Lignite Exacerbates Nitrous Oxide Emissions from New Zealand Pastoral Systems

A dissertation
submitted in partial fulfilment
of the requirements for the Degree of
Bachelor of Science with Honours

at
Lincoln University
by
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Lincoln University
2013

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Abstract

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Lignite is sold in New Zealand as a soil amendment that purportedly improves soil fertility and reduces nitrate (NO_3^-) leaching from urea. Its use may increase due to recent research that showed lignite reduces the threat of cadmium (Cd) in pasturelands. There is no information on how lignite affects the production of nitrous oxide (N_2O), a greenhouse gas with a global warming potential some 300 times greater than carbon dioxide. This work aimed to test the hypothesis that lignite would reduce N_2O emissions by binding ammonium (NH_4^+) in soils amended with urea and biosolids. A lysimeter trial using a closed chamber method was used to measure N_2O flux from a Lismore stony silt loam soil sown with *Lolium multiflorum* Lam. (Italian ryegrass pasture). Treatments comprised control (no amendment), urea (200 kg N/ha equivalent), and biosolids (400 kg N/ha equivalent). Each treatment was replicated three times, with and without lignite addition (20 tonnes/ha) equivalent. Lignite significantly increased N_2O emissions from urea treated lysimeters, thereby falsifying the hypothesis that lignite would reduce N_2O emissions. Cumulative N_2O emissions were 242 g N_2O-N/ha from the urea + lignite treatment compared to 125 g N_2O-N/ha from urea only treatment. Emissions from all other treatments were below 100 g N_2O-N/ha. Lignite significantly reduced NO_3^- from 193 in the urea treatment to 148 kg/ha in the urea + lignite treatment, but had no effect on leaching from the control (0.5 kg/ha) or biosolids treatment (3 kg/ha). The reduction in NO_3^- from the urea treatment was proportional to the cation exchange capacity (CEC) of the added lignite. The lack of effect on the biosolids treatment was consistent with the high NO_3^- concentration initially present in the biosolids. The unexpected increase in N_2O emissions from the urea + lignite treatment warrants further testing of N_2O evolution in contrasting soils amended with lignite.

Keywords: biosolids, brown coal, humates, nitrate leaching, nitrogen cycle, lignite, *Lolium multiflorum* Lam., sewage sludge

Acknowledgements

Firstly, I would like to specially thank my supervisor Brett Robinson for his patient guidance and insightful suggestions during all stages of this year. To my other supervisor Timothy Clough, thank you for your help, guidence and advice along the way.

A huge thank you to Dharini Paramashivam for your help with sample collection and analysis of the leachate trial. Your company was always welcomed and appreciated, particularily out in the field.

For the wonderful and effcient lab and technical support, thanks Manjula Premaratne, Teresa Parayil, Lynne Clucas, Roger Cresswell, Neil Smith, Roger Atkinson and Trevor Hendry. Thank you to Amal Torky for being able to find anything and anyone and always with a smile.

I would also like to thank all my fellow postgrad collegues for providing valuable clarification on various subjects and many laughs along the way.

Thank you to all my friends who have endlessly encouraged me through the year. Cheers to Chantelle Fisher, Alice O’Brien and Marie Macfarlane for your support and humour paricularily in my final few weeks of study.

Lastly to my family who have always believed in me and have been so supportive throughout my time at university. Thank you.

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Chapter 1

Introduction

1.1 Nitrogen fluxes from soil and environmetnal degregation

Nitrous oxide (N_2O) is a potent greenhouse gas (GHG) and a precursor to compounds involved in stratospheric ozone depletion (IPCC, 2007; Ravishankara et al., 2009). It has a global warming potential 298 times that of carbon dioxide (CO_2) over a period of 100 years and levels in the atmosphere have now risen to 319 parts per billion (ppb) (IPCC, 2007). Rapidly rising concentrations of GHG's are caused by anthropogenic activities, which exacerbate the greenhouse effect; thus evoking potentially irreversible changes in the global climate system. (Wrage et al., 2001). Nitrate (NO_3^-) leaching and water contamination have also become a major concern worldwide, particularly in developed countries where agriculture is intensifying (Bijay et al., 1995). High concentrations of NO_3^- in drinking water are harmful to human health, predominantly for infants less than 1 year of age. This has resulted in the establishment of drinking water standards, limiting the NO_3^- concentration in drinking water to 10 - 11.3 mg NO_3^- N/L. In addition, where high concentrations of NO_3^- drain into surface water bodies, deterioration in surface water quality is common. Implications from this include eutrophication, algal blooms, fish poisoning and reduced ascetic value. Water bodies may be classified as eutrophic when the total N concentration reaches 0.4 – 6 mg N/L (Di and Cameron, 2002b).

