Luo *et al.*, 2015).

Abbreviations

C = carbon
CCH = closed chamber
CO_2 = carbon dioxide
CV = coefficient of variation
d = day
ds = days
FTIR = Fourier transform infrared spectroscopy
GC = gas chromatography
h = hour
M = month
MS = manure system
N = nitrogen
NH_3 = ammonium
ODC = open dynamic chamber
SLR = slurry
TDL = Tuneable Diode Laser absorption spectrometer
yr = year
yrs = years
wk = week
wks = weeks

denitrifiers (Chadwick *et al*., 2011). Abalos *et al.* (2016) found that N_2O fluxes associated with freeze-thaw events were reduced when manure was applied in spring. However, applying manure in spring also implies higher N availability when soil temperature is rising and rainfall events are frequent, enhancing soil microbial activity. As a consequence, the highest N_2O peaks of the experimental period were measured for the spring treatment after significant rainfall events (Abalos *et al*., 2016). Bell *et al.* (2016) applied slurry and farmyard manure of cattle, broiler litter and layer manure on winter wheat. Mean annual N_2O emissions were greater in autumn (2 kg N_2O-N.ha^{-1}) than in spring (0.35 kg N_2O-N.ha^{-1}) applications, and in the spring experiment they were significantly lower from cattle slurry than from other treatments.

Allen *et al*. (1996) measured nitrous oxide (N_2O) emissions from different soils under grass after treatment with cow dung and urine in two seasons. N_2O emission rates were much higher during autumn-winter than during spring-summer, and in the case of well-drained soil were substantial for both excreta types (207 mg N_2O-N.kg^{-1} of deposited dung and 197 mg N_2O-N.kg^{-1} of urine in autumn-winter). The ratio of nitrogen released as N_2O to the amount of N excreted by the livestock varied from 0 % (summer) to 0.8-2.3 % (winter), consistent with loss rates observed for mineral fertilizers (Allen *et al*., 1996).

The evaluation models must include adequate flexibility to predict cold soil emissions as well as emissions under tropical conditions. Some recent studies indicate that many of the published direct estimates of N_2O emissions from agricultural fields may be further underestimated because they did not account for cold season N_2O emissions, which can be substantial (Mosier *et al*., 1998ab).

CONCLUSION

N_2O emissions from soils are the largest contributor to global greenhouse gas emissions. Nitrous oxide emissions are moderated by many factors, but the most important are temperature, water-filled pore space, available soil carbon, soil pH and soil nitrate. Nitrous oxide emissions from soils are highest when soil aeration is limited (wet or compacted soil conditions) and the availability of soil mineral N is high. Recent studies have shown that avoiding soil compaction or increasing soil drainage can substantially reduce N_2O emissions from soils.

Animal wastes from husbandry are an excellent nutrient source. Applying manure or effluents to agricultural fields has been shown to increase crop yields, improve the water-holding capacity of the soil and enhance soil fertility.

However, for efficient use of manure some considerations have to be made. Technology for applying manure or effluents to the land must take into account external factors when predicting N_2O releasing following manure application. Manure applied to frozen soil may be carried off to lakes and streams during thaws or during winter or early spring rains. To minimize this risk when soils are frozen, manure has to be applied only to relatively flat fields. N_2O volatilization can be reduced considerably by the use of optimum application with shallow injection compared with surface spreading. Conditions favouring N_2O losses are more often met in fall and winter than in spring and summer. Manure should be applied as soon as possible after plant cutting to reduce potential injury to the re-growth; applying when the soil is not wet, manure spreaders cause compaction on the wet soils.

An extended review revealed that more data are needed to better quantify emissions from manure management, therefore, a further research is required.

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