1

Emissions of Nitrous Oxide (N_2O) and Di-Nitrogen (N_2) from the Agricultural Landscapes, Sources, Sinks, and Factors Affecting N_2O and N_2 Ratios

M. Zaman, M.L. Nguyen, M. Šimek, S. Nawaz,
M.J. Khan, M.N. Babar and S. Zaman
Ballance Agri-Nutrients Limited, Tauranga,
New Zealand

1. Introduction

Nitrous oxide (N_2O) is one of the key greenhouse and ozone (O_3) depleting gas, constituting 7% of the anthropogenic greenhouse effect. On a molecular basis, N_2O has 310 and 16 times higher global warming potential than that of CO_2 and CH_4 respectively over a 100-year period. To develop mitigation tools for N_2O emissions, it is imperative to understand the processes of nitrogen (N) transformation and N_2O and di-nitrogen (N_2) production in soils as influenced by different land uses, management and environmental conditions. The aim of our chapter is to examine the current information and understanding of the sources of N_2O and N_2 production and the factors affecting N_2O:N_2 ratio from the agricultural landscapes. Nitrous oxide concentration has increased by 20% from 270 ppbv since 1750 to a current level of 322 ppbv and continues to increase currently by 0.3% per year. Intensification of agricultural and human activities, such as the increased use of synthetic fertilizer (103 M ton of N worldwide in 2010), increasing human population and changes in their diet, inefficient use of irrigation water, increased crop production, deposition of animal excreta (urine + dung) from grazing animals, excessive application rates of farm effluents and animal manures to croplands and pastures, and management practices that enhance soil organic N mineralization and C decomposition including cultivation, residues removal or burning, and following no crop rotation are to be blamed for the increased N_2O emissions of 17.7 T g of N per year to the atmosphere. This book chapter focuses on the following sub-sections including nitrogen transformations, processes of N_2O and N_2 production across the agricultural landscape, challenges in N_2O measurements and estimates across the agricultural landscape, factors affecting N_2O and N_2 emissions and possible mitigating options, conclusions and references.

2. Nitrogen transformations

Nitrogen is an essential nutrient controlling the diversity, dynamics, and functioning of many terrestrial, freshwater and marine ecosystems. Agricultural ecosystems rely on N

inputs from a variety of sources including synthetic chemical fertilizers, predominantly urea which accounts for more than 50% of the total world N consumption, organic wastes (farm dairy effluent, animal excreta, plant residues and sewage sludge) and atmosphere (biological fixation of atmospheric N through symbiotic and non-symbiotic microorganisms) to sustain productivity. A detailed description of N cycling in agricultural ecosystems is beyond the scope of this chapter and for details on N transformations, N dynamics, sources of N inputs, and losses, the readers are referred to research papers, articles and review written by these authors (Ledgard et al., 1999; Saggar et al., 2004b, 2005, 2009, 2011; deKlein & Eckard 2008; Ledgard & Luo 2008; Luo et al., 2010); however a brief description of the various microbial and enzymatic processes involved in N cycling is given below.

2.1 A brief biochemistry of N mineralization

Nitrogen transformations within soil-plant-water and atmospheric systems refer to N cycling. As will be discussed in section 3, N cycling provides precursors like ammonium (NH_4^+) and nitrate (NO_3^-) for the production of N_2O and N_2 in soil. A simple schematic diagram of the N inputs, losses and transformation processes is presented in Fig. 1 The key N transformation processes within soil, plant and atmospheric systems include mineralization (gross and net), immobilization, nitrification (gross and net), denitrification, ammonia (NH_3) volatilization, NH_4^+ fixation and NO_3^- leaching. The first four processes (i.e. mineralization, immobilization, nitrification and denitrification) are of microbial and enzymatic origin (biotic), while the last three (i.e. NH_3 volatilization, NH_4^+ fixation and NO_3^- leaching) involve only chemical and physical processes (abiotic). Nitrogen mineralization is a sequence of microbial and enzymatic activities which involves the conversion of organic N (eg. protein, amino acids, amines, amides, urea, chitin and amino sugars) into an inorganic form of N (mainly NH_4^+), which then serves as a substrate for a diverse group of micro-organisms and for nitrification (Zaman et al., 1999 a, b; 2004; Zaman & Change, 2004). The

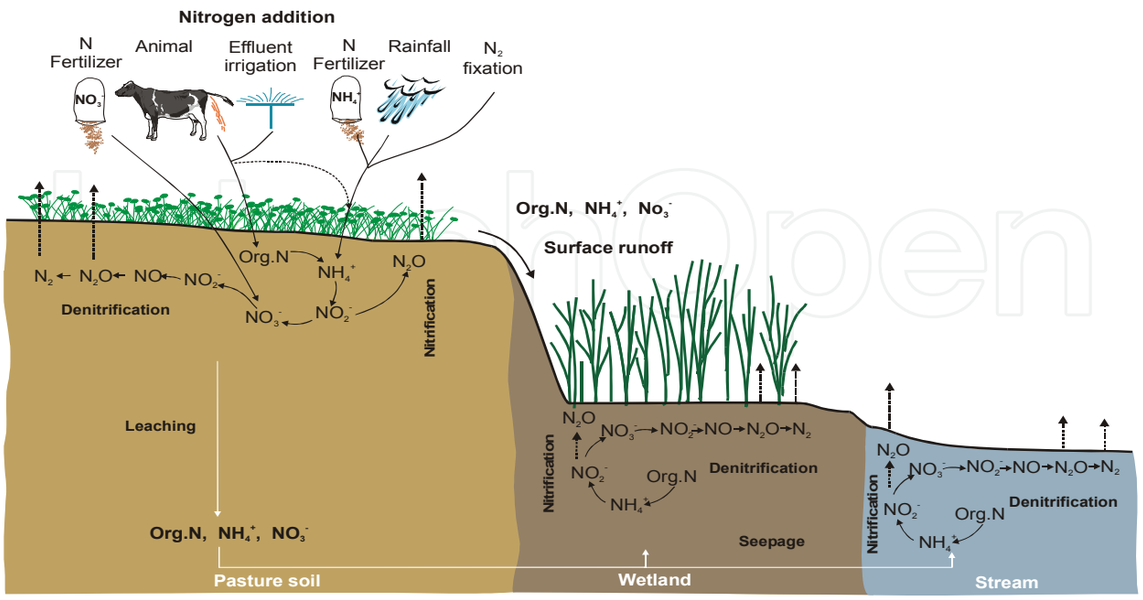
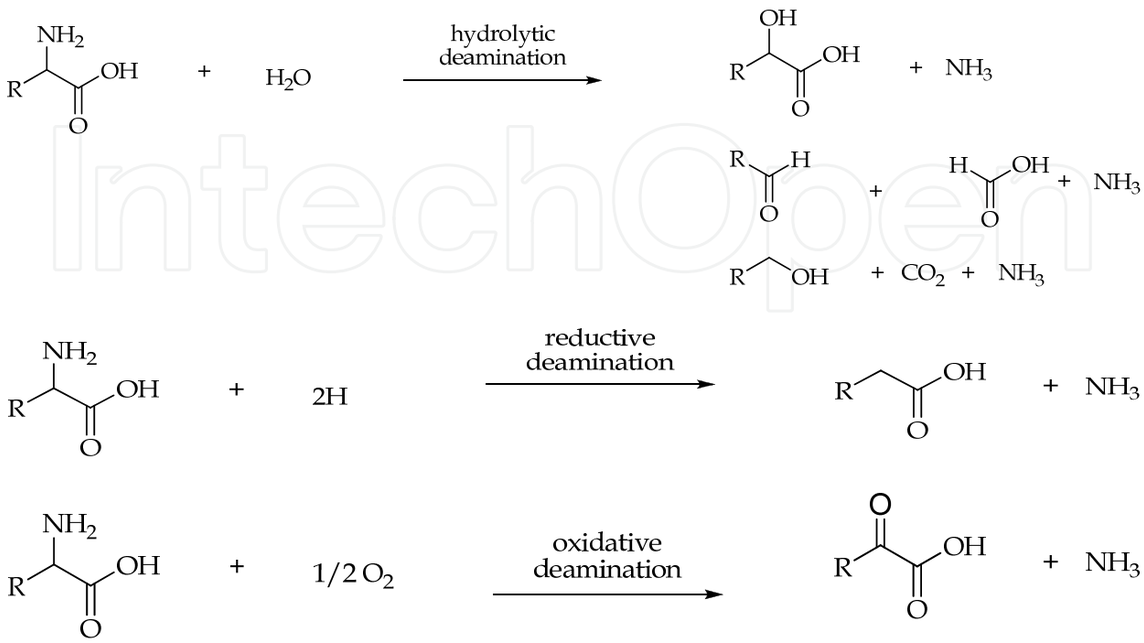


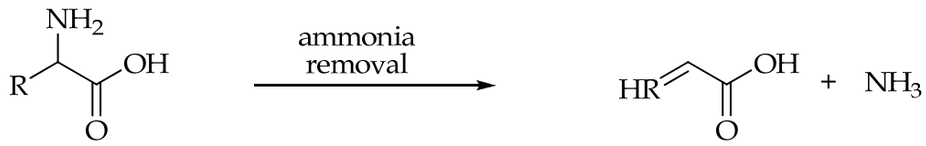
Fig. 1. N inputs, losses and transformation processes across the agricultural landscape (Zaman et al., 2008b).

immobilization process is the opposite of mineralization, where mineral N (NH_4^+ and NO_3^-) and even organic N (amino acids) are consumed by a diverse group of microorganisms to synthesize their protein and grow in number. These diverse groups of microorganisms are mostly heterotrophic (consume organic C) bacteria, fungi, and actinomycete, which produce a wide variety of extracellular and intra-cellular enzymes (e.g. protease, deaminase and urease) in soil. They then carry out the hydrolysis of high molecular weight organic compounds like protein into low molecular weight organic compounds such as amino acids, as shown in Eq. 2.1.1

(2.1.1)

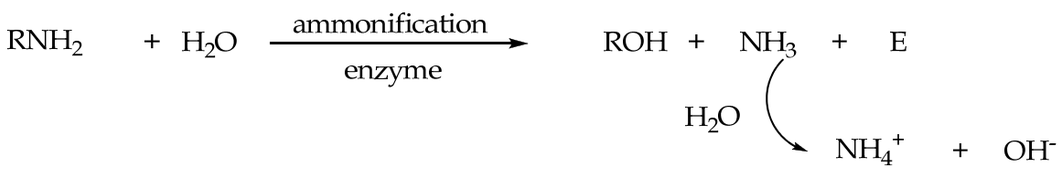
The low molecular weight organic compounds such as amino acids, amines and amides produced after proteolytic decomposition or after the application of organic residues or wastes are then subjected to microbial and enzymatic decomposition such as deamination which is carried out either by extracellular deaminase (Ladd & Jackson, 1982; Zaman et al., 1999 a, b) or by direct assimilation within the microbial cell (Barak et al., 1990; Barraclough, 1997). A large number of heterotrophic microorganisms are capable of carrying out the deamination of amino acids, both within and outside the microbial cell. Deaminases hydrolyse the NH_2-N attached to the α-C of an amino acid to NH_3 and CO_2. The amino acids are deaminated at different rates through four different reactions, depending on their side chains, as shown below in Eq. 2.1.2. Some amino acids are reported to be readily mineralized, while others take longer to mineralize (Alef & Kleiner, 1986).





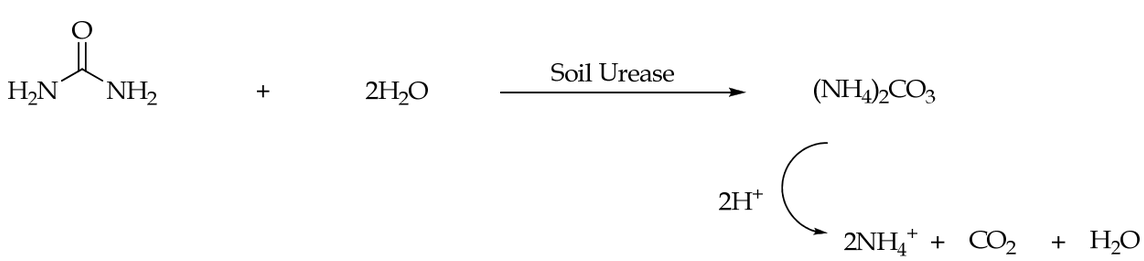
(2.1.2)

Whether an amino acid is used for an energy source by microorganisms or as a building block for protein synthesis depends on the available N and soluble organic C at the micro-site where the microbial reaction occurs (Mengel, 1996). After deamination has occurred within the cell, the removal of NH_4^+ is carried out by enzymes such as glutamate dehydrogenase and coenzyme nicotine adenine dinucleotide (NADH). Ammonium produced by deamination is always associated with the production of new microbial biomass, and the extent of NH_4^+ immobilization or accumulation in the soil depends on the micro-organism's C:N ratio (Mengel, 1996; Paul & Clark, 1996) and the available soil mineral N and organic C. The turnout of microbial biomass is reported to be fast and the new microbial biomass die after reaching a certain limit, thus serving as a substrate for enzymes and other groups of microorganisms. This turnover of microorganisms releases the NH_4^+ again. Thus the dead biomass, which is prone to biological decomposition (Jenkinson & Ladd, 1981), serves as the main source of NH_4^+ production in soil (Azam et al., 1986). The non-proteinaceous cell wall constituents of bacteria and fungi, such as amino sugar and chitin, are first depolymerised by chitinase to glucose amines. These are then attacked by kinases, and this process finally releases the NH_4^+ in soil as shown in Eq. 2.1.3.



(2.1.3)

Similarly urea ($CO(NH_2)_2$, from (i) urine deposition of grazing animals, (ii) the application of urea fertilizer or (iii) from production of hydrolytic decomposition of proteinaceous materials in soil, undergoes fast hydrolysis (Zaman et al., 2008a & 2009) and the hydrolysis is usually completed within 1 to 2 days by urease enzymes. These ubiquitous enzymes are found in soils, many plants and plant litters (Freney & Black, 1988) and in most species of bacteria, yeast and fungi (Sumner, 1953). Urease catalyzes the hydrolysis of urea to NH_4^+ (Eq. 2.1.4) and carbamate ions, which result in the production of carbon dioxide (CO_2) and NH_4^+.



(2.1.4)

The active site of urease contains two-nickel (II) atoms, which are linked by a carbamate bridge. Two imidazole N atoms are bound to each Ni atom; a carboxylate group and a water molecule fill the remaining coordination site of the metal ion. The ability to hydrolyze urea is found to vary from 17 to 70% for soil bacteria and from 78 to 98% for soil fungi (Lloyd & Sheaffe, 1973; Roberge & Knowles, 1967). Although soil urease is considered to be of microbial origin (Skujins, 1976), there is evidence to suggest that some urease activity may be derived from plants (Frankenberger & Tabatabai, 1982). However, there is no direct evidence for the production of urease by plant roots (Estermann & McLaren, 1961).

3. Processes of N_2O and N_2 production across the agricultural landscape

Gaseous N emissions from the agricultural landscape (arable, pasture and wetland soils) occur as NH_3, nitric oxide (NO also called nitrogen oxide), nitrogen dioxide (NO_2), N_2O and N_2. Quantifying N_2O emission is of particular interest to those countries, which are signatories to the Kyoto Protocol, since it is one of the key greenhouse gases constituting 7% of the anthropogenic greenhouse effect. On a molecular basis, N_2O has 310 and 16 times higher global warming potential than that of CO_2 and methane (CH_4) respectively over a 100-year period (IPCC, 2007). The global atmospheric concentration of N_2O has increased from 270±7 in the pre-industrial-period (1750) to a current level of 322 ppbv representing a 20% increase. Over the last two decades a nearly linear increase of 0.26% in the concentration of N_2O has been measured (Saggar et al., 2009). Moreover, due to its relative stability, (150 years) after emission from the soil surface and transport through the troposphere, N_2O acts as a source of NO in the stratosphere, and thus indirectly accelerates depletion of ozone (O_3), a substance that protects the biosphere from harmful ultraviolet (UV) radiation (Crutzen, 1981; Duxbury, 1994). The total estimated emissions of N_2O are about 17.7 Tg N per year, but there are large uncertainty ranges in each of the individual sources. About 70% of N_2O emissions come from the bacterial breakdown of N in soils and in the oceans. Globally, soils in areas of natural vegetation, especially in the tropics, and the oceans account for N_2O emissions of about 6.6 and 3.8 Tg N per year respectively; while human activities account for the remaining 30% of N_2O emissions, or about 6.7 Tg N per year (Denman, 2007). Factors blamed for the increased N_2O emissions of 17.7 T g of N per year to the atmosphere include; a rapid increase in human population (according to the latest United Nations population estimates, 77 million more people each year are being added to the current world population of 6.98 billion), intensification of agricultural and human activities, such as the increased use of synthetic fertilizer (103 million ton of N worldwide in 2010) (IFA 2011), inefficient use of irrigation water and N fertilizers (both synthetic and organic), increased grassland areas for livestock which cover 117 million km^2 of vegetated lands that provide forage for over 1800 million livestock units and wildlife (World Resources Institute 2000). The other factors include increased animal stocking rates (>3 cows per ha) and intensive gazing, which results in deposition of huge amounts of N via animal excreta (urine + dung), farm management practices that enhance soil organic N mineralization and decomposition of organic C (deep cultivation, crop residues removal or burning, and following no crop rotation) and the increased consumption of dairy products worldwide especially in fast growing economies like China and India (Robertson et al., 1989; Duxbury et al., 1993; Šimek & Cooper, 2001; Rochester, 2003; Denman et al., 2007; IPCC, 2010; Zaman & Blennerhassett., 2010; Zaman & Nguyen., 2010). Nitrous oxide can also be produced during nitric acid production and fossil fuel combustion, but the amount of N_2O

from fossil fuel varies with the fuel type and technology. Fossil fuel combustion and industrial processes are responsible for N_2O emissions of around 0.7 Tg N per year (Denman, 2007). Other important sources include human sewage and the burning of biomass and biofuels.

Across the agricultural landscape, several microbial processes can occur simultaneously to produce harmful N_2O and non-greenhouse N_2 in soils (pasture and arable) and sediments (drain, ditch, wetland and stream). These microbial processes are regulated by various soil, environmental and management factors, therefore making it difficult to control the rates of N_2O and N_2 production and their ratios (Paul & Beauchamp, 1989; Stevens et al., 1997; Zaman et al., 2007, 2008 b,c; Zaman & Nguyen, 2010). The aim of our review is to examine current information and understanding of the sources of N_2O and N_2 production and factors affecting N_2O:N_2 ratio in agricultural landscape, to enable management practices to be devised that minimize N losses as N_2O emission to the atmosphere.

Soil microbial processes, which account for major N_2O production include; nitrification (Inubushi et al., 1996), denitrification (Tiedje, 1988; Firestone & Davidson, 1989; Smith, 1990; Cavigelli & Robertson, 2001) and dissimilatory NO_3^- reduction to NH_4^+ (DNRA) (Silver et al., 2001). These three microbial processes may occur in soils and sediments across the landscape depending on the physical (moisture contents or O_2 level) and chemical conditions [N form (i.e. NH_4^+ and NO_3^-), pH and C contents] in their micro-sites. Details of each of these processes are given below:

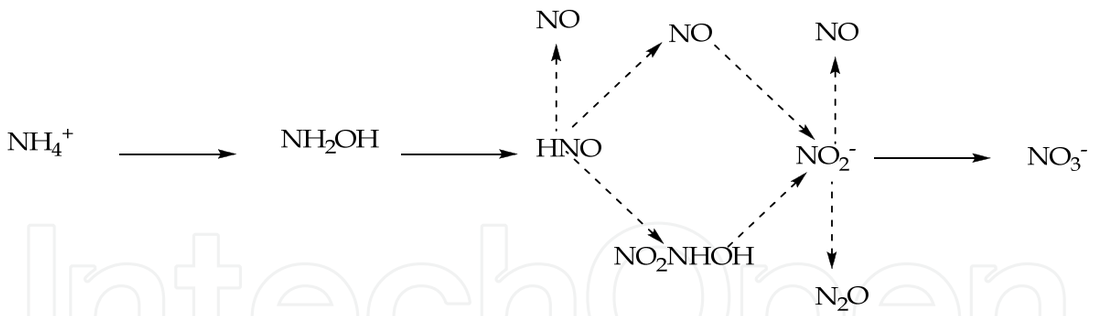
3.1 Nitrification

Autotrophic nitrification, a strictly aerobic process, is carried by chemolitho-autotrophic bacteria which use O_2 as a terminal electron acceptor. In the first step, NH_4^+ is oxidized to NO_2^- by ammonia oxidizing species of the genus *Nitrosomonas,* while in the second step, NO_2^- oxidation to NO_3^- is facilitated by *Nitrobacter* and *Nitrococcus* (Bremner & Blackmer, 1981; Watson et al. 1981) as shown in Eq. 3.1.1 Other genera including *Nitrosococus, Nitrosospira* and subgenera *Nitrosobolus, and Nitrosovibrio* also have the ability to autotrophically oxidize NH_3 to NO_2^-:

$$2NH_4^+ + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2NO_2^- + 2H_2O + 4H^+$$

$$2NO_2^- \xrightarrow{\text{Nitrobacter}} 2\,NO_3^- \qquad (3.1.1)$$

In addition to NO_2^- production during the first stage of autotrophic nitrification, several intermediate and unstable compounds such as hydroxylamine (NH_2OH) and nitroxyl (NOH) are also formed. Ammonia oxidizers consume relatively large amounts of molecular O_2 during this first stage, causing anaerobic conditions in the microsites, which then lead to a reduction of NO_2^- to N_2O and N_2 (Poth & Focht, 1985; Firestone & Davidson, 1989; Zart & Bock, 1998; Colliver & Stephenson, 2000) as shown in Eq. 3.1.2.



(3.1.2)

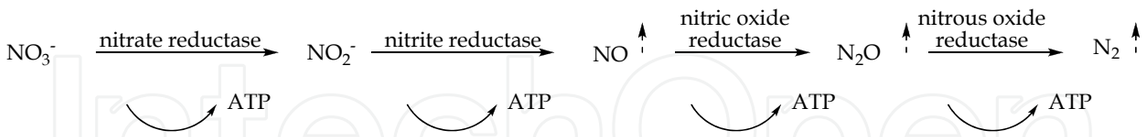
Broken lines show the unconfirmed pathways of the biological reaction.

Heterotrophic nitrification, the oxidation of reduced N compounds or NH_4^+ to NO_3^- in the presence of O_2 and organic C, can also produce N_2O from NO_2^- and typically occurs in acidic soils (Wood, 1990). However, high rates of heterotrophic nitrification relative to autotrophic nitrification have been measured in a riparian wetland soil with a pH close to 7, which was exposed to O_2 (Matheson et al., 2003). Production of N_2O via heterotrophic nitrification is poorly understood because autotrophic and heterotrophic nitrification can occur simultaneously in a given soil and it is difficult to separate the end products of these two processes without using ^{15}N tracers (Matheson et al., 2003). Sufficient soil O_2 levels [(optimum at water filled pore space (WFPS) of 60%)], adequate NH_4^+ concentrations, a favorable soil temperature above 5°C (optimum 25 to 35°C), and soil pH above 5 (optimum 7 to 9) are among the known soil and environmental conditions which control the rate of autotrophic nitrification (Linn & Doran 1984; Grundmann et al., 1995; Whitehead, 1995; Zaman et al., 1999a; Šimek., 2000; Zaman & Chang, 2004; Zaman et al., 2007; Saggar et al., 2009; Zaman et al., 2009; Zaman & Nguyen, 2010). Among these factors, NH_4^+ and O_2 concentrations are considered the most critical factors affecting autotrophic nitrification (Zaman et al., 2007). Thus autotrophic nitrification is expected to be a dominant N transformation process in well-drained pastoral or arable systems, where soils are oxygenated (at or around field capacity or at 60% WFPS) and NH_4^+ is abundant [(e.g., excreta deposition after animal grazing, after the application of organic wastes, and NH_4^+-based synthetic fertilizer like urea, di-ammonium phosphate (DAP), ammonium sulphate, and liquid ammonia or as a result of increased mineralization of soil organic N compounds)] (Zaman et al., 1999a,b; Zaman & Chang, 2004; Zaman et al., 2007; 2008a; 2009; Zaman & Nguyen 2010). However, nitrification can also occur in waterlogged areas at a slower rate where wetland vegetation releases O_2 from roots (Armstrong, 1964). At the sediment-plant root interface, nitrifying bacteria are supplied with O_2 from plants and NH_4^+ from the surrounding sediment. There is evidence to suggest that autotrophic denitrification can proceed at a pH around 4, because soil aggregates protect bacterial cells against nitrous acid toxicity (De Boer et al., 1991).

3.2 Denitrification

Denitrification is predominantly a microbial process by which NO_3^- and NO_2^- are reduced to N_2O and N_2 in a respiratory metabolism. During respiratory denitrification, denitrifiers couple reduction of N-oxides to oxidation of organic C under anaerobic conditions and

produce adenosine tri-phosphate (ATP) by phosphorylation (Firestone, 1982; Linn & Doran, 1984; Tiedje, 1988, Smith, 1990; Cavigelli & Robertson, 2001). Four different reductase enzymes are involved in a complete denitrification reaction. These enzymes are usually distributed in different microorganisms as shown in Eq. 3.2.1.



(3.2.1)

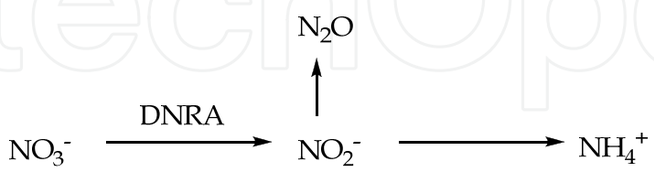
Denitrifiers are usually aerobic bacteria; however they prefer to use N-oxides at a low O_2 level (Tiedje, 1988). Biological denitrification thus requires; NO_3^- as a substrate (more than 2 mg NO_3^--N per kg of soil) as an electron acceptor, absence of O_2, which is related to a high soil moisture content >60% WFPS, available organic C as an electron donor, suitable soil pH, which generally ranges from 5 to 8 (optimum at 7) and a soil temperature range between 5 and 30 ^oC (optimum 25 ^oC) (Ryden & Lund, 1980; Ryden, 1983; Goodroad & Keeney, 1984; Scholefield et al., 1997; Barton et al., 1999; Swerts et al., 1997; Aulakh et al., 2001; Zaman et al., 2004; Zaman et al., 2007, 2008 b c, 2009; Zaman & Nguyen, 2010). However, the most critical factors are the NO_3^- concentrations, anaerobic conditions and the availability of soluble organic C (Zaman et al., 2007; 2008bc). Thus denitrification is expected to be an important N transformation process in areas where soils and sediments are subject to water logging (making them anaerobic), where they contain sufficient organic C and intercept inputs of NO_3^- or NO_2^- in groundwater or where there is excess nitrate after application of nitrate based fertilizers, or after nitrification (eg. 3.1.1). These areas include; urine patches in grazed pastures, where up to 1,000 kg N ha^{-1} can be found (Saggar et al., 2009; Zaman & Blennerhassett., 2010), riparian wetlands (Nguyen et al., 1999; Matheson et al., 2003), drains and ditches, and stream or river channels (Garcia-Ruiz et al., 1998; Bronson & Fillery, 1998; Mcmahon & Dennehy, 1999; Walker et al., 2002; Groffman et al., 2002; Zaman et al., 2008b&c, Zaman & Nguyen, 2010). However denitrification can also occur in less obviously waterlogged areas within the agricultural landscape due to the existence of anaerobic micro-sites such as in the center of soil aggregates (Parkin, 1987) or in areas of localized high O_2 consumption (hot spots), which are created by decaying organic C (Burton et al., 1999; Godde & Conrad, 2000; Khalil et al., 2002; Mosier et al., 2002). Depending on soil physical and chemical conditions, other processes like chemo-denitrification can result in substantial production of N_2O.

3.3 Dissimilatory NO_3^- reduction to NH_4^+ (DNRA)

DNRA is the 3rd biological process, which is known to produce considerable amounts of N_2O as a byproduct under anaerobic conditions (Tiedje, 1988; Silver et al., 2001) as shown in Eq. 3.3.1

Conditions required for DNRA are similar to those required for denitrification and besides anaerobiosis include available NO_3^- and organic C (Tiedje, 1988). DNRA has been found in anaerobic sludge and animal rumen, and also in lake littoral sediments, riparian wetland soil (Matheson et al., 2002) and tropical forest soils (Silver et al., 2001). Matheson et al., (2002) has also shown that DNRA is likely to be a more important process of NO_3^-

transformation relative to denitrification under more reducing (O_2 limited) conditions, since the microbes capable of DNRA are fermentative, and are able to grow in the absence of O_2 contrary to predominantly aerobic denitrifiers. Silver et al. (2001) reported that in upland tropical forest soils, DNRA accounted for 75% of the turnover of the NO_3^- pool and N_2O emission rates via DNRA, were 3 times greater than the combined N_2O and N_2 fluxes from nitrification and denitrification. Within the agricultural landscape, DNRA is likely to be an important N transformation process in wetland or stream sediments but may also occur in slow-draining upland soils where anaerobic sites are prevalent.



(3.3.1)

As discussed above, while nitrification and DNRA produce only N_2O, denitrification produces both N_2O and N_2. Stevens and Laughlin (1998) hypothesized that N_2O produced by various processes might form one common pool before being reduced to N_2 by nitrous oxide reductase. However, there is limited information available about the bulk reduction of N_2O to N_2.

4. Challenges in N_2O measurements and estimates across the agricultural landscape

Nitrous oxide emission and estimation across the different agricultural landscapes (arable, pasture, and wetland) is extremely variable (both spatially and temporally), thus posing the greatest challenge to researchers, modellers and policy makers to accurately predict N_2O emissions. Among the different field and laboratory methods, the static chamber method has most widely been used to determine the rate of N_2O emissions from soil because these chambers are easy to design, portable, compact, easy to install, and can be readily adapted to take gas measurements in the presence of animals and growing crops (Saggar et al., 2009). Readers are referred to Saggar et al (2009) for detailed information on the static chamber method. Other methods, including the sub-surface measurement of N_2O emissions (Arah et al., 1991; Gut et al., 1998; Clark et al., 2001), the Push and Pull technique of Addy et al. (2002) modified by Zaman et al., 2008b to quantify N_2O and N_2 emissions from wetland soils and the estimation approach of the Intergovernmental Panel on Climate Change (IPCC) have also been used to quantify N_2O emissions.

Few studies have carried out simultaneous measurements of N_2 and N_2O across the agricultural landscape. This is probably due to a lack of robust, easy and less expensive measurements and analytical methods. The most commonly used methods for measuring production of N_2 and N_2O in and their emission from the soils, include a technique based on the acetylene (C_2H_2) inhibition of N_2O reduction (Tiedje et al., 1988) and methods using substrates enriched in ^{15}N which allow subsequent ^{15}N gas determination by isotope-ratio mass spectrometry (Mosier & Klemedtsson, 1994). These methods are not only expensive but far from perfect and have some serious biological implications. For example, C_2H_2 inhibition method needs paired soil samples (with or without C_2H_2), which is not only time

consuming and expensive to analyze but a small amount of C_2H_2 (1%) can block nitrification and thus underestimates denitrification in NO_3^- limited soils. Denitrifiers after repeated exposure to C_2H_2 adapt to C_2H_2 and use it as a source of C, which stimulates denitrification rates. Therefore both paired soil samples need to be discarded after 24 hrs of incubation to avoid this problem. In addition, acetone, which is added to C_2H_2 as stabilizer, also acts as a source of C for denitrifiers (Gross & Bremner, 1992) and needs to be removed before injecting C_2H_2 into soil cores or incubation jars. The most problematic step of this technique however, is to successfully achieve a uniform distribution of the desired concentration of C_2H_2 in microsites inhabited by denitrifiers if intact soils cores are used (Zaman & Nguyen, 2010). Similarly a lack of inhibitory effect of C_2H_2 on *Nitrosospira briensis*, one of the common ammonia-oxidizing bacteria in soils, observed by Wrage et al., (2004) also poses a challenge, especially in soil treated with ammonium-based fertilizer where N_2O production via nitrifier-denitrification is likely to be overestimated. Thus although the technique of C_2H_2 inhibition has been widely used in laboratory conditions, when sieved soils or small monoliths were deployed, it has rarely been used in field conditions. To avoid the inhibitory effects of C_2H_2 on nitrification and denitrification, recently there has been an increasing interest in developing isotopic methods, which enable researchers to measure both N_2O and N_2 concurrently and identify the source of N_2O production from various microbial processes including nitrification, denitrification and DNRA (Stevens et al., 1997; Matheson et al., 2003; Sutka et al., 2006). N_2O production during nitrification and denitrification involves significant isotopic discrimination (ε = 35–60‰ and 28–33‰, respectively) (Robinson, 2001). Tilsner et al. (2003) reported that N_2O emitted during denitrification under controlled laboratory conditions was highly depleted in ^{15}N (–40.8 ± 5.7‰). Similarly Stevens et al. (1997) differentially labelled the NH_4^+ and NO_3^- pools simultaneously with ^{15}N, and periodically measured their individual ^{15}N enrichments and N_2O emission. A random distribution of ^{15}N in N_2O indicated a single source of origin whereas a non-random distribution indicated the two or more sources of N_2O origin. Despite the fact that the isotopic method permits the fractional contribution of each pathway to N_2O production and concurrent measurements of both N_2O and N_2, few researchers have used this method due to the high cost of ^{15}N-substrates and ^{15}N gases analyses, limited access to gas chromatograph with isotope-ratio mass spectrometers, and the difficulties associated with the uniform labeling of N pools in drier soils. Recently Mondini et al (2010) developed a robust automated dynamic closed chamber technique for concurrent measurement and analysis of N_2O, CO_2 and CH_4 under laboratory conditions. In their system, a gas chromatograph is connected to a fully computerised sampling system composed of 16 sample jars and 2 multiposition valves. For further details on these various methods, the readers are referred to the above mentioned papers.

In the estimation approach, the IPCC divides N_2O emissions from the agricultural landscape into direct and indirect emissions. Direct N_2O emission refers to N_2O derived from applied fertilizer and manure N, which is believed to increase with fertilizer use. Under the United Nations Framework Convention for Climate Change (UNFCCC), the majority of the countries use the IPCC default value of the 1% as emission factor (EF) (IPCC, 2006) from agricultural soils receiving synthetic fertilizers, farm dairy effluents (FDE), organic wastes and N fixed via biological fixation by leguminous crops (Bouwman et al., 2002; Stehfest & Bouwman 2006). However, a wide range of direct N_2O emissions (i.e. 3 to 22% of applied N) across the agricultural landscape have been reported in the literature (Corre et al., 1996;

Lovell & Jarvis, 1996; Velthof et al., 1996; Jambert et al., 1997; Goossens, et al., 2001; De Klein et al., 2003**;** Zaman et al. 2007; 2008b, c; Saggar et al., 2007b; Zaman & Nguyen, 2010) which is greater than the 1% EF value of the IPCC. A comprehensive review collected by Saggar et al., (2009) indicated that N_2O emissions from synthetic fertilizers range between 0.1 and about 2% of applied N. The large variations in the EF could be related to differences in soil types, time of fertilizer application, climatic conditions, weather patterns and form of synthetic fertilizers (ammonium and nitrate-based chemical fertilizers), animal urine and different protocols of N_2O measurement such as static chambers, C_2H_2 inhibition, micrometeorological, and isotopic methods. Crutzen et al (2007) also reported that the IPCC methodology seriously underestimates N_2O emissions from agriculture. Their estimates, using known global atmospheric removal rates and concentration growth of N_2O, show an overall EF of 3–5%, whereas the EFs estimated for direct and indirect emissions using IPCC methodology cover only part of these emissions. Saggar et al (2009) further argued that the IPCC approach is limited by a number of uncertainties in emission factors, and in indirect emissions, limited data on the type and amount of N excreted by grazing animals, and in spatial and temporal variability of N_2O emissions. Furthermore, the IPCC methodology does not allow for any mitigation options such as the use of urease or nitrification inhibitors and others. It is therefore critical to collect more data to validate the IPCC emission factor for N_2O emission from agricultural soils, which may enable us to accurately predict the global N_2O budget.

According to the IPCC, indirect N_2O emission consists of 3 parts; N_2O emissions associated with atmospheric N deposition [N_2O (G)], human waste [N_2O (S)], and with N lost via surface runoff and leaching [N_2O (L)]. Indirect N_2O emissions represent 1/3 of the total agricultural emissions, and the majority (75% of the total indirect emission) come from riparian zones (riparian wetlands, drainage ditch and stream sediments), where NO_3^- in leachate and NH_4^+ in runoff from farmland are microbially converted to N_2O and N_2 (Groffman, 2002; Zaman et al., 2007; Zaman et al., 2008b,c Zaman and Nguyen, 2010). N_2O emission rates from riparian wetlands are generally higher than those of agricultural soils (Lowrance et al., 1984; Pinay et al., 1993; Zaman et al., 2008c) which could be attributed to the higher C in riparian soils and enriched NO_3^- inputs from surrounding areas via seepage and groundwater flow to riparian zones. Given the potentially higher N_2O emission rates from wet soils c.f. dry soils in agricultural landscapes, and the general lack of data from wet soils, there is a clear need for more data on N_2O emission rates from riparian wetlands. Limited studies have been conducted to measure the rate of N_2O emissions from streams and rivers. Garcia-Ruiz et al. (1999) found that N_2 production ranged from 0.05-0.27 μmol N m^{-2} h^{-1} in the Swale-Ouse River system to 570 μmol N m^{-2} h^{-1} in the River Wiske. In the River Wiske, N_2O production accounted for up to 80% of total N gas production. Using the current IPCC methodology, approximately 40% of indirect N_2O emissions (emissions not accounted for from direct N sources such as fertilizers and applied animal urine) are derived from streams, rivers and estuaries.

5. Factors affecting N_2O and N_2 emissions and possible mitigating options

As reviewed in Section 3 (Processes of N_2O and N_2 production across the agricultural landscape), autotrophic and heterotrophic nitrification and DNRA produce only N_2O; while

denitrification produces both N_2O and N_2. The emissions of N_2O and N_2 and their ratios are affected by various soil and management factors, including mineral N concentration, available C, soil pH, soil aeration status, soil temperature and their interactions as shown in Table 5.1.

Factors	Management	Impact	Management practices
Soil NH_4^+ & NO_3^- concentration	Decrease	Reduce nitrification & denitrification and lower N_2O:N_2	Use urease and nitrification inhibitors to enhance fertilizer use efficiency; split N fertilizer application to synchronize plant N demand and to minimize N losses; avoid over grazing; manipulation of animal diet; use of constructed or natural riparian wetland, improving water use efficiency to avoid anaerobicity
Soil organic C	Increase	Improve soil health, facilitate denitrification and thus lower N_2O:N_2	Sequester more C by adopting management practices including zero or minimum tillage, retention of crop residues, mulching, application of organic and farm wastes, biochar, and applying chemical fertilizers with organic amendments
Soil pH	Increase	Facilitate nitrification and denitrification and thus lower N_2O:N_2	Regular liming each year or if possible with every N fertilizer application
Soil aeration and water status	Improve	Facilitate nitrification and denitrification and thus lower N_2O:N_2	Improving soil structure via C sequestration, avoiding soil compaction; improving soil drainage condition and also water use efficiency

Table 5.1. Factors affecting N_2O and N_2 emissions and their ratios.

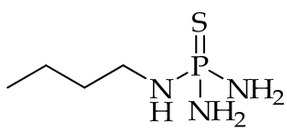
In the section below, an attempt has been made to discuss these soil and management factors. Understanding these factors may help us to design mitigating tools to reduce the rate of N_2O production and to lower N_2O:N_2 ratios.

5.1 Soil NH_4^+ and NO_3^- concentrations

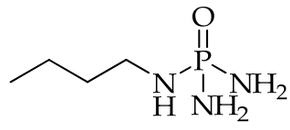
The amount of mineral N, both NH_4^+ and NO_3^-, are critical for the production of N_2O, N_2 and their ratio. The amount of NH_4^+ in soil under aerobic soil conditions, and hence its availability for nitrification, can directly regulate N_2O emission via nitrifier-denitrification (Webster & Hopkins, 1996; Wrage et al., 2001; Dalal et al., 2003; Ma et al., 2007), while NO_3^- is used as a substrate by both denitrification and DNRA and thus affects N_2O production **(**Webster and Hopkins, 1996; Zaman et al., 2008c). A higher level of NO_3^- in soil is also known to result in incomplete denitrification and thus higher N_2O:N_2 due to suppression of nitrous oxide reductase activity, the enzyme responsible for microbial conversion of N_2O to N_2 (Eq. 3.2.1). To mitigate N_2O emissions, researchers during the past two decades focused mainly on reducing the rate of nitrification while little work has been done to exert control on the denitrification level. For example, to reduce N_2O emissions from applied urea, ammonium based fertilizers or urine N, researchers have developed different mitigation technologies including the use of N inhibitors to reduce the entry of mineral N from applied fertilizer/urine into the available N pool, application of soil amendments like zeolites to capture soil NH_4^+ and controlled release and split applications of N fertilizers to match crop N demand. Among these options, coating chemical fertilizers with N inhibitors or applying N inhibitors on their own to treat urine patches in grazed pastures have received the most attention. The two major classes of N inhibitors are urease inhibitors (UIs) and nitrification inhibitors (NIs). Urease inhibitors retard the hydrolysis of soil-applied urea and delay the entry of urea-N into the NH_4^+ pool, which is likely to produce less N_2O via nitrification due to the limited availability of NH_4^+ (Watson, 2000; Xu et al., 2000; Zaman et al., 2008a; Zaman et al., 2009) as shown earlier in Eq. 2.1.4. Such a reduction in urea hydrolysis also limits the opportunity for nitrite (NO_2^-) accumulation in the soil, which is known to produce N_2O (Eq. 3.1.2).

Decisions about N fertilizer application are usually dependent on the availability of water, and the N application rate is determined by crop growth stage and the productivity goals. Fast urea hydrolysis starts within hours of urea fertilizer application or after deposition of urine from grazing animals and is completed within 1 to 3 days, during which time a significant amount of NH_3 (up to 30% of the applied N) is lost. UI like N-(n-butyl) thiophosphoric triamide (nBTPT) or Agrotain® applied at a very low concentration (0.01%) with urea fertilizer is reported to delay such fast urea hydrolysis by 7 to 9 days (Watson et al., 2008), which has implications for worldwide urea use in pasture and cropping systems where there is a high risk of NH_3 loss due to low moisture and high temperature, especially during summer or early autumn. Such a delay in urea hydrolysis allows more time for rainfall or irrigation water to wash the applied urea from surface soil and thus minimizes the risk of NH_3 emissions. After application, nBTPT is quickly converted to its oxygen analog N-(n-butyl) phosphoric triamide) (NBPT) (Eq. 5.1.1), which is the actual UI (McCarty et al., 1989; Christianson et al., 1990; Creason et al., 1990), and it is bound and moves along with urea molecule in the soil (Christianson & Howard, 1994). The conversion of nBTPT to NBPT is rapid, occurring within minutes/hours in aerobic soils (Byrnes & Freney, 1995), but can take several days in the floodwater of tropical soils. NBPT forms a tridentate ligand with the urease enzyme, blocking the active site (Manunza et al., 1999).

In addition to reduced nitrification, Agrotain is also known to reduce N_2O emission indirectly through reduced NH_3 volatilization (Watson et al., 1990; 1994 a & b, 1998, 2008;



N-(*n*-butyl)thiophosphoric triamide (*n*BTPT)



N-(*n*-butyl)phosphoric triamide (Oxygen analogue)

(5.1.1)

Chadwick et al., 2005; Meneer et al., 2008; Sanz-Cobena et al., 2008; Singh et al., 2008; Zaman et al., 2008a & 2009; Zaman & Blennerhassett., 2010). Ammonia itself is not a greenhouse gas, but it can act as a secondary source of N_2O production after its deposition on land (Martikainen, 1985) and thus contributes indirectly to climate change. To our knowledge, New Zealand is the only country that has included NH_3 reduction from Agrotain treated urea in its national inventory on N_2O. Sherlock et al. (2008) after a literature search on NH_3 emission, recommended to the New Zealand Ministry of Agriculture and Forestry (MAF) that a specific value of 0.1 for $Frac_{GASM}$ and $Frac_{GASF}$ be considered for adoption. In New Zealand, studies where nBTPT (0.025% w/w) was applied reduced NH_3 emissions by 43% from urea and by 48% from urine (Singh et al., 2008; Meneer et al., 2008; Zaman et al., 2008a & 2009; Zaman & Blennerhassett 2010). Based on these estimates of reductions in NH_3 emission from nBTPT treated urea applications, a New Zealand specific value of 0.06 for $Frac_{GASF}$ is recommended for adoption where fertilizers containing the urease inhibitor, nBTPT are applied. Saggar et al. (2010) recommended to MAF that where NBTPT is applied with urea, $Frac_{GASF}$ should be calculated as follows,

$$FracGASF = [(FN_{UI}) \times 0.06] + [(FN - FN_{UI}) \times 0.10]$$

Where $\mathbf{Frac_{GASF}}$ is the fraction of total fertilizer N emitted as NH_3, **FN** is the total amount of applied fertilizer N, $\mathbf{FN_{UI}}$ is the amount of applied fertilizer N treated with the urease inhibitor, nBTPT. Changing the $Frac_{GASF}$ from 0.1 to 0.06 for the current use of 18.4 Gg N of Agrotain treated urea reduces indirect N_2O emissions by 0.012 Gg, which equates to 3.6 Gg $CO_{2\text{-equiv.}}$ However, assuming all urea is applied with nBTPT in New Zealand, changing the $Frac_{GASF}$ from 0.1 to 0.06 will reduce the indirect N_2O emissions by 0.14 Gg, which equates to 43.4 Gg $CO_{2\text{-equiv.}}$

Nitrification inhibitors are compounds (both natural and synthetic) that delay bacterial oxidation of NH_4^+ either by temporarily suppressing the activities of nitrifiers or killing them in the soil, thus maintaining the applied N in more stable form (i.e. NH_4^+-N). Slowing down nitrification in soils lowers N_2O production associated with nitrifier-denitrification (Webster & Hopkins, 1996; Wrage et al., 2001; Ma et al., 2007), or indirectly by reducing the amount of NO_3^- substrate available for denitrification. Among the many synthetic NIs, only nitrapyrin or N-Serve (NP) (2-chloro-6-(tri-chloromethyl) pyridine), dicyandiamide (DCD) and 3,4-Dimethylpyrazol-phosphate (DMPP) have gained substantial practical and commercial importance in agricultural and horticultural crop production.

Nitrapyrin because of its high volatility needs to be injected into the soil. Therefore nitrapyrin may be a preferred NI where injecting chemical fertilizers or farm dairy effluent (FDE) into the soil is a common practice. Unlike nitrapyrin, DCD is relatively soluble in

water, non-volatile, cheap and can be easily treated/coated onto solid ammonium based N fertilizers such as urea, diammonium phosphate (DAP); ammonium nitrate (NH_4NO_3) and ammonium sulfate $(NH_4)_2SO_4$ or directly added into FDE to improve their N use efficiency and minimize N losses. However after application, separation of DCD from applied NH_4^+, DCD leaching, and its rapid decomposition with increasing soil temperature are reported to lower its efficacy. Contrary to this, DMPP has several advantages over DCD and nitrapyrin. Lower application rates (0.5 to 1.0 kg of the active compound ha^{-1}) are needed to achieve optimal nitrification inhibition to reduce N_2O emissions and NO_3^- leaching. After application, DMPP is less prone to leaching and remains effective much longer than that of DCD (Weiske et al., 2001; Zerulla et al., 2001).

In intensive agricultural system like grazed pastures, other mitigation options including feeding dairy cows with low N feed such as palm kernel and maize silage instead of high N pastures to reduce the amount of N in animal excreta, using winter feed pads and restricted grazing to avoid soil compaction and to minimize urine depositions during critical times (winter) (de Klein et al., 2006), natural and constructed riparian wetlands to intercept N entering from adjacent pasture soils and to process it before entering water bodies (Zaman et al., 2008b), applying lime or zeolite as soil amendments to reduce N_2O emissions and shift the balance between harmful N_2O and non-greenhouse N_2 (Zaman et al., 2007, 2008c; Zaman & Nguyen, 2010), adding salts to animal feed to increase urine volume and spread (Ledgard et al., 2007), increasing the hippuric acid concentration in urine by manipulating animal feed (Bertram et al., 2009) have been suggested as additional mitigation tools.

5.2 Soil available organic C concentration

Soil organic C is another important controller of N_2O and N_2 production in soils and sediments as denitrifiers are strictly heterotrophs and use available organic C as electron donor and indirectly affects O_2 concentrations of aerobic soils (Groffman et al., 1987). However the effect of available C on the amounts of N_2O and N_2 produced in and emitted from the soils, as well as on the ratio between the two gases, is reported to vary with soil NO_3^- concentration and WFPS (Zaman et al., 2007, 2008b,c). In anaerobic zones of non-fertilized soils, NO_3^- availability may control the denitrification rates as discussed above in section 5.1, while in soils with high NO_3^- inputs (i.e. after application of chemical fertilizers and FDE or urine patches after grazing), available soil organic C would be the main driver of N_2O and N_2 production via denitrification (Tiedje, 1988). Applying urea fertilizer with C source (wheat straw and green manure) was reported to substantially reduce N_2O emission compared to urea fertilizer alone (Aulakh et al., 2001) possibly due to the microbial immobilization (Tiedje, 1988) or DNRA (Matheson et al., 2002). Zaman et al., (2008b) during an incubation study observed that wetland soils treated with KNO_3 emitted more N_2 emissions than those of the pasture soils which they attributed to the availability of highly enriched organic C and high WFPS in wetland soils. Weier et al. (1993) also measured N_2O and N_2 emissions from 4 soils treated with a range of available C (0, 180 and 360 kg ha^{-1}), NO_3^--N (0, 50 and 100 kg ha^{-1}) and WFPS (60, 75 and 90%). They reported that N_2 emission was favored at the highest available C rate of 360 kg C ha^{-1} and 90%WFPS, while the higher NO_3^- concentration inhibited the conversion of N_2O to N_2, resulting in higher N_2O:N_2 ratios. Similarly Yao et al. (2002) observed a negative correlation between N_2O emission and soil organic C from N fertilized wheat crop. The N_2O:N_2 ratio could be explained by an

interaction of C availability, NO_3^- concentration and enzyme status (Swerts et al., 1996). There are reports that the N_2O:N_2 ratios are lower in the rhizosphere, which provides more available organic C in the form of root exudates and root debris, and is characterized by low partial pressure of O_2 (due to O_2 consumption by plant roots) (Casella et al., 1984).

Depending on the management practices, agricultural soils can act as a source or sink for atmospheric CO_2. Improved land management practices in croplands and grasslands can store up to 1 Gt C in the soil on an annual basis (IPCC, 2000). It is therefore possible to store between 100 to 1000 kg SOC ha^{-1} $year^{-1}$ depending on the climate, soil and vegetation types, and site-specific soil management practices. Improved land management practices like zero or minimum tillage, retention of crop residues via crop rotation and mulching, application of FDE, organic residues and manure, following crop rotation especially with N fixing crops and avoiding burning crop residues after harvest may offer potential mitigation tool to sequester more C in the soils to offset the increase in atmospheric CO_2 as well as to improve soil fertility, soil structure, aggregate stability, pore size geometry and distribution, water and nutrients holding capacity and soil quality (increased microbial and enzymatic activities). Such improvement in soil physical and chemical fertility and health will minimize conducive conditions like anaerobicity and soil compaction which stimulate denitrification. Increased soil C may also help to shift the balance between harmful N_2O and non-greenhouse gas N_2 during denitrification as the activity of nitrous oxide reductase enzymes is stimulated by available soil C.

5.3 Soil pH

Soil pH is among the key regulators of the microbiological processes that affect N_2O and N_2 production and their ratios. Nitrification activity is generally higher with higher soil pH (> 6) (Bremner & Blackmer, 1981; Bramley & White, 1989). The critical soil pH threshold for nitrification is 5; however, nitrification can occur even at a soil pH of 4.5 due to acid-adapted nitrifier strains (Bouwman, 1990). Denitrification has been reported to occur over a wide range of soil pH values (5 to 8) (Weier & Gilliam, 1986; Ramos, 1996; Flessa et al, 1998); however, laboratory experiments with artificially adjusted soil pH suggest, that under optimized conditions (very low pO_2, NO_3^- and glucose amendments), denitrification can proceed even at pHs below 4 or above 10 (Šimek & Hopkins, 1999, Šimek et al., 2002). Numerous laboratory and field studies have shown that soil pH affects N_2O and N_2 and the ratio of these gases (e.g. Weier & Gilliam, 1986; Stevens & Laughlin, 1998). Under controlled environment experiments, we found that raising soil pH to 7 through lime application significantly increased N_2 emission from pasture and wetland soils treated with urine, urea and KNO_3 at 200 kg N ha^{-1} rate (Zaman et al., 2007 & 2008c). More recently in a field experiment, a similar trend of enhanced N_2 after raising soil pH to 7 was observed in pasture soils treated with urea/urine (Zaman & Nguyen, 2010). This idea is further supported by our studies on cattle pasture soil (Hynšt et al., 2007). At the site with the greatest animal impact, the ratio of N_2 to N_2O produced during denitrifying enzyme activity (DEA) measurements was five-fold higher, and the pH was 2 units higher, compared to the site with the least animal impact, which indicated that soil conditions were favourable for production of N_2 rather than N_2O in the area where excretal returns and treading was intense.

Types of chemical N fertilizers are also likely to regulate N_2O:N_2 ratios, as NH_4^+ based fertilizers (i.e. ammonium sulphate, ammonium nitrate, and mono-ammonium phosphate)

are reported to lower soil pH after their application (Thornton et al., 1996; Mulvaney et al., 1997; Nobre, 2001; Cai et al., 2002). For example, Mulvaney et al. (1997) have reported that ammonium-based fertilizers with soil acidifying effects produce a higher N_2O:N_2 ratio compared to alkaline forming fertilizers (anhydrous ammonia, urea or di-ammonium phosphate). Most researchers attribute high N_2O and low N_2 emissions in acidic conditions to the suppression of nitrous oxide-reductase at low soil pH (inhibition at soil pH 4.5) (Kostina et al., 1996; Daum & Schenk 1998; Flessa et al., 1998; Stevens and Laughlin, 1998; Zaman et al., 2007). It is also likely that all denitrifying enzymes are susceptible at low soil pH and produce N_2O from intermediate products (Nagele & Conrad, 1990). However, the extensive review conducted by Šimek and Cooper (2002) reported that the lower rates of N_2 and high N_2O:N_2 ratio at low soil pH could be due to lower amounts of soil organic C and mineral N available to the denitrifying population under acid conditions rather than a direct effect of low pH on denitrification enzymes. Regardless of the biochemical reasons for changes in soil pH on N_2 emission, raising soil pH through application of soil amendment like lime appears to offer a mechanism for mitigation of N_2O (Šimek et al., 2002; Zaman et al., 2007, 2008b, Zaman & Nguyen, 2010).

5.4 Soil aeration and water status

Soil aeration, namely O_2 concentration and gas exchange between soil and atmosphere, affects all microbial N transformation processes including nitrification, denitrification, and DNRA. Control of the denitrification enzymes, especially nitrous oxide reductase, represents the key mitigation option for the rate of N_2O production and can therefore shift the balance between harmful N_2O and non-greenhouse N_2 production across the agricultural landscape (Smith & Tiedje, 1979; Mosier et al., 1986; Robertson & Tiedje, 1987; Henrich & Haselwandter, 1997; Bollmann & Conrad, 1998; Mosier et al., 2002).). In soil, O_2 concentration changes with soil moisture content and organic matter decomposition by soil microorganisms. After rainfall or applying irrigation water, soils become temporarily anaerobic; the extent and duration of anaerobiosis differs with soil types (drainage class). Fine-textured soils with a higher clay content are reported to remain anaerobic for a longer period of time at low WFPS than coarse-textured soils because of the greater number of micro pores in the former (Barton et al., 1999). Therefore fine-textured soils with poorly drained conditions are likely to emit more N_2O for a longer period than those of coarse-textured soils with well-drained conditions (Groffman & Tiedje, 1989; Aulakh et al., 1991; Clayton et al., 1997; Dobbie & Smith, 2001; Saggar et al., 2004a). At higher O_2, partial pressure (>0.5 vol. %), nitrification is expected to proceed, provided there is sufficient water for optimum activity of nitrifiers (Linn & Doran, 1984; Bollmann & Conrad, 1998); if the soil WFPS increases (and pO_2 decreases), the rate of N_2O production and the proportion of N_2O to NO_3^- produced also increases (Smith et al., 2003). Under such specific conditions at WFPS>60%, nitrification is considered to be the predominant source of N_2O as opposed to denitrification or DNRA (Inubushi et al., 1996). Although DNRA is understood to be an anaerobic process, information about the critical levels of WFPS or O_2 for DNRA is lacking in the literature. Denitrification becomes a major source of N_2O and N_2 production at lower O_2 partial pressure (<0.5 vol. %) and higher WFPS (>60%) (Davidson, 1993; Scholefield et al., 1997; Bronson & Fillery, 1998; Khalil et al., 2002). In such scenarios, more aerobic soils are likely to produce mainly N_2O because denitrification reductases (Eq. 3.2.1) especially nitrous oxide reductase is reported to be sensitive to soil O_2 level, while anaerobic soils and

sediments will generate both N_2O and N_2. A number of studies have reported higher amounts of N_2 than N_2O at lower O_2 partial pressure and WFPS above 70% (Eriksen & Hartwig, 1993; Dendooven et al., 1999; Kwong et al 1999, Khalil et al., 2002). Aulakh et al. (2001) reported that gaseous N losses as N_2O after application of urea (120 kg ha^{-1}) to flooded rice were 8 to 10 times higher than those of upland wheat because of the anaerobic conditions in the former. Recently we found that riparian wetland soils treated with NO_3^--N (200 kg N ha^{-1} rate) emitted 4 and 8 times more N_2O and N_2 respectively than pasture soils during 28-day incubation (Zaman et al., 2008 c). However, the relative production of N_2O and N_2 in anaerobic or aerobic soil conditions is not that simple since O_2 level or WFPS is only one of the many known soil and management factors which affect this relationship (Fillery, 1983; Scholefield et al., 1997; Stevens & Laughlin, 1998; Zaman et al., 2008b). In their comprehensive review on emissions of N_2O and NO from fertilized fields published, Bouwman et al. (2002) concluded that restricted drainage and fine texture favors N_2O emissions. Thus our current understanding of the processes of N_2O and N_2 production in anaerobic and aerobic soil conditions is limited. At this stage we can only suggest that improving soil drainage conditions and avoiding soil compaction through use of the heavy farm machinery and grazing animals (pugging) in wet soil conditions (especially in winter) could help to maintain aerobicity in soils, which in turn may reduce N_2O emission rates through nitrification, denitrification and DNRA (Bhandral et al., 2003, 2007b. Luo et al., 2008b).

Apart from the above mentioned factors, temperature is also known to affect N_2O production and the N_2O:N_2 ratio (Cho et al., 1997; Daum et al (1997, Muller et al., 2002). However, controlling soil temperature is mostly beyond the ability of farmers. Manipulation of the interaction between mineral N supply (NH_4^+ and NO_3^-), organic C, soil aeration and pH offers the best hope for minimizing N_2O emission from soils. Similarly the export of N via surface and sub-surface runoff from upland to water bodies can be minimized by using riparian zones (both natural and constructed) along river and stream banks. Since denitrification is considered to be the major NO_3^- removal process in wetland, proper management of wetlands include, regular application of lime to keep the pH above 6.5, sequestering C to build C reserves, and exclusion of grazing animals to minimize N inputs are essential. All these management practices are known to stimulate the activity of nitrous oxide reductase, which will help to result in emissions of more N_2 than N_2O as discussed above.

6. Conclusions

Nitrogen is the most dynamic plant, microbial and animal nutrient which affects the diversity, dynamics, and functioning of many terrestrial, freshwater and marine ecosystems. Gaseous N losses in the form of N_2O are undesirable because N_2O is an important greenhouse gas and is also involved in the depletion of stratospheric ozone. Nitrification, denitrification and DNRA are the main microbial processes for N_2O production across the agricultural landscape which can sometimes operate concurrently in a given soil system. N losses as N_2O across the agricultural landscape are extremely variable and range from about 1% to more than 20 % of the applied N. Such losses are generally higher from wetland soils than those from pasture or arable soils. The critical soil and management factors affecting the rates of N_2O and N_2 production and their ratios are concentration of mineral N, soil

organic C, soil pH, and soil aeration status. N_2 production dominates over that of N_2O at lower mineral NO_3^- content, increasing organic C contents, increasing soil pH (above 6.5), lowering O_2 partial pressure or increasing WFPS; above 70%. Manipulation of these factors offers potential tools for mitigation of N_2O.

7. Acknowledgments

The senior author acknowledges the financial assistance for page charges by Ballance Agri-Nutrients Ltd. We also acknowledge Sharon Long for her assistance in proof reading this chapter and the unknown reviewers for their positive comments.

8. References

Addy, K. Kellogg, D.O. Gold, A.J. Groffman, P.M. Ferendo, G. & Sawyer, C. (2002). In situ pushpull method to determine ground water denitrification in riparian zones. *Journal of Environmental Quality,* 31, pp. 1017-1024.

Alef, K. Kleiner, D. (1986). Arginine ammonification, a simple method to estimate microbial activity potential in soils. *Soil Biology and Biochemistry,* 18, pp. 233-235.

Arah, J.R.M. Smith, K.A. Crichton, L.J. & Li, H.S. (1991). Nitrous oxide production and denitrification in Scottish soils. *Journal of Soil Science,* 42, pp. 351-367.

Armstrong, W. (1964). Oxygen diffusion from the roots of some British bog plants. *Nature,* 264, pp.801-802.

Aulakh, M.S. Doran, J.W. & Mosier, A.R. (1991). In-field evaluation of four methods for measuring denitrification. *Soil Science Society of America Journal,* 55, pp. 1332-1338.

Aulakh, M.S. Khera, T.S. Doran, J.W. & Bronson, K.F. (2001). Denitrification, N_2O and CO_2 fluxes in rice, wheat cropping system as affected by crop residues, fertilizer N and legume green manure. *Biology and Fertility of Soils,* 34, pp. 375-389.

Azam, F. Malik, K.A. & Hussain, F. (1986). Microbial biomass and mineralization-immobilization of nitrogen in some agricultural soils. *Biology and Fertility of Soils,* 2, pp. 157-163.

Barak, P. Molina, J.A.E. Hadas, A. & Clapp, C.E. (1990). Mineralization of amino acids and evidence of direct assimilation of organic nitrogen. *Soil Science Society of America Journal,* 54, pp. 769-774.

Barraclough, D. (1997). The direct or MIT route for nitrogen immobilization, An 15N mirror image study with leucine and glycine. *Soil Biology and Biochemistry,* 29, pp. 101-108.

Barton, L. McLay, C.D.A. Schipper, L.A. & Smith, C.T. (1999). Annual denitrfication rates in agricultural and forest soils, a review. *Australian Jurnal of Soil Research,* 37, pp. 1073-1093.

Bertram, J.E. Clough, T.J. Sherlock, R.R. Condron, L.M. O'Callaghan, M. Wells, N.S. & Ray, J.L. (2009). Hippuric acid and benzoic acid inhibition of urine derived N_2O emissions from soil. *Global Change Biology,* 15, pp. 2067-2077.

Bhandral, R. Saggar, S. Bolan, N.S. & Hedley, M.J. (2003). Nitrous oxide fluxes in soil as influenced by compaction. *Proceedings of the New Zealand Grassland Association,* 65, pp. 265-271.

Bhandral, R. Saggar, S. Bolan, N.S. & Hedley, M.J. (2007). Transformation of nitrogen and nitrous oxide emission from grassland soils as affected by compaction. *Soil and Tillage Research,* 94, pp. 482-492.

Bolan, N.S. Saggar, S. Luo, J. Bhandral, R. & Singh, J. (2004). Gaseous emissions of nitrogen from grazed pastures, processes, measurements and modelling, environmental implications, and mitigation. *Advances in Agronomy,* 84, pp. 37-120.

Bollmann, A. & Conrad, R. (1998). Influence of O_2 availability on NO and N_2O release by nitrification and denitrification in soils. *Global Change Biology,* 4, pp. 387-396.

Bouwman, A.F. (1990). Soils and the greenhouse effect, Proceedings of the International Conference Soils and the greenhouse effect, International Soil Reference and Information Centre ISRIC. John Wiley and Sons, New York, pp. 575.

Bouwman, A.F. Boumas, L.J.M. & Batjes, N.H. (2002). Emissions of N_2O and NO from fertilized fields, Summary of available measurement data. *Global Biogeochemical Cycles,* 16, pp. 1-13.

Bramley, R.G.V. & White, R.E. (1989). The effect of pH, liming, moisture and temperature on the activity of nitrifiers in a soil under pasture. *Australian Journal of Soil Research,* 27, pp. 711-724.

Bremner, J.M. & Blackmer, A.M. (1981). Terestrial nitrification as a source of atmospheric nitrous oxide, In: Delwiche, C.C. (Ed.), Denitrification, Nitrification and Atmospheric Nitrous Oxide. Willey and Sons, New York, pp. 151-170.

Bronson, K.F. & Fillery, I.R.P. (1998). Fate of nitrogen-15-labelled urea applied to wheat on a waterlogged texture-contrast soil. *Nutrient Cycling in Agroecosystems,* 51, pp. 175-183.

Cai, G. White, R.E. Chen, D. Fan, X.H. Pacholski, A. Zhu, Z.L. & Ding, H. (2002). Gaseous nitrogen losses from urea applied to maize on a calcareous fluvo-aquic soil in the North China Plain. *Australian Journal of Soil Research,* 40, pp. 737-748.

Casella, S. Leporini, C. & Nuti, M.P. (1984). Nitrous oxide production by nitrogen-fixing fast growing rhizobia. *Microbial Ecology,* 10, pp. 107-114.

Cavigelli, M.A. & Robertson, G.P. (2001). Role of denitrifier diversity in rates of nitrous oxide consumption in a terrestrial ecosystem. *Soil Biology and Biochemistry,* 33, pp. 297-310.

Cho, C.M. Burton, D.L. & Chang, C. (1997). Denitrification and fluxes of nitrogenous gases from soil under steady oxygen distribution. *Canadian Journal of Soil Science,* 77, pp. 261-269.

Christianson, C.B. & Howard, R.G. (1994). Use of soil thin-layer chromatography to assess the mobility of the phosphoric triamide urease inhibitors and urea in soil. *Soil Biology and Biochemistry,* 26, pp. 1161-1164.

Clark, M. Jarvis, S. & Maltby, E. (2001). An improved technique for measuring concentration of soil gases at depth in situ. *Communications in Soil Science and Plant Analysis,* 32, pp. 369-377.

Clayton, H. McTaggart, I.P. Parker, J. Swan, L. & Smith, K.A. (1997). Nitrous oxide emission from fertilised grassland, A 2-year study of the effects of N fertilizer form and environmental conditions. *Biology and Fertility of Soils,* 25, pp. 252-260.

Corre, M.D. Van Kessel, C. & Pennock, D.J. (1996). Landscape and seasonal patterns of nitrous oxide emissions in a semiarid region. *Soil Science Society of America Journal,* 60, pp. 1806-1815.

Creason, G.L. Byrnes, B.H. & Carmona, G. (1990). Urease inhibitory activity associated with N-butyl thiophosphoric triamide is due to formation of its oxon analog. *Soil Biology and Biochemistry,* 22, pp. 209-211.

Crutzen, P.J. (1981). Atmospheric chemical processes of the oxides of nitrogen including nitrous oxide, In: Delwidche, C.C. (Ed.), Denitrification, Nitrification and Atmospheric Nitrous Oxide. John Wiley, New York, pp. 17-44.

Crutzen, P.J. Mosier, A.R. Smith, K.A. & Winiwarter, W. (2007). N_2O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. *Atmospheric Chemistry and Physics Discussions,* 7, pp. 11191-11205.

Dalal, R. C. W. Wang, G. P. Robertson, & Parton, W. J. (2003). Nitrous Oxide Emission from Australian Agricultural Lands and Mitigation Options: A Review. *Australian Journal of Soil Research*, 41, pp. 165-195.

Daum, D. & Schenk, M.K. (1998). Influence of nutrient solution pH on N_2O and N_2 emissions from a soilless culture system. *Plant and Soil,* 203, pp. 279-287.

Daum, D. Schenk, M.K. & Roeber, R.U. (1997). Extent and N_2O/N_2 ratio of gaseous nitrogen losses from a soilless culture system. *Acta Horticulture,* 450, pp. 519-526.

Davidson, E.A. (1993). Soil water content and the ratio of nitrous oxide to nitric oxide emitted from soil, In: Oremland, R.S. (Ed.), *The Biogeochemistry of Global Change, Radiatively Active Trace Gases*. Chapman and Hall, New York, pp. 369-386.

De Boer, W. Klein Gunnewiek, P.J.A. Veenhuis, M. Bock, E. & Laanbroek, H.J. (1991). Nitrification at low pH by aggregated chemolithotrophic bacteria. *Applied and Environmental Mikrobiology,* 57, pp. 3600-3604.

de Klein, C.A.M. Barton, L. Sherlock, R.R. Li, Z. & Littlejohn, R.P. (2003). Estimating a nitrous oxide emission factor for animal urine from some New Zealand pastoral soils. *Australian Journal of Soil Research,* 41, pp. 381-399.

de Klein, C.A.M. & Eckard, R.J. (2008). Targetted technologies for nitrous oxide abatement from animal agriculture. *Australian Journal of Experimental Agriculture,* 48, pp. 14-20.

de Klein, C.A.M. Smith, L.C. & Monaghan, R.M. (2006). Restricted autumn grazing to reduce nitrous oxide emissions from dairy pastures in Southland, New Zealand. *Agriculture Ecosystems and Environment,* 112, pp. 192-199.

Dendooven, L. Murphy, M.E. & Catt, J.A. (1999). Dynamics of the denitrification process in soil from the Brimstone farm experiment, UK. *Soil Biology and Biochemistry,* 31, pp. 727-734.

Denman, K.L. (2007). Climate change: the physical science basis, In: Solomon, S. Qin, D. Manning, M. Marquis, M. Averyt, K. Tignor, M.M.B. Miller, H.L.J. (Eds.), Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, pp. 499-587.

Dobbie, K.E. & Smith, K.A. (2003). Impact of different forms of N fertilizers on N_2O emission from intensive grassland. *Nutrient Cycling in Agroecosytems,* 67, pp. 37-46.

Duxbury, J.M. Harper, L.A. & Mosier, A.R. (1993). Contributions of agroecosystems to global climate change, Agricultural Ecosystem Effects on Trace Gases and Global Climate Change. *American Society of Agronomy*, pp. 1-18.

Eriksen, A.B. & Holtan-Hartwig, L. (1993). Emission spectrometry for direct measurement of nitrous oxide and dinitrogen from soil. *Soil Science Society of America Journal,* 57, pp. 738-742.

Esterman, E.F. & McLaren, A.D. (1961). Contribution of rhyzosplane organisms to total capacity of plants to utilize organic nutrients. *Plant and Soil,* 15, pp. 243-260.

Fillery, I.R.P. (1983). Biological denitrification, In: Freney, J.R. Simpson, J.R. (Eds.), Gaseous Loss of Nitrogen from Plant-Soil Systems. Martinus Nijhoff/Dr. W.Junk Publishers, The Hague, pp. 33-64.

Firestone, M.K. (1982). Biological denitrification, In: Stevenson, F.J. (Ed.), Nitrogen in Agricultural Soils. American Society of Agronomy Inc., Crop Science Society of America, Inc., Soil Science Society of America, Inc.Publisher Madison, Wisconsin, USA, pp. 289-326.

Firestone, M.K. & Davidson, E.A. (1989). Microbiological basis of NO and N_2O production and consumption in soil, In: Andreae, M.O. Schimel, D.S. (Eds.), Report for the Dahlem Workshop on Exchange of the Trace Gases between Terrestrial Ecosystems and the Atmosphere. John Wiley and Sons, Berlin pp. 7-22.

Flessa, H. Wild, U. Klemisch, M. & Pfadenhauer, J. (1998). Nitrous oxide and methane fluxes from organic soils under agriculture. *European Journal of Soil Science,* 49, pp. 327-335.

Frankenberger, W.T. & Tabatabai, M.A. (1982). Amidase and urease activities in plants. *Plant and Soil,* 64, pp. 153-166.

Freney, J.R. & Black, A.S. (1988). Importance of ammonia volatilization as a loss process, In: Wilson, J.R. (Ed.), Advances in Nitrogen Cycling in Agricultural Ecosystems. CAB International, Wallingford, UK, pp. 156-173.

Garcia-Ruiz, R. Pattinson, S.N. & Whitton, B.A. (1998). Denitrification and nitrous oxide production in sediments of the Wiske, a lowland eutrophic river. *Science of the Total Environment*, 210-211, pp. 307-320.

García-Ruiz, R. Pattinson,S.N. Whitton, B.A. 1999. Nitrous oxide production in the river Swale–Ouse, North–East England, *Water Research*, 33 (5), pp. 1231-1237.

Godde, M. & Conrad, R. (2000). Influence of soil properties on the turnover of nitric oxide and nitrous oxide by nitrification and denitrification at constant temperature and moisture. *Biology and Fertility of Soils,* 32, pp. 120-128.

Goodroad, L.L. & Keeney, D.R. (1984). Nitrous oxide production in aerobic soils under varying pH, temperature and water content. *Soil Biology and Biochemistry,* 16, pp. 39-43.

Goossens, A. de Visscher, A. Boeckx, P. & van Cleemput, O. (2001). Two year field study on the emission of N_2O from coarse and middle, textured Belgian soils with different land use. *Nutrient Cycling in Agroecosystems,* 60, pp. 23-34.

Groffman, P.M. (1987). Nitrification and denitrification in soil, a comparison of incubation, enzyme assay and enumeration techniques. *Plant and Soil,* 97, pp. 445-450.

Groffman, P.M. (2002). Non-CO_2 greenhouse gases, Scientific understanding, control options and policy aspects, In: Van Ham, J. Baede, A.P.M. Guicherit, R. Williams-Jacobes, J.G.F.M. (Eds.), Proceedings of the Third International Symposium, Mechanisms,

Rates and Assessment of N_2O in Groundwater, Riparian Zones and Rivers Maastricht, The Netherlands, pp. 159-166.

Groffman, P.M. Gold, A.J. Kellog, D.Q. & Addy, K. (2002). Mechanisms, rates and assessment of N_2O in groundwater, riparian zones and rivers, In: Van Ham, J. Baede, A.P.M. Guicherit, R. Williams-Jacobse, J.G.F.M. (Eds.), Proceedings of the Third International Symposium on Non-CO_2 Greenhouse Gases, Scientific Understanding, Control Options and Policy Aspects. Millpress, Rotterdam, Maastricht, The Netherlands, pp. 159-166.

Groffman, P.M. & Tiedje, J.M. (1989). Denitrification in north temperate forest soils, spatial and temporal patterns at the landscape and seasonal scale. *Soil Biology and Biochemistry,* 21, pp. 613-620.

Gross, P.J. & Bremner, J.M. (1992). Acetone problems in use of the acetylene blockage method for assessment of denitrifying activity in soil. *Communications in Soil Science and Plant Analysis,* 23, pp. 1345-1358.

Grundmann, G.L. Renault, P. Rosso, L. & Bardin, R. (1995). Differential effects of soil water content and temperature on nitrification and aeration. *Soil Science Society of America Journal,* 59, pp. 1342-1348.

Gut, A. Blatter, A. Fahrni, M. Lehmann, B.E. Neftel, A. & Staffelbach, T. (1998). A new membrane tube technique METT for continuous gas measurements in soils. *Plant and Soil,* 198, pp. 79-88.

Henrich, M. & Haselwandter, K. (1997). Denitrification and gaseous nitrogen losses from an acid spruce forest soil. *Soil Biology and Biochemistry,* 29, pp. 9-10.

Hynšt, J. Brůček, P. & Šimek , M. (2007). Nitrous oxide emissions from cattle-impacted pasture soil amended with nitrate and glucose. *Biology and Fertility of Soils,* 43, pp. 853-859.

IFA. (2010). International Fertiliser Association statistics, Nitrogen Fertilizer Consumption by Region, In: Wilson, J.R. (Ed.), Advances in Nitrogen Cycling in Agricultural Ecosystems.

Inubushi, K. Naganuma, H. & Kitahara, S. (1996). Contribution of denitrification and autotrophic and heterotrophic nitrification to nitrous oxide production in andosols. *Biology and Fertility of Soils* 23, pp. 292-298.

IPCC. (2007). Climate Change, Mitigation of Climate Change, Contribution of Working Group III to the Intergovernmental Panel on Climate Change, Fourth Assessment Report, Cambridge.

Jambert, C. Serca, D. & Delmas, R. (1997). Quantification of N, losses as NH_3, NO, and N_2O and N_2 from fertilized maize fields in southwestern France. *Nutrient Cycling in Agroecosystems,* 48, pp. 91-104.

Jenkinson, D.S. & Ladd, J.N. (1981). Microbial biomass in soils, measurement and turn over, In: Paul, E.A. Ladd, J.N. (Eds.), Soil Biochemistry. Marcel Dekker, New York, pp. 415-471.

Kanakidou, M. Keller, M. Melillo, J.M. & Zavaria, G.A. (1989). Trace gas exchange and the chemical and physical climate, critical interactions, In: Andreae, M.O. Schimel, D.S. (Eds.), Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere. John Wiley & Sons Ltd. Chichester, pp. 303-320.

Khalil, M.I. Rosenani, A.B. van Cleemput, O. Fauziah, C.I. & Shamshuddin, J. (2002). Nitrous oxide emissions from an ultisol of the humid tropics under maize, groundnut rotation. *Journal of Environmental Quality,* 31, pp. 1071-1078.

Kostina, N.V. Stepanov, A.L. & Umarov, M.M. (1996). Impact of environmental factors of nitrous oxide reduction in some soil types. *Eurasian Soil Science,* 28, pp. 175-184.

Kwong, K.F.N.K. Bholah, A. Veerapen, S. & Singh, V. (1999). Gaseous nitrogen losses from soils under sugar cane in Mauritius, In: Kumar, V. (Ed.), Proceedings of the XXIII ISSCT Congress, New Delhi, India, pp. 70-79.

Ladd, J.N. & Jackson, R.B. (1982). Biochemistry of ammonification, In: Stevenson, F.G.S. (Ed.), Nitrogen in Agricultural Soil. American Society of Agronomy Madison Wisconsin, pp. 173-228.

Ledgard, S.F. & Luo, J. (2008). Nitrogen cycling in intensively grazed pastures and practices to reduce whole-farm nitrogen losses, Multifunctional Grasslands in a Changing World, Organizing Committee of 2008 IGC/IRC Conference. Guangdong People's Publishing House, pp. 292-297.

Ledgard, S.F. Menneer, J.C. Welten, B. Kear, M.J. Dexter, M.M. Lindsey, S.B. Betteridge, K. Crush, J.R. & Pacheco, D. (2007). New nitrogen mitigation technologies for evaluation in the lake Taupo catchment, In: L.D. C. L.J. Y. (Eds.), Proceedings of the Workshop "Design Sustainable Farms, Critical Aspects of Soil and Water Management. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand, pp. 19-24.

Ledgard, S.F. Penno, J.W. & Sprosen, M.S. (1999). Nitrogen inputs and losses from clover/grass pastures grazed by dairy cows, as affected by nitrogen fertilizer application. *Journal Agricultural Science Cambridge,* 132, pp. 215-225.

Linn, D.M. & Doran, J.W. (1984). Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. *Soil Science Society of America Journal,* 48, pp. 1267-1272.

Lloyd, A.B. & Sheaffe, M.J. (1973). Urease activity in soils. *Plant and Soil,* 39, pp. 71-80.

Luo, J. & Ledgard, S.F. (2008). A test of a winter farm management option for mitigating nitrous oxide emissions from a dairy farm. *Soil Use and Management,* 24, pp. 121-130.

Ma, W.K. Schautz, A. Fishback, L.A.E. Bedard-Haughn, A. Farrell, R.E. & Siciliano, S.D. (2007). Assessing the potential of ammonia oxidizing bacteria to produce nitrous oxide in soils of a high arctic lowland ecosystem on Devon Island, Canada. *Soil Biology and Biochemistry,* 39, pp. 2001-2013.

Manunza, B. Deiana, S. Pintore, M. & Gessa, C. (1999). The binding mechanism of urea, hydroxamic acid and N-(N-butyl)-phosphoric triamide to the urease active site. A comparative molecular dynamics study. *Soil Biology and Biochemistry,* 31, pp. 789-796.

Martikainen, P.J. (1985). Nitrous oxide emission associated with autotrophic ammonium oxidation in acid coniferous forest soil. *Applied and Environmental Microbiology,* 50, pp. 1519-1525.

Matheson, F.E. Nguyen, M.L. Cooper, A.B. & Burt, T.P. (2003). Short-term nitrogen transformation rates in riparian wetland soil determined with nitrogen-15. *Biology and Fertility of Soils,* 38, pp. 129-136.

Matheson, F.E. Nguyen, M.L. Cooper, A.B. Burt, T.P. & Bull, D.C. (2002). Fate of 15N-nitrate in unplanted, planted and harvested riparian wetland soil microcosms. *Ecological Engineering,* 19, pp. 249-264.

McMahon, P. Dennehy, K. & Sandstrom, M. (1999). Hydraulic and geochemical performance of a permeable reactive barrier containing zero-valent Iron, Denver Federal Center. *Ground Water* 37, pp. 396-404.

Mengel, K. (1996). Turnover of organic nitrogen in soils and its availability to crops. *Plant and Soil*, 181, pp. 83–93.

Mondini, C. Sinicco, T. Cayuela, M.L. Sanchez-Monedero, M.A. 2010.A simple automated system for measuring soil respiration by gas chromatography. *Talanta*, 81, pp. 849–855

Mosier, A.R. Doran, J.W. & Freney, J.R. (2002). Managing soil denitrification. *Journal of Soil and Water Conservation,* 57, pp. 505-513.

Mosier, A.R. Guenzi, W.D. & Schweizer, E.E. (1986). Soil losses of dinitrogen and nitrous oxide from irrigated crops in Northeastern Colorado. *Soil Science Society of America Journal,* 50, pp. 344-348.

Mosier, A.R. & Klemedtsson, L. (1994). Measuring denitrification in the field, In: Weaver, R.W. (Ed.), *Methods of Soil Analysis Part 2 SSSA Book Series, Madison*, WI, pp. 1047-1065.

Muller, C. Martin, M. Stevens, R.J. Laughlin, R.J. Kammann, C. Ottow, J.C.G. & Jager, H.J. (2002). Processes leading to N_2O emissions in grassland soil during freezing and thawing. *Soil Biology and Biochemistry,* 34, 1325-1331.

Mulvaney, R.L. Khan, S.A. & Mulvaney, C.S. (1997). Nitrogen fertilizers promote denitrification. *Biology and Fertility of Soils,* 24, pp. 211-220.

Nägele, W. & Conrad, R. (1990). Influence of soil- pH on the nitrate-reducing microbial populations and their potential to reduce nitrate to NO and N_2O. *FEMS Microbial Ecology,* 74, pp. 49-57.

Nguyen, M.L. Rutherford, J.C. & Burns, D. (1999). Denitrification and nitrate removal in two contrasting riparian wetlands, In: Tomer, M. Robinson, M. Gielen, G. (Eds.), Modelling of Land Treatment Systems. Proceedings of the 20th New Zealand Land Treatment Collective Technical Session. New Zealand Forest Research Institute, Rotorua, NZ New Plymouth, NZ, pp. 127-131.

Nobre, A.D. Keller, M. Crill, P.M. & Harriss, R.C. (2001). Short-term nitrous oxide profile dynamics and emissions response to water, nitrogen and carbon additions in two tropical soils. *Biology and Fertility of Soils,* 34, 363-373.

Parkin, T.B. (1987. Soil microsites as a source of denitrification variability. *Soil Science Society of America Journal,* 51, pp. 1194-1199.

Paul, E.A. & Clark, E. (1996). Ammonification and nitrification, In: Paul, E.A. Clark, E. (Eds.), *Soil Microbiology and Biochemistry*. Academic Press, Inc. , USA, pp. 182-196.

Paul, J.W. & Beauchamp, E.G. (1989). Effect of carbon constituents in manure on denitrification in soil. *Canadian Journal of Soil Science,* 69, pp. 49-61.

Pinay, G. & Decamps, H. (1988). The role of riparian woods in regulating nitrogen fluxes between the alluvial aquifer and surface waters, A conceptual model. *Regulated Rivers Research and Management* 2, pp. 507-516.

Poth, M. & Focht, D.D. (1985). 15N kinetic-analysis of N_2O production by Nitrosomonas europaea, an examination of nitrifier denitrification. *Applied and Environmental Microbiology,* 49, pp. 1134-1141.

Ramos, C. (1996). Effect of agricultural practices on the nitrogen losses to the environment. *Fertilizer Research,* 43, pp. 183-189.

Robertson, G.P. Andreae, M.O. Bingemer, H.G. Crutzen, P.J. Delmas, R.A. Duyzer, J.H. Fung, I. Harriss, R.C. Kanakidou, M. Keller, M. Melillo, J.M. & Zavaria, G.A. (1989). Group report ?race gas exchange and the chemical and physical climate: critical interactions. In: Andreae, M.O. and Schimel, D.S. (eds), Exchange of trace gases between terrestrial ecosystems and the atmosphere. pp. 303 – 320. John Wiley & Sons Ltd. Chichester.

Roberge, M.R. & Knowels, R. (1967). The ureolytic microflora in a black spruce (*Picea mariana* Mill) humus. *Soil Science Society of America Proceedings,* 31, pp. 76-79.

Robertson, G.P. & Tiedje, J.M. (1987). Nitrous oxide sources in aerobic soils, nitrification, denitrification and other biological processes. *Soil Biology and Biochemistry,* 19, pp. 187-193.

Robinson D. (2001). Delta N-15 as an integrator of the nitrogen cycle. *Trends in Ecology and Evolution,* 16, pp. 153–162.

Rochester, I.J. (2003). Estimating nitrous oxide emissions from flood-irrigated alkaline grey claysna. *Australian Journal of Soil Research,* 41, pp. 197-206.

Ryden, J.C. (1983). Denitrification loss from a grassland soil in the field receiving different rates of nitrogen as ammonium. *Journal of Soil Science,* 34, pp. 355-365.

Ryden, J.C. & Lund, L.J. (1980). Nature and extent of directly measured denitrification losses from some irrigated vegetable crop production units. *Soil Science Society of America Journal,* 44, pp. 505-511.

Saggar, S. Andrew, R.M. Tate, K.R. Hedley, C.B. Rodda, N.J. & Townsend, J.A. (2004a). Modelling nitrous oxide emissions from New Zealand dairy grazed pastures. *Nutrient Cycling in Agroecosystems,* 68, 243-255.

Saggar, S. Bolan, N.S. Bhandral, R. Hedley, C. & Luo, J. (2004b). Emissions of methane, ammonia and nitrous oxide from animal excreta deposition and farm effluent application in grazed pastures. *New Zealand Journal of Agricultural Research,* 47, pp. 513-544.

Saggar, S. Bolan, N.S. Singh, J. & Blard, A. (2005). Economic and environmental impacts of increased nitrogen use in grazed pastures and the role of inhibitors in mitigating nitrogen losses. *New Zealand Science Review,* 62, pp. 62-67.

Saggar, S. Hedley, C.B. Giltrap, D.L. & Lambie, S.M. (2007). Measured and modelled estimates of nitrous oxide emission and methane consumption from sheep-grazed pasture. *Agriculture Ecosystems and Environment,* 122, pp. 357-362.

Saggar, S. Luo, J. Giltrap, D.L. & Maddena, M. (2009). Nitrous oxide emissions from temperate grasslands, processes, measurements, modelling and mitigation, In: Adam, I.S. Barnhart, E.P. (Eds.), Nitrous Oxide Emissions Research Progress. Nova Science Publishers, Inc. , pp. 1-66.

Sanz-Cobena, A. Misselbrook, T.H. Arce, A. Mingot, J.I. Diez, J.A. & Vallejo, A. (2008). An inhibitor of urease activity effectively reduces ammonia emissions from soil treated

with urea under Mediterranean conditions. *Agriculture Ecosystem and Environment,* 126, pp. 243-249.

Scholefield, D. Hawkins, J.M.B. & Jackson, S.M. (1997). Use of a flowing helium atmosphere incubation technique to measure the effects of denitrification controls applied to intact cores of a clay soil. *Soil Biology and Biochemistry,* 29, pp. 1337-1344.

Sherlock, R.R. Goh, K.M. Jewell, P. & Clough, T.J. (2009). Review of New Zealand specific FracGASM and FracGASF emission factors, Reports for Ministry of Agriculture and Forestry, pp. 52.

Silver, W.L. Herman, D.J. & Firestone, M.K. (2001). Dissimilatory nitrate reduction to ammonium in upland tropical forest soils. *Ecology,* 82, pp. 2410-2416.

Šimek, M. (2000). Nitrification in soil - terminology and methodology review. *Rostlinna-Vyroba,* 46, pp. 385-395.

Šimek, M. & Cooper, J.E. (2002). The influence of soil pH on denitrification, progress towards the understanding of this interaction over the last 50 years. *European Journal of Soil Science,* 53, pp. 345-354.

Šimek, M. & Hopkins, D.W. (1999). Regulation of potential denitrification by soil pH in long-term fertilized arable soil. *Biology and Fertility of Soils,* 30, pp. 41-47.

Šimek, M. Jíšová, L. & Hopkins, D.W. (2002). What is the so-called optimum pH for denitrification in soil? *Soil Biology and Biochemistry,* 34, pp. 1227-1234.

Singh, J. Saggar, S. Giltrap, D.L. & Bolan, N.S. (2008). Degradation kinetics of dicyandiamide in three soils and its effect on nitrous oxide emission and microbial biomass, An incubation study. *Australian Journal of Soil Research,* 46, pp. 517-525.

Skujins, J.J. (1976). Extracellular enzymes in soils. CRC. *Critical Review of Microbiology,* 4, pp. 383-421.

Smith, K.A. Ball, T. Conen, F. Dobbie, K.E. & Rey, A. (2003). Exchange of greenhouse gases between soil and atmosphere, interactions of soil physical factors and biological processes. *European Journal of Soil Science,* 54, pp. 779-791.

Smith, M.S. & Tiedje, J.M. (1979). Phases of denitrification following oxygen depletion in soil. *Soil Biology and Biochemistry,* 11, pp. 261-267.

Stevens, R.J. Laughlin, R.J. Burns, L.C. Arah, J.R.M. & Hood, R.C. (1997). Measuring the contributions of nitrification and denitrification to the flux of nitrous oxide from soil. *Soil Biology and Biochemistry*, 29, pp.139-151.

Stevens, R.J. & Laughlin, R.J. (1998). Measurement of nitrous oxide and di-nitrogen emissions from agricultural soils. *Nutrient Cycling in Agroecosystems,* 52, pp. 131-139.

Sutka, R.L. Ostrom, N.E. Ostrom, P.H. Breznak, J.A. Gandhi, H. Pitt, A.J. & Li, F. (2006). Distinguishing nitrous oxide production from nitrification and denitrification on the basis of isotopomer abundances. *Applied and Environmental Microbiology*, 72, pp. 638–644.

Swerts, M. Merckx, R. & Vlassak, K. (1996). Influence of carbon availability on the production of NO, N_2O, N_2 and CO_2 by soil cores during anaerobic incubation. *Plant and Soil,* 181, pp. 145-151.

Swerts, M. Merckx, R. & Vlassak, K. (1997). Denitrification, N_2,fixation and fermentation during anaerobic incubation of soils amended with glucose and nitrate. *Biology and Fertility of Soils,* 23, pp. 229-235.

Thornton, F.C. Bock, B.R. & Tyler, D.D. (1996). Soil emissions of nitric oxide and nitrous oxide from injected anhydrous ammonium and urea. *Journal of Environmental Quality,* 25, pp. 1378-1384.

Tiedje, J.M. (1988). Ecology of denitrification and dissimilatory nitrate reduction to ammonium, In: Zehnder, J.B. (Ed.), Biology of Anaerobic Microorganisms. Wiley, New York, pp. 179-244.

Tilsner, J. Wrage, N. Lauf, J. & Gebauer, G. (2003). Emission of gaseous nitrogen oxides from an extensively managed grassland in NE Bavaria, Germany. *Biogeochemistry*, 63 (3), pp. 249-267.

Walker, J.T. Geron, C.D. Vose, J.M. & Swank, W.T. (2002). Nitrogen trace gas emissions from a riparian ecosystem in southern Appalachia. *Chemosphere,* 49, pp. 1389-1398.

Watson, C.J. (2000). Urease activity and inhibition principles and practice, Proceedings International Fertiliser-Society No. 454. International Fertiliser Society, UK, pp. 1-40.

Watson, C.J. Akhonzada, N.A. Hamilton, J.T.G. & Matthews, D.I. (2008). Rate and mode of application of the urease inhibitor N-n-butyl thiophosphoric triamide on ammonia volatilization from surface-applied urea. *Soil Use Management,* 24, pp. 246-253.

Watson, C.J. Miller, H. Poland, P. Kilpatrick, D.J. Allen, M. Garrett, M.K. & Christianson, C.B. (1994a). Soil properties and the ability of the urease inhibitor N-n-butyl thiophosphoric triamide NBTPT to reduce ammonia volatilization from surface-applied urea. *Soil Biology and Biochemistry,* 26, pp. 1165-1171.

Watson, C.J. Miller, H. Poland, P. Kilpatrick, D.J. Allen, M.D.B. Garrett, M.K. & Christianson, C.B. (1994b). Soil properties and the ability of the urease inhibitor N-N-butyl thiophosphoric triamide Nbtpt to reduce ammonia volatilization from surface-applied urea. *Soil Biology and Biochemistry,* 26, pp. 1165-1171.

Watson, C.J. Stevens, R.J. & Laughlin, R.J. (1990). Effectiveness of the urease inhibitor Nbpt N-normal-butyl thiophosphoric triamide for improving the efficiency of urea for ryegrass production. *Fertilizer Research,* 24, pp. 11-15.

Watson, S.W. Valos, F.W. & Waterbury, J.B. (1981). The family nitrobacteraceae, In: Starr, M.P. Stolp, H. Trupe, H.G. Below, A.P. Shlegel, H.G. (Eds.), The Prokaryotes, A handbook on Habits, Isolation, and Identification of Bacteria. Springer-Verlag, Berlin.

Weier, K.L. Doran, J.W. Power, J.F. & Walters, D.T. (1993). Denitrification and the dinitrogen/nitrous oxide ratio as affected by soil water, available carbon, and nitrate. *Soil Science Society of America Journal,* 57, pp. 66-72.

Weier, K.L. & Gilliam, J.W. (1986). Effect of acidity on denitrification and nitrous oxide evolution from Atlantic Coastal Plain soils. *Soil Science Society of America Journal,* 50, pp. 1202-1205.

Weiske, A. Benckiser, G. Herbert, T. & Ottow, J.C.G. (2001). Influence of nitrification inhibitor 3,4-dimethylpyrazole phosphate DMPP in comparison to dicyandiamide DCD on nitrous oxide emissions, carbon dioxide fluxes and methane oxidation during 3 years of repeated application in field experiments. *Biology and Fertility of Soils,* 34, pp. 109-117.

Whitehead, D.C. (1995). Grassland Nitrogen. CAB International, Wallingford, UK.

Wood, P.M. (1990). Autotrophic and heterotrophic mechanisms for ammonia oxidation. *Soil Use and Management,* 6, pp. 78-79.

World Resources Institute (2000). World Resources 2000–2001. World Resources Institute, Washington D.C.

Wrage, N. Velthof, G.L. Beusichem, M.L. & van Oenema, O. (2001. Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biology and Biochemistry,* 33, pp. 1723-1732.

Wrage, N. Velthof, G.L. Laanbroek, H.J. & Oenema, O. (2004). Nitrous oxide production in grassland soils, assessing the contribution of denitrification. *Soil Biology and Biochemistry,* 36, pp. 229-236.

Xu, X. Zhou, L. Cleemput, O.V. & Wang, Z. (2000). Fate of urea-15N in a soil-wheat system as influenced by urease inhibitor hydroquinone and nitrification inhibitor dicyandiamide. *Plant and Soil,* 220, pp. 261-270.

Zaman, M. & Blennerhassett, J.D. (2010). Effects of the different rates of urease and nitrification inhibitors on gaseous emissions of ammonia and nitrous oxide, nitrate leaching and pasture production from urine patches in an intensive grazed pasture system. *Agriculture Ecosystems and Environment,* 136, pp. 236-246.

Zaman, M. & Chang, S.X. (2004). Substrate type, temperature, and moisture content affect gross and net soil N mineralization and nitrification rates in agroforestry systems. *Biology and Fertility of Soils,* 39, pp. 269-279.

Zaman, M. Di, H.J. & Cameron, K.C. (1999a). Gross N-mineralization and nitrification rates and their relationships to enzyme activities and soil microbial biomass in soils treated with dairy shed effluent and ammonium fertilizer in the field. *Soil Use and Management,* 15, pp. 188-194.

Zaman, M. Di, H.J. Cameron, K.C. & Frampton, C.M. (1999b). Gross N mineralization and nitrification rates and their relationships to enzyme activities and soil microbial biomass in soils treated with dairy shed effluent and ammonium fertilizer at different water potentials. *Biology and Fertility of Soils,* 29 (2), pp. 178–186.

Zaman, M. & Nguyen, M.L. (2010). Effect of lime or zeolite on N_2O and N_2 emissions from a pastoral soil treated with urine or nitrate-N fertiliser under field conditions. *Agriculture Ecosystems and Environment,* 136, pp. 254-261.

Zaman, M. Nguyen, M.L. Blennerhassett, J.D. & Quin, B.F. (2008a). Reducing NH_3, N_2O and NO_3-N losses from a pasture soil with urease or nitrification inhibitors and elemental S-amended nitrogenous fertilizers. *Biology and Fertility of Soils,* 44, pp. 693-705.

Zaman, M. Nguyen, M.L. Gold, A.J. Groffman, P.M. Kellogg, D.Q. & Wilcock, R.J. (2008b). Nitrous oxide generation, denitrification and nitrate removal in a seepage wetland intercepting surface and subsurface flows from a grazed dairy catchment. *Australian Journal of Soil Research,* 46, pp. 565-577.

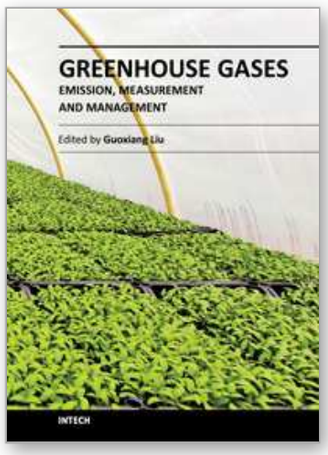
Zaman, M. Nguyen, M.L. Matheson, F. Blennerhassett, J.D. Quin, B.F. (2007). Can soil amendments zeolite or lime shift the balance between nitrous oxide and dinitrogen emissions from pasture and wetland soils receiving urine or urea-N? *Australian Journal of Soil Research,* 45, pp. 543-553.

Zaman, M. Nguyen, M.L. & Saggar, S. (2008c). N_2O and N_2 emissions from pasture and wetland soils with and without amendments of nitrate, lime and zeolite under laboratory condition. *Australian Journal of Soil Research,* 46, pp. 526-534.

Zaman, M. Saggar, S. Blennerhassett, J.D. & Singh, J. (2009). Effect of urease and nitrification inhibitors on N transformation, gaseous emissions of ammonia and nitrous oxide, pasture yield and N uptake in grazed pasture system. *Soil Biology and Biochemistry,* 41, pp. 1270-1280.

Zart, D. & Bock, E. (1998). High rate of aerobic nitrification and denitrification by Nitrosomonas eutropha grown in a fermentor with complete biomass retention in the presence of gaseous N_2O or NO. *Archives of Microbiology,* 169, pp. 282-286.

Zerulla, W. Barth, T. Dressel, J. Erhardt, K. Locquenghien, K.H.V. Pasda, G. Radle, M. & Wissemeier, A.H. (2001). 3,4-Dimethylpyrazole phosphate DMPP-a new nitrification inhibitor for agriculture and horticulture, an introduction. *Biology and Fertility of Soils*, 34, pp. 79-84.



Greenhouse Gases - Emission, Measurement and Management
Edited by Dr Guoxiang Liu

ISBN 978-953-51-0323-3
Hard cover, 504 pages
Publisher InTech
Published online 14, March, 2012
Published in print edition March, 2012

Understanding greenhouse gas sources, emissions, measurements, and management is essential for capture, utilization, reduction, and storage of greenhouse gas, which plays a crucial role in issues such as global warming and climate change. Taking advantage of the authors' experience in greenhouse gases, this book discusses an overview of recently developed techniques, methods, and strategies: - A comprehensive source investigation of greenhouse gases that are emitted from hydrocarbon reservoirs, vehicle transportation, agricultural landscapes, farms, non-cattle confined buildings, and so on. - Recently developed detection and measurement techniques and methods such as photoacoustic spectroscopy, landfill-based carbon dioxide and methane measurement, and miniaturized mass spectrometer.

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

IntechOpen