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Review Article

Factors Influencing Methane (CH_4) and Nitrous oxide (N_2O) Emissions from Soils: A Review

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Abstract: Methane (CH_4) and nitrous oxide (N_2O) are the two most important non-carbon dioxide (CO_2) greenhouse gases (GHGs) that play a critical role in shaping the global climate. Their concentrations in the atmosphere have been significantly increased by human activities. CH_4 has contributed to an estimated 18–20% of post-industrial anthropogenic global warming and is 25 times more effective in absorbing radiation that atmospheric CO_2. Its production and consumption in soils is affected by numerous factors including water table depth. Nitrous oxide is one of the key ozone (O_3) depleting gases, constituting 7% of the anthropogenic greenhouse effect. On a molecular basis, N_2O has 298 and 16 times higher global warming potential than that of CO_2 and CH_4 respectively over a 100-year period. Nitrous oxide is produced in soils by denitrification and nitrification processes. It is affected by many physical and biochemical factors such aeration/moisture status of the soil.

Keywords: Emission, greenhouse gases, methane, nitrous oxide, soil

Introduction

Greenhouse gases (GHGs) methane (CH_4) and nitrous oxide (N_2O) are the two most important non-carbon dioxide (CO_2) greenhouse gases. GHGs in the atmosphere play a critical role in shaping the global climate, and human activities have significantly modified the concentrations of these gases. Methane (CH_4) is the second most prevalent greenhouse gas from human activities after CO_2 (Schimel and Gulledge; 1998; Van den Pol-van Dasselaar *et al*., 1999). It is emitted by natural sources such as wetlands (IPCC 2007), as well as anthropogenic activities such as biomass burning, rice production, fossil fuel exploitation, digestive processes in ruminants, sewage treatment plants and landfill use (Crutzen, 1991; Lelieveld *et al*., 1998; IPCC 2007). The concentration of CH_4 in the atmosphere has risen from the pre-industrial level of 0.75 µmo1 mol^{-1} (Lelieveld *et al*., 1998; Schimel 2000; Smith *et al*., 2003). The growth rate in CH_4 concentration is changing considerably and the very large and interannual variations in CH_4 concentration remain unexplained; thus present an important challenge to the research community (Fowler *et al*. 2009; IPCC 2007). CH_4 has contributed to an estimated 18–20% (Hütsch 2001; Knittel and Boetius, 2009; Zhuang *et al*., 2009) of post-industrial global warming (Brzezińska *et al*., 2012). Weight to weight, the comparative impact of CH_4 on climate change is 25 times greater than CO_2 over a 100-year period, which means that 1 kg of CH_4 is 25 times more effective in absorbing radiation as 1 kg of atmospheric CO_2 (IPCC, 2007). A total of 600 Tg CH_4 are estimated to be released to the atmosphere globally (Lelieveld *et al*., 1998; Smith 2005), with wetland soils, rice paddies and the raising of livestock contributing 70% of the emissions (IPCC 2007).

After CO_2 and CH_4, N_2O is the third most important greenhouse gas. It is naturally present in the atmosphere as part of the earth's nitrogen cycle, and has a variety of natural sources. In nature, it is emitted from soils and oceans. Nitrous oxide emissions from human activities include the cultivation of soil, the production and use of fertilizers, and the burning of fossil fuels and other organic material. Nitrous oxide is not stored in significant amounts through natural processes or actively taken out of the atmosphere. As a powerful GHG in the troposphere it contributes to ozone depletion in the stratosphere (Cicerone 1987). Its concentration in the atmosphere has increased from the industrial revolution level of 0.275 µmo1 mol^{-1} to the current level of 0.320 µmo1 mol^{-1} due to emissions from different sources. It has been increasing at an average global concentration of 0.2 to 0.3% in recent decades (Flessa *et al*., 1995; Conrad, 1996; Mosier *et al*., 1998a). Nitrous oxide molecules stay in the atmosphere for an average of 120 years before being removed by a sink or destroyed through chemical reactions. The impact of one kilogram of N_2O on warming the atmosphere is 298 times than 1 kilogram of CO_2 over a time period of 100 years (IPCC, 2007). The concentrations of CH_4 and N_2O in the atmosphere result from the balance between processes contributing to uptake and release (von Arnold *et al*., 2005). Together with CO_2, they are considered the primary causes of global climate change (IPCC, 2007).

