**Factors Influencing Methane (CH\textsubscript{4}) and Nitrous oxide (N\textsubscript{2}O) Emissions from Soils: A Review**

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**Abstract:** Methane (CH\textsubscript{4}) and nitrous oxide (N\textsubscript{2}O) are the two most important non-carbon dioxide (CO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{3}) depleting gases, constituting 7% of the anthropogenic greenhouse effect. On a molecular basis, N\textsubscript{2}O has 298 and 16 times higher global warming potential than that of CO\textsubscript{2} and CH\textsubscript{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 as aeration/moisture status of the soil.

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

**Introduction**
Greenhouse gases (GHGs) methane (CH\textsubscript{4}) and nitrous oxide (N\textsubscript{2}O) are the two most important non-carbon dioxide (CO\textsubscript{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\textsubscript{4}) is the second most prevalent greenhouse gas from human activities after CO\textsubscript{2} (Schimel and Gullede; 1998; Van den Pol-van Dalselaat 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\textsubscript{4} in the atmosphere has risen from the pre-industrial level of 0.75 µmol mol\textsuperscript{-1} (Lelieveld et al., 1998; Schimel 2000; Smith et al., 2003). The growth rate in CH\textsubscript{4} concentration is changing considerably and the very large and interannual variations in CH\textsubscript{4} concentration remain unexplained; thus present an important challenge to the research community (Fowler et al., 2009; IPCC, 2007). CH\textsubscript{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\textsubscript{4} on climate change is 25 times greater than CO\textsubscript{2} over a 100-year period, which means that 1 kg of CH\textsubscript{4} is 25 times more effective in absorbing radiation as 1 kg of atmospheric CO\textsubscript{2} (IPCC, 2007). A total of 600 Tg CH\textsubscript{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\textsubscript{2} and CH\textsubscript{4}, N\textsubscript{2}O 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 µmol mol\textsuperscript{-1} to the current level of 0.320 µmol mol\textsuperscript{-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\textsubscript{2}O on warming the atmosphere is 298 times than 1 kilogram of CO\textsubscript{2} over a time period of 100 years (IPCC, 2007). The concentrations of CH\textsubscript{4} and N\textsubscript{2}O in the atmosphere result from the balance between processes contributing to uptake and release (von Arnold et al., 2005). Together with CO\textsubscript{2} they are considered the primary causes of global climate change (IPCC, 2007).

**Sources and sinks for atmospheric CH\textsubscript{4}**
A source is any process or activity through which CH\textsubscript{4} is released into the atmosphere. Both natural processes and human activities release CH\textsubscript{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\textsubscript{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\textsubscript{4} emissions from anthropogenic and natural sources are about 600 Tg CH\textsubscript{4} yr\textsuperscript{-1} (Lelieveld et al., 1998; Smith 2005; Whalen 2005; Prather and Hsu 2010). Major sources of CH\textsubscript{4} include the ruminant animal population (about 15% of the calculated annual CH\textsubscript{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\textsubscript{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 methopilic, able to function in temperature ranging from 20 to 40°C (Topp and Pattey, 1997). Once CH₄ unicellular organisms belonging to phylogenetic domain Archea (Garcia, 1990). Most methanogens are methopilic, able to function in temperature ranging from 20 to 40°C (Topp and Pattey, 1997). Once CH₄ is produced, it can be released into the atmosphere through any of the three following pathways: (i) diffusion of dissolved CH₄ along the concentration gradient, (ii) transport via the aerenchyma of vascular plants, or (iii) release of CH₄ 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 CH₄ 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 CH₄ becomes one of several non-greenhouse compounds that are then removed from the atmosphere through precipitation or another means.

Methane is consumed (oxidized to CO₂) by methane-oxidizing bacteria (methanotrophs) (Singh and Tate, 2007) in many soils which is the main CH₄ 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; Sjögren et al., 2007). This process simply exchanges one greenhouse gas for another. However, CH₄ is much more powerful than CO₂ 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 emissions one greenhouse gas for another. However, CH₄ is much more powerful than CO₂ 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 emissions one greenhouse gas for another. However, CH₄ is much more powerful than CO₂ 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 emissions.

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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; Tuttiala 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 (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 CH₄ production (Valentine et al., 1994; Zhuang et al., 2004) and consumption (Einola et al., 1998; Visvanathan et al., 1999). Although increasing soil temperature influences both CH₄ 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 (Kahababata 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 al., 2003) and net ecosystem exchange of CO₂ (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 CH₄ 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 120 kg N ha⁻¹ year⁻¹ as NH₄NO₃ and observed that CH₄ 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 CH₄ fluxes. The increase in methane fluxes from nitrogen fertilised soil has been attributed to nitrogen’s ability to inhibit CH₄ 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; Kähkönä et al., 2002).

Land use change and Management

Land use changes such as converting forests and grasslands to arable land decreases the oxidation of CH₄ (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 CH₄ consumption after land use changes has been attributed to the disturbance on the population and activity of soil microorganisms responsible for CH₄ 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 CH₄ 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 N₂O fluxes

Soil temperature

Nitrification and denitrification rates increase with increasing temperature (Granli and Boeckman, 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 N₂O production; it may affect microbial processes by stimulating N₂O 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 Boeckman (1994). Temperature exerts more control over soil N₂O 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 N₂O 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 N₂O emissions from all soil types. It influences the release of N₂O 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 N₂O 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 O₂ diffusion. The diffusion of oxygen in water is 1×10⁻¹⁰ 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) N₂O production increased when soil moisture content was increased from 0.1 to 0.3 cm cm⁻³. The process of nitrification is important in N₂O 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; Scholfeld 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 (Grossman and Tiedje, 1989; Aulakh et al, 1991; Clayton et al, 1997; Dobbie and Smith, 2003; Saggart 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 (Bowman, 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 (Klemmedtsson 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 Beece 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 Beece (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 (Kliwer 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$_2O$ (Ray 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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