In New Zealand, anthropogenic N_2O emissions and NO_3^- leaching are primarily due to agricultural activities. Since 1990 there has been a 25.5% increase in N_2O emissions from agricultural soils (Ministry for the Environment, 2012). The biotic processes of nitrification and denitrification in the soil are considered the main mechanisms in which N_2O and NO_3^- are produced. However, small amounts of N_2O can be generated through non biological processes including the chemical decomposition of nitrite (NO_2^-) and hydroxylamine (Henault et al., 2012). Increases in nitrogen (N) fertiliser use and consequently in animal excreta are the primary sources of N_2O and NO_3^- found in agricultural soils in New Zealand (Cameron et al., 2013). Recently, the application of biosolids as a fertiliser for agricultural soils, or to rebuild those that are degraded is an area also generating interest. Biosolids represent an important source of organic matter and soil nutrients, in particular phosphorus (P) and N (Robinson et al.,2011). Future use of mineral fertilisers alone may not be adequate to support sustainable agriculture, thus land application of biosolids may offer an alternate solution. However, this would require significantly higher rates of application, which may result in N losses similar to traditional practices. Nitrogen losses from biosolids amended soils are highly variable (Knowles et al., 2011; Obi and Ebo, 1995).

The loss of N from agricultural soils in the form of N_2O and NO_3^- represents an important economic loss to producers and consumers of agricultural products (van Zwieten et al., 2009). Improved nutrient use efficiency requires techniques to keep applied nutrients in the topsoil and therefore in the main root zone of the crop. This requires a technology that is viable over large areas, is cost effective to apply and leaves the soil fertile. Soil amendments, such lignite, high in organic matter may be a feasible way to maintain soil fertility over a long period of time (Lehmann et al., 2003). The incorporation of lignite into agricultural soils could therefore retain N in the soil for longer and reduce the risk of N loss resulting from biological N transformations.

1.2 Lignite as a soil condtioner

Lignite (brown coal) is defined as a carbon (C) rich product that is an intermediate state between peat and coal (Zein El-Abedine and Hosny, 1982). Abundant worldwide, lignite is primarily mined for energy production. However; its low calorific value currently limits the large scale economic use of this resource, making it a relatively low cost candidate for pollution remediation (Pehlivan and Arslan, 2006). Studies have proven lignite to be an effective amendment for soils that are degraded and/or have low fertility. Recently, it has been found to reduce plant uptake of cadmium (Cd) therefore it may be an important amendment to New Zealand pastures (Simmler et al., 2013).

Currently no scientific studies have investigated the effect such amendments could have on the inhibition of the N cycle, and therefore N_2O emissions and N leaching. Despite this, products known as Black Urea and HuMates are currently being marketed as an amendment, which reduces N loss from agricultural soils (Advanced Nutrients, n.d.; HuMates, n.d.). Black urea consists of a coating comprised of humic and fulvic acids, amino acids, melanines, peptides and polysaccharides which are derived from lignite materials (Figure 1.1) (Advanced Nutrients, n.d.). Unpublished trials suggest that black urea could reduce the N and P application rates by 15 – 35% by locking N in the soil when applied at rates ranging between 200 and 300 kg/ha (Agricultural Research Trust, 2009). This has been attributed to the coating bonding with urea and its mineralised products (NH_4^+) thus reducing volatilisation and leaching of N from the soil.

In a greenhouse pot trial, van Vuuren and Claassens (2009) investigated the efficacy of black urea compared to other N sources on maize (*Zea mays* L.) growth. van Vuuren and Claassens (2009) suggest that black urea increased the yield by 46% compared to standard urea. This paper investigated plant growth and no data was available on the effect of black urea on N loss via emissions or leaching. It was suggested that black urea is best suited for grain crops as well as sugar fruit and vegetables. No information was available on the outcome of black urea application on grazed pasture (van Vuuren and Claassens, 2009).