Sources and sinks for atmospheric CH_4

A *source* is any process or activity through which CH_4 is released into the atmosphere. Both natural processes and human activities release CH_4. Methane sink is a reservoir that takes it up from another part of its natural cycle. Methane has both natural sources such as wetlands, gas hydrates, permafrost, termites, oceans, freshwater bodies, non-wetland soils and other sources such as wildfires. Anthropogenic or human activities that produce CH_4 include fossil fuel production and transport, livestock and manure management, rice cultivation, and waste management (i.e., landfills and the burning of biomass) (Crutzen 1991; Lelieveld *et al*. 1998). Estimated total global annual CH_4 emissions from anthropogenic and natural sources are about 600 Tg CH_4 yr^{-1} (Lelieveld *et al*., 1998; Smith 2005; Whalen 2005; Prather and Hsu 2010). Major sources of CH_4 include the ruminant animal population (about 15% of the calculated annual CH_4 release), rice paddies (20%), gas loss during coal mining and oil production (14%), biomass burning (10%), and natural wetlands (24%) (Cicerone and Oremland 1988, Whalen 2005).

Soils are the most important biological sources and sinks for atmospheric CH_4 (Le Mer and Roger 2001; Dutaur and Verchot 2007). Methane is produced under water saturated conditions present in wetlands by anaerobic decomposition of organic material

by methanogenic bacteria (Lloyd *et al*., 1998; Hou *et al*., 2000; Yavitt and Williams, 2000). Methanogens are strictly anaerobic unicellular organisms belonging to phylogenetic domain *Archea* (Garcia 1990). Most methanogens are methophilic, able to function in temperature ranging from 20 to 40°C (Topp and Pattey 1997). Once CH_4 is produced, it can be released into the atmosphere through any of the three following pathways: (i) diffusion of dissolved CH_4 along the concentration gradient, (ii) transport via the aerenchyma of vascular plants, or (iii) release of CH_4- containing gas bubbles, i.e., ebullition (Chanton 2005). Methane emitted from the soil to the atmosphere is the net balance between production and consumption controlled by methanogens and methanotrophs (Sundh et al., 1994; Chan and Parkin 2001; Dutaur and Verchot 2007; Chen *et al*., 2009).

Sinks for atmospheric CH_4 were estimated to be 580 Tg yr^{-1} due to hydroxyl radicals (OH) oxidation and via microbial oxidation in soils (Whalen 2005). Methane's reaction with hydroxyl radicals is often counted as methane sinks (Wang and Ineson 2003), but technically, it does not result in methane storage or removal from the atmosphere. They initiate a series of chemical reactions by which CH_4 becomes one of several non-greenhouse compounds that are then removed from the atmosphere through precipitation or another means.

Methane is consumed (oxidized to CO_2) by methane-oxidizing bacteria (methanotrophs) (Singh and Tate 2007) in many soils which is the main CH_4 biological sink in terrestrial ecosystems (Adamsen and King 1993; Sundh *et al*., 1994; Castro et al, 1995; Butterbach-Bahl *et al*., 1998; Roura-Carol and Freeman 1999; Smith *et al*., 2000; Sjögerten et al, 2007). This process simply exchanges one greenhouse gas for another. However, CH_4 is much more powerful than CO_2 as a GHG. Oxidation of atmospheric methane by methanotrophic bacteria in well-drained soils accounts for about 10% (Topp and Pattey 1997) of the global methane sink, that is about 22−100 Tg yr^{-1} (Smith *et al*., 2000; Castaldi *et al*., 2006; Dutaur and Verchot 2007). CH_4 is also oxidized in wetland soils but at comparatively low rates in the interface of the soil before it is released into the atmosphere (Ding *et al.*, 2003). An estimated 37% of atmospheric methane consumed in terrestrial ecosystems is oxidized in temperate and tropical forest soils (Steudler et al., 1989).

Sources and sinks for atmospheric N_2O

Land surfaces are the main source of atmospheric N_2O; thus, changes in land-use practices modify soil emissions and influence N_2O concentration in the atmosphere (Kroeze *et al*., 1999). It is estimated that roughly half of the global N_2O emissions are anthropogenic (Davidson, 1991; Khalil and Rasmussen, 1992; Hutchinson, 1995; Prasad, 1997). Soils are the most important global sources of atmospheric N_2O (Williams *et al*., 1992; Bouwman *et al*., 1993). Nitrous oxide is produced by microbial processes of nitrification and denitrification (Regina et al., 1996; Bremner1997; Machefert et al., 2002; Mosier et al., 2004; Koponen et al., 2006) and dissimilatory NO_3^- reduction to NH_4^+ (Silver *et al*., 2001) in soils. The two microbial processes are controlled by environmental factors, cropping systems, soil management practices (Ellert and Janzen, 2008), inorganic or organic fertilization and by soil moisture content (Zou et al., 2007). Denitrification is an anoxic process that is important in producing and releasing N_2O in saturated organic soils (Smith et al., 1998; Dobbie et al., 1999; Ruser et al., 2001), whereas nitrification or the oxidation of ammonium (NH_4^+) or ammonia (NH_3) to nitrate via nitrite (Bollman and Conrad 1998; McLain and Martens 2005) is important in aerobic soils (Wrangle *et al*., 2001).

Approximately 80% of the global N_2O emissions from human activities are contributed by agriculture, more than half of which is released directly from agricultural soils and animal systems and the indirect emissions from soil through loss of nitrogen to aquatic system and atmosphere (Groffman *et al*., 1998; Mosier *et al*., 1998b; Kroeze *et al*., 1999; McMahon and Dennehy 1999; Gödde and Conrad 2000; Reay *et al*., 2004). Annual emissions from agricultural system amounts to 6.3 Tg N_2O-N yr^{-1} (Mosier *et al*., 1998b). The increase in emissions from agriculture is primarily caused by increased N input into agricultural soils (Mosier *et al*., 1998b). The use of nitrogenous fertilizer has risen sharply worldwide in recent years. This is expected to increase further to meet the food demand of the growing population. Consequently, the emission of N_2O from the soil would also increase (Sangeetha *et al*., 2009).

Factors that affect methane fluxes

Water table depth

Methane production and consumption in soils is affected by numerous factors. These include water table position (Moore and Roulet 1993; Roulet *et al*., 1993; Granberg *et al*., 1997; Tuittiala *et al*., 2000; Frenzel and Karofeld., 2000, Yang *et al*., 2006; Ding and Cai 2007) which determines the partitioning between aerobic and anaerobic zone in wetland sediments (Moore and Roulet, 1993). The position of the water table influence methane emissions in a number of ways. The water table depth must be at a level where organic matter is within an anaerobic environment. If the water table is not at a level where organic matter is within an anaerobic environment, methane oxidation will occur (Freeman et al., 1993; Roulet et al., 1993; Martikainen et al., 1995; Nykänen et al., 1998; Sundh et al., 2000; Minkkinen et al., 2002). Once a sufficient water table is met for methane production, changes in water table position will influence methane flux in two ways (Long 2006). First, a fluctuation in water table will either increase or decrease the anaerobic soil volume where methane production occurs. A higher or elevated water table will cause a larger soil volume for methane production, whereas a lowered table will cause a smaller soil volume for methane production. Secondly, fluctuations in water table depth will either increase or decrease the aerobic soil volume, where methane oxidation occurs. An increase in water table depth will increase the soil volume where methane oxidation occurs; whereas a decrease in water table depth will decrease the soil volume where methane oxidation occurs. With a higher water table causing a larger soil volume for methane production and a smaller soil volume for methane oxidation, an increase in water table position is commonly associated with an increase in net methane emission to the atmosphere (Verma *et al*., 1992). Conversely, a decrease in water table position will cause a decrease in net methane emission to the atmosphere (Moore and Roulet, 1993; Roulet *et al*., 1993). Furthermore, the water table depth can reach a point where the level of oxidation exceeds production, and there is a net influx of methane to the ecosystem (Roulet *et al*., 1993).

Soil Temperature and substrate availability

In addition to water table, the production and consumption of methane is also influenced by soil temperature (Crill et al., 1988; Dunfield *et al*., 1993; Castro *et al*., 1995; Alford *et al*., 1997; Komulainen *et al*., 1998; Heyer and Berger 2000). Methane is produced by the anaerobic breakdown, or digestion, of organic material by methanogenic bacteria. The bacterial activity is closely related to temperature and different types of bacteria have adapted their activity to different temperature ranges. An increase in soil temperature can increase both CH_4 production (Valentine *et al*., 1994; Zhuang *et al*., 2004) and consumption (Einola et al., 2007; Visvanathan *et al*., 1999). Although increasing soil temperature influences both CH_4 production and oxidation, it has been shown to increase net methane fluxes from peatlands (Alford *et al*., 1997; Crill *et al*., 1988; Hargreaves *et al*., 2001; Heyer and Berger, 2000; Macdonald *et al*., 1998; Sachs *et al*., 2008).

Methane fluxes increase with increased soil temperature, but results differ in the observed relationship between temperature and methane emissions. A linear dependence of methane generation at low temperatures has been reported in some studies (Kaharabata *et al*., 1998; Macdonald *et al*., 1998; Sharpe and Harper, 1999; Heyer and Berger 2000). Other studies report an exponential dependence of methane emission rate on temperature (Husted, 1994; Khan *et al*., 1997; Macdonald *et al*., 1998; Sommer *et al*., 2000; Hargreaves *et al*., 2001; Sachs *et al*., 2008; Wille *et al*., 2008). Methane production and consumption rates are also influenced by substrate availability which drives carbon mineralisation (Svenson and Sundh, 1992; Whiting and Chanton, 1993; Christensen *et al*., 2003; Strom *et a*l., 2003) and net ecosystem exchange of CO_2 (Joabsson *et al*., 1999, Dunfield *et al*, 1993). The carbon substrates provide methanogenic microorganisms with molecules to metabolize in order to produce energy.

Nitrogen fertilisation

Mineral nitrogen affects CH_4 fluxes in many ecosystems (Steudler *et al*., 1989; Sitaula *et al*., 1995; Cai *et al*., 1997; Suwanwaree and Robertson 2005). Steudler *et al*. (1989) applied 120kg N ha^{-1} $year^{-1}$as NH_4NO_3 and observed that CH_4 emissions were enhanced by 33%. Suwanwaree and Robertson (2005) added N to a forest site at 100 kg ha^{-1} and observed a 60% increase in CH_4 fluxes. The increase in methane fluxes from nitrogen fertilised soil has been attributed to nitrogen's ability to inhibit CH_4 oxidizing soil microorganisms (Van den Pol-van Dasselaar *et al*., 1999) or by changing the composition of the soil microbial community (Saari et al., 1997; Van den Pol-van-Dasselaar *et al*., 1999; Kähkonen *et al*., 2002).

Land use change and Management

Land use changes such as converting forests and grasslands to arable land decreases the oxidation of CH_4 (Dobbie and Smith 1996;; Smith *et al*., 2000; Ball *et al*., 2002; Merino *et al*., 2004; Tate *et al*., 2007). A mixed deciduous forest in Scotland was found to consume 2.19 to 2.97 mg m^{-2} day^{-1}, compared to 0.82 mg m^{-2} day^{-1} consumed in an adjacent cultivated land used for arable agriculture (Dobbie and Smith 1996). The decrease in CH_4 consumption after land use changes has been attributed to the disturbance on the population and activity of soil microorganisms responsible for CH_4 oxidation (Knief *et al*., 2003; Seghers *et al*., 2003; *Tate et al*., 2007). Soils than have been out of cultivation for a long time were found to consume CH_4 ten times faster than their recently cultivated counterparts (Willison *et al*., 1995). Drainage experiments conducted in peatland soils have shown that lowering the water table depth improve aeration on the peat surface and increases oxidation of methane (Roulet *et al*., 1993; Glen *et al*., 1993; Martikainen *et al*., 1995; Nykänen *et al*., 1995).

Factors affecting Soil N_2O fluxes

Soil temperature

Nitrification and denitrification rates increase with increasing temperature (Granli and Bøckman, 1994; Skiba *et al*., 1998; Smith *et al*., 1998; Koponen *et al*., 2006). Soil temperature controls many biological processes in soils and in the case of N_2O production; it may affect microbial processes by stimulating N_2O producing soil microorganisms. Studies indicate that denitrification proceeds at temperatures as low as –4°C and that temperatures above 5°C are required for the rates to be significant are cited by Granli and Bøckman (1994). Temperature exerts more control over soil N_2O production in soils that are not limited by soil moisture and substrate availability (Skiba *et al*., 1998; Smith *et al*., 1998). However, lack of relationship between N_2O emission and temperature has been observed in some studies (Willers *et al*., 1993; Sommer *et al*., 2000).

Soil moisture and aeration

Soil-water content influences N_2O emissions from all soil types. It influences the release of N_2O from soil through regulating the reactions of oxidation and reduction (Bollmann and Conrad, 1998). Soil moisture can directly or indirectly influence denitrification by providing a suitable environment for microbial growth and activity, preventing the supply of oxygen to micro sites by filling soil pores, releasing available C and N substrates during wetting and drying cycles and through provision of a diffusion medium through which substrates and products are moved to and away from soil microorganisms (Aulakh *et al*., 1992). It has been shown that after rainfall and irrigation, denitrification rate increases due to decrease oxygen diffusion into the soil (Ryden and Lund, 1980; Ruser et al., 2001). Therefore, the rate of N_2O emission increases with increasing soil moisture content from air dry to field capacity (Sitaula and Bakken, 1993; Dobbie and Smith, 2001).

Oxygen inhibits denitrification (Knowles, 1982) and the effect of soil moisture on denitrification occurs through its control over O_2 diffusion. The diffusion of oxygen in water is 1×10^4 times slower. Thus wet soils are more anaerobic with higher rates of denitrification and decreased nitrification. Denitrification can also occur in well-aerated soils in the presence of anaerobic micro sites (Müller *et al*., 1997; Russow *et al*., 2009). In soil incubation studies conducted in a laboratory by Goodroad and Keeney (1984) N_2O production increased when soil moisture content was increased from 0.1 to 0.3 cm cm^{-3}. The process of nitrification is important in N_2O emissions in well aerated coarse-textured soils with <60% water filled pore space (WFPS) (Skiba *et al*., 1992; Skiba and Ball 2002; Bollmann and Conrad 1998; Bouwman *et al*., 2002; Mexiner and Yang, 2004). However, fine- textured soils which are poorly aerated provide conditions that favour denitrification (Groffman and Tiedje, 1991; Dobbie *et al*., 1999). Thus

denitrification becomes a major source of N_2O emissions at lower oxygen partial pressure (<0.5 vol. %) and higher WFPS (>60%) (Davidson, 1993; Scholefield *et al*., 1997; Bronson and Fillery, 1998; Khalil *et al*., 2002). The WFPS depends on the balance between the amount of water entering the soil from precipitation or irrigation and the combined effect of evapo-transpiration and drainage (Dobbie and Smith 2003, 2006). Poorly drained fine soils are likely to emit more N_2O for a longer period than their well-drained coarse textured counterparts (Groffman and Tiedje, 1989; Aulakh *et al.*, 1991; Clayton *et al*., 1997; Dobbie and Smith, 2003; Saggar *et al*., 2004).

Soil pH

Soil pH is one of the regulators of microbiological processes that influence N_2O production. Nitrification activity generally increases with soil pH (Bremner and Blackmer, 1981; Bramley and White, 1989). The optimal pH for nitrification is approximately 7 to 8 (Haynes, 1986). Soil fertilised with NH_4^+ and incubated under aerobic conditions revealed that N_2O production increased significantly with increasing pH up to about 8 (Wang and Rees, 1996). Although the critical threshold for nitrification is 5, it has been shown to occur at a soil pH of 4.5 due to acid-adapted nitrifier strains (Bouwman, 1990) which show that acidity also favours N_2O production in soils (Martikainen and Boer, 1993). At soil pH above 8.2, nitrite accumulates in the soil, and is then reduced to N_2O because competitive biological oxidation of nitrite by *Nitrobacter* is prohibited (Chalk and Smith, 1983). Denitrification can occur over a wide range of soil pH values (5 to 8) (Weier and Gilliam, 1986; Ramos, 1996; Flessa *et al*, 1998).

Nitrogen fertilisation

The differences in N_2O emissions between fertilised and unfertilised soils are particularly evident in soils which have low available mineral N (Castaldi and Aragosa, 2002; Rees *et al*., 2006). Denitrification and nitrification rate increases in nitrogen (N) fertilised systems (Klemedtsson *et al*., 1997; Flessa *et al*., 1998; Kaiser *et al*., 1998; Baggs *et al*., 2003; Weitz *et al*., 2001; Ruser *et al*., 2006; Bremer, 2007; Sangeetha et al., 2009) because N provides a substrate for production of N_2O. The rate at which N_2O is produced and emitted from N fertilized soil depend on the amount and type of N fertiliser, application rates and method of application, soil types and environmental conditions (Granli and Bockman 1994; Castaldi *et al*., 2006). Cochran *et al*. (1981) and Hutchinson and Brams (1992) reported larger N_2O emissions from soils fertilized with anhydrous NH_3 than those that received fertilizer containing NO_3^- or NH_4^+. Sangeetha *et al* (2009) observed that nitrification is limited by the formation of NH_4^+ from mineralisation under normal field conditions.

Mapanda *et al*. (2010) reported average emissions of 3.3–3.4 μg N_2O-N m^{-2} hr^{-1} of N_2O-N from cropped land on clay and sandy loam soils in Zimbabwe. The low fluxes could be attributed to low organic carbon in the soil (Castaldi et al., 2006), and high N uptake by crops which leaves very little N available for denitrification (Mapanda *et al*., 2011). Atmospheric N deposition also increases N_2O emissions (Brumme and Beese 1992; Butterbach-Bahl *et al*., 1998; Gundersen *et al*., 1998; Skiba and Smith 2000). Nitrous oxide emissions from forests that had received significant quantities of N deposition in the temperate zone of Europe were found to be 2 to 5 times more than in their counterparts that had received low deposition (Butterbach-Bahl *et al*., 1998). Brumme and Beese (1992) recorded N_2O emissions of 5.6 kg N_2O-N ha^{-1} $year^{-1}$ from a beech forest in Germany that had received N deposition at a rate of 35 kg N ha^{-1} $year^{-1}$.

Land use and management

Drainage of fertile peat soils for agriculture and forestry in the boreal and temperate region increases N_2O emissions (Kliewer and Gilliam 1995; Regina *et al.,* 1998; Liikainen *et al*., 2002) by enhancing the rate of decomposition of organic matter (Updegraff *et al*., 1995) which increases N substrate. Any nitrogen lost through drainage, however, may be susceptible to loss as N_2O (Reay *et al*., 2004). Mounding a silvicultural practice used to establish tree plantations in wet planting sites has a potential of inducing N_2O emissions because it mixes or buries the litter and the organic layer beneath the mineral layer (Saari et al., 2004). This increases the organic matter decomposition rates (Mann 1986; Davidson and Ackerman 1993) which may release N (Vitousek and Matson 1985; Fox et al., 1986; Vitousek *et al*., 1992), thus enhancing the production and emission of N_2O. The conversion of deforested land or grasslands to agricultural use can increase N_2O emission when N fertilizers are used (Nyamadzawo *et al*., 2012).

Conclusion

The atmospheric concentrations of CH_4 and N_2O have increased significantly during the past several decades due to anthropogenic activities. CH_4 from soil from soil to the atmosphere is the balance between production and consumption. Methane emitted from the soil to the atmosphere is the balance between production and consumption by methanogens and methanotrophs which are affected by numerous factors that include; soil water table depth, soil temperature, soil moisture content, etc. N_2O is an important constituent of the atmosphere because it is not only the dominant source of ozone (O_3) destroying odd nitrogen in the stratosphere but also a greenhouse gas. The gas is produced by numerous processes in soils of which denitrification and nitrification are considered to be the most significant. The emission of nitrous oxide from the soil is affected by moisture content, oxygen, soil pH, soil texture, temperature, fertilizer application etc.

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