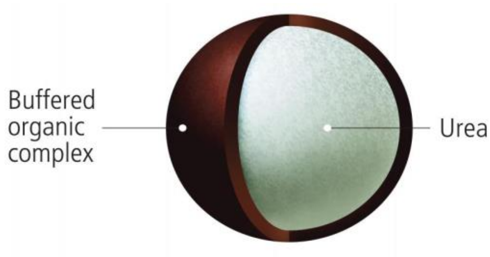

Figure 1-1. Black urea granule, with organic coating purported to improve nutrient efficacy in soil (AdvancedNutrients, n.d.).

1.3 Potential effects of lignite on soil nitrogen

Soil chemistry

The pathways of N loss and prospective sites where lignite could manipulate the N cycle are in agricultural soils are illustrated in Figure 1.2. By limiting the concentration of NH_4^+ available for nitrification and thence denitrificantion, the potential for NO_3^- leaching and N_2O emissions may be reduced. The addition of lignite may also create conditions conducive to N immobilisation in the soil. Should this occur, low concentrations of mineral N, may limit microbial activity in the soil conducive to N loss from the soil system. However, the extent to which N immobilisation would influence N available for plant uptake also needs to be considered.

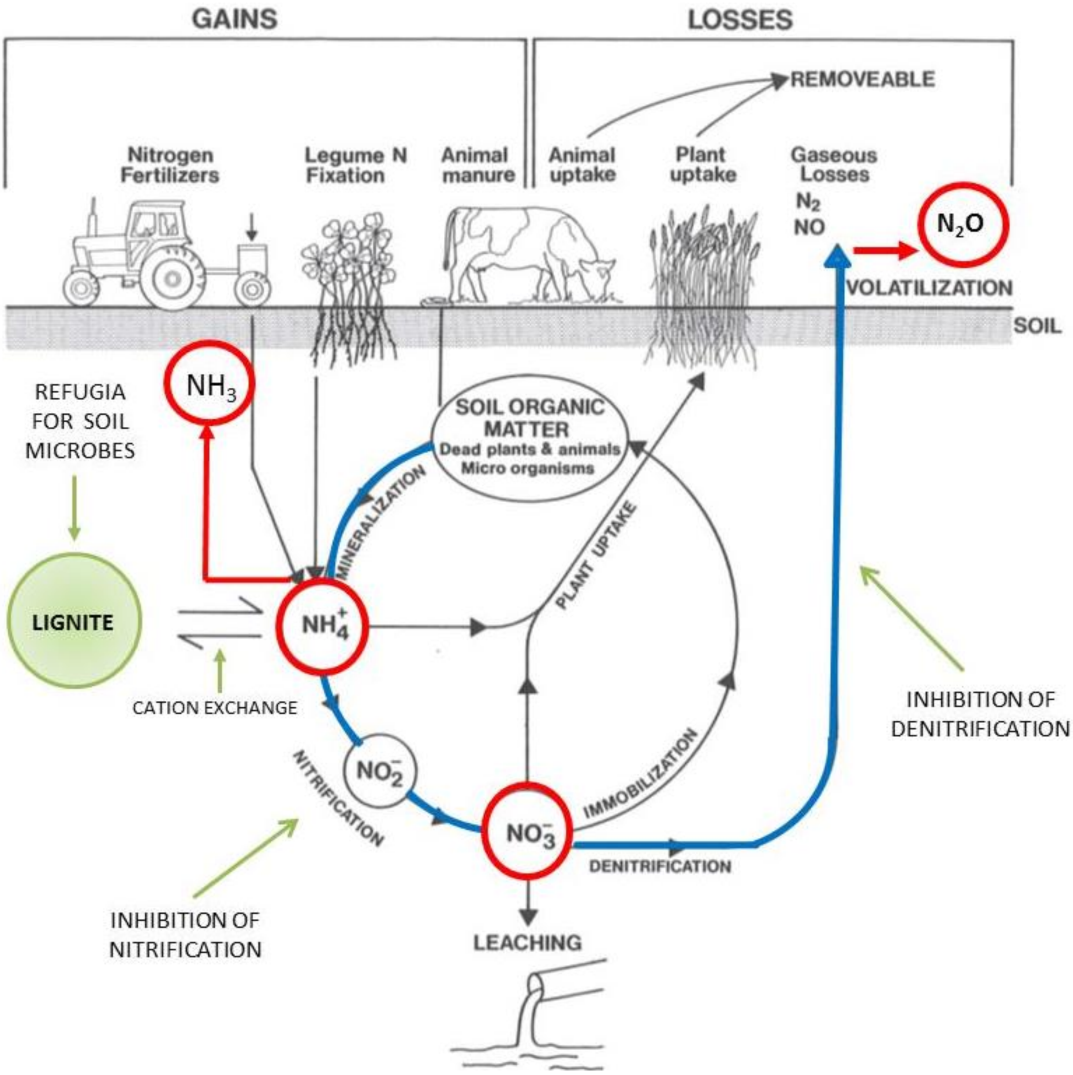

Figure 1-2. The N cycle in the soil-plant systems showing the microbiological processes that could be influenced by lignite amendment (blue), sources of N loss (red) and potential sites of inhibition by lignite addition (green). Adapted from McLaren & Cameron (1996).

Lignite may influence N_2O emissions from agricultural soils by both its chemical composition, and from specific physical properties. The most important mechanism by which lignite could influence the N cycle is via its ability to act as a porous system, allowing for absorption and ion exchange between the soil solution and solid phase (Kwiatkowska et al., 2008). Lignite contains a large portion of humic and fulvic acids (Pehlivan and Arslan, 2006). These exhibit similar characteristics to their equivalents in soil (Kwiatkowska et al., 2008). The ability of lignite to participate in ion exchange can be attributed to the many carbonyl (C=O) carboxyl (COOH) and phenolic hydroxyl (OH) functional groups associated with its structure (Arpa et al., 2000). Carboxyl groups of lignite increasingly dissociate between pH 2.5 and 7.0 while phenolic groups dissociate at a higher pH between 8.0 and 13.5 therefore the number and type of negatively charged functional groups available to participate in ion exchange could vary substantially, depending on the pH value of the surrounding environment.

Therefore, the viability of lignite as a soil amendment may vary over a range of pH values (Pehlivan and Arslan, 2006).

The functional groups associated with lignite can increase the cation exchange capacity (CEC) of a soil (Hue and Adams, 1984; Pehlivan and Arslan, 2006). The CEC of various lignite samples have been reported to range from 40 to 400 meq/100g (Jochová et al., 2004; Pentari et al., 2009). Ammonium (NH_4^+) in the soil carries a positive charge therefore an increase in soil CEC could bind NH_4^+ rendering it less available for nitrification. Ammonium, when removed from soil solution is no longer available as a substrate for microbial transformations. Ardakani et al. (1974) found that the abundance of *Nitrosomonas* bacteria involved in nitrification is strongly correlated to substrate supply provided all soil conditions are favourable. Because substrate supply is an important factor controlling nitrification in soil (Sherlock, 1992; Zhang et al., 2008), the rate at which nitrification occurs could be reduced via an increase in NH_4^+ retention, therefore retaining N in the soil for longer.

The removal of NH_4^+ ions from aqueous solution has been observed using activated lignite modified by oxidation. As the concentration of NH_4^+ increased, the removal efficiency decreased due to saturation of adsorption sites on the lignite (Vassileva et al., 2009). Currently, no studies have investigated NH_4^+ adsorption using lignite in soil. Under field condition, other ions in the soil may compete for exchange sites thereby reducing the efficiency of NH_4^+ adsorption and potentially the availability of other essential plant and animal elements. This was observed by Pusz (2007) when investigating the removal of Cd from soil solution when lignite was used as a fixing additive. Cadmium in soil solution was decreased due to adsorption with lignite functional groups however, the availability of plant essential elements, zinc (Zn) and copper (Cu), was also inhibited.

Kwiatkowska et al. (2008) found that seven years after application, soil amended with lignite had a higher C content, slightly higher N content and a higher C:N ratio than the control soil. The C:N ratio has a critical influence on N mobility within a soil. Lignite sludge in particular is characterised by a high total carbon content (34%) and high C:N ratio (68:1) (Domene et al., 2010; Dželetović et al., 2009). While ratios will vary depending on the origin and treatment of various lignite, evidence indicates that the removal of N substrate could result in a reduction of N_2O emissions. However, the immobilisation of mineral N will also limit the amount of N available for plant uptake. This could have undesirable consequences for plant growth and production (Tahir et al., 2011). If lignite were applied to soil on a larger scale across New Zealand, such questions are of crucial importance.

Soil micobes

It has yet to be determined whether lignite will have a positive effect on nitrifying and denitrifying bacteria in the soil. The rate of denitrification shows a positive response to increasing carbon and water-soluble carbon in the soil (Burford and Bremner, 1975; Wrage et al., 2001). When other soil factors are conducive to denitrification this can generate conditions favourable to high N_2O emission (Singh et al., 2010). In contrast, Rumpel and Kögel-Knabner (2004) & Domene et al. (2010) suggest that competition with other micro-organisms in the soil such as heterotrophic bacteria and fungi could limit denitrifier activity. Vallini et al. (1997) investigated the effect of humic acids derived from leonardite had on the activity and growth of *Nitrosomonas europaea* and *Nirtrobactor agilis* bacteria using cultured mediums. Results indicated an increase in NH_4^+ and NO_2^- oxidation and cell growth of nitrifying bacteria when leonardite was present. This was attributed to an increase in microbial membrane permeability favouring better utilisation of nutrients.

Equally unclear is whether lignite will provide refugia for soil microbes. The highly porous nature of lignite is similar to that of another carbonaceous amendment; biochar, which has been found to have both positive and negative effects on nitrifier and denitrifier activity (Atkinson et al., 2010; Knowles et al., 2011; O'Neill et al., 2009). Kolb et al. (2009) suggest that if microbes were to seek refugia within these micropores, microbe growth would be restricted due to reliance on diffusion to bring in any necessary nutrients and gasses.

Soil physics

Changes in soil structure, aeration and water holding capacity (WHC) occur following lignite application due to humic substances and the porous nature of the material (Dick et al., 2002; Gómez-Serrano et al., 2004). Lignite application to soil has been linked to improved soil aggregation especially in degraded soils where coal derived humic aids have increased soil aggregation by up 40 – 120% (Piccolo and Mbagwu, 1990; Piccolo et al., 1996). Where soil aeration is improved, a reduction in denitrification may occur. This was observed in the findings of (Yanai et al., 2007) where N_2O losses were higher when the soil was at 83% WFPS compared to only 73% WFPS. Alternatively, lignite has the ability to adsorbed both hydrophobic and hydrophilic molecules depending on the available functional groups on the surface of the lignite. Where hydrophilic groups attract water an increase in water retention could occur. (Richards et al., 1986) found that the high portion of meso and macro pores associated with lignite increased the water holding capacity of a sandy soil. However, there was no increase in plant available water suggesting that water is held under high tension by lignite particles. The retention of water in lignite-amended soils will be affected by soil type and its initial moisture content. In extremely dry soils, an increase in soil moisture may stimulate nitrifying bacteria while promoting denitrification in soils that already have high water contents. Possible adverse effects may occur if lignite is found to block soil pores and/or alter water movement throughout the profile when large quantities of hydrophobic compounds are present (Gerke et al., 2001; Richardson and Wollenhaupt, 1983).

1.4 Summary of potential effects on the nitrogen cycle

Table 1.1 summarises the mechanisms that may be affected by the incorporation of lignite into agricultural soils, and the potential benefits, which may result from these interactions.

Table 1-1. Proposed effects lignite could have on N transformations and N_2O emissions in New Zealand agricultural soils.

Mechanism	Soil process affected	Impact on N_2O emission
Increase in soil CEC	Nitrification	Decrease
Increase in soil WHC	Nitrification and denitrification	Increase or decrease
Alteration of microbial communities and biomass	Nitrification and denitrification	Increase or decrease
Increase in soil carbon	Mineralisation	Decrease
Alteration of soil pH	Nitrification and denitrification	Increase or decrease

1.5 Hypothesis

I hypothesise that the addition of lignite to soil will reduce N_2O emissions by limiting the concentration of NH_4^+ available for nitrification and thence denitrificantion. I would also expect that lignite would cause a significant reduction in NO_3^- leaching from soils amended with biosolids and urea.

1.6 Aims

The aim of this study was to investigate the effect of lignite on N_2O emissions in New Zealand pasturelands. Specifically, this investigation sought to determine N-fluxes in a low fertility soil, sown in *Lolium multiflorum* Lam. amended with biosolids and urea, with and without lignite.

I seek to test the concept that lignite could be used at agriculturally relevant application rates to significantly reduce the threat of N loss associated with agriculture in New Zealand. However, this is a short-term study. Therefore, even given a positive result, further work will be required to clarify management practices associated with lignite addition to soil.

Chapter 2

Background

Part A

2.1 Nitrous oxide importance

Naturally occurring N compounds can be described as non-reactive or reactive. Non-reactive N occurs as N_2 while reactive N (Nr) includes all inorganic (NO_3^-, NO_x, N_2O, NH_3, NH_4^+) and organic N compounds. Several forms of Nr contribute directly or indirectly to global climate change (Galloway et al., 2003). Nitrous oxide is of particular importance as it is classed as one of the three major anthropogenic greenhouse gasses after CO_2 and CH_4 (de Klein and Ledgard, 2005).

Greenhouse gases are atmospheric gases that absorb and re-emit long-wave radiation back to Earth's surface (Pinares-Patino et al., 2009). These are critically important for the regulation of Earth's surface temperature, as without them, the average temperature would be -19^{o}C instead of the current 14^{o}C (IPCC, 2007). Ice core data has shown that the atmospheric concentration of N_2O far exceeds pre industrial values (Figure 2.1). Since the industrial revolution the concentration of N_2O in the atmosphere has risen from a pre-industrial value of 270 ppb (parts per billion) to a value of 319 ppb in 2005 (IPCC, 2007). The N_2O molecule has an atmospheric residence time of 114 years and can be converted into ozone depleting gasses such as nitric oxide (NO) and nitrogen dioxide (NO_2) within the stratosphere (IPCC, 2007; Ravishankara et al., 2009).

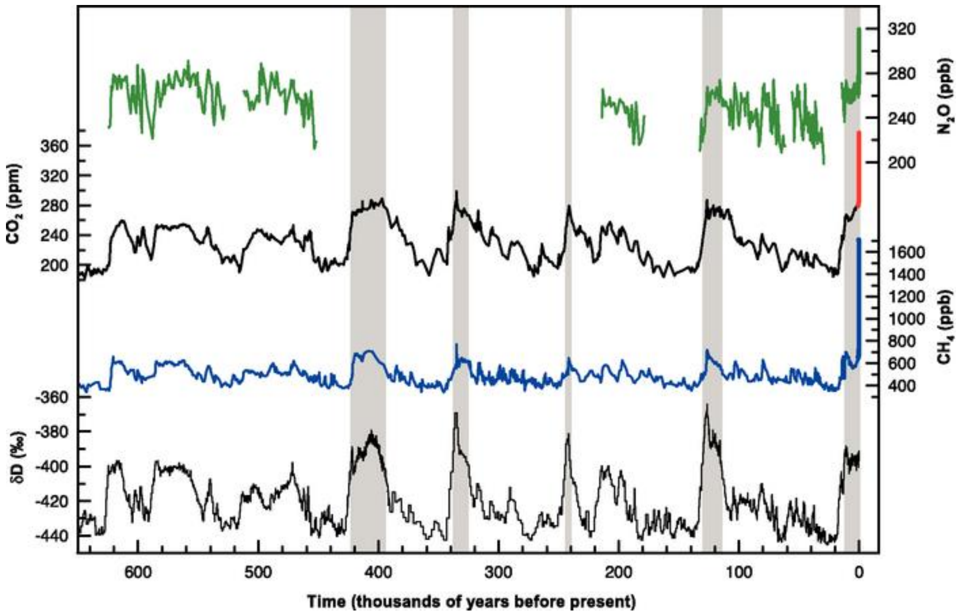

Figure 2-1. Variations of deuterium in antarctic ice, which is a proxy for local temperature, and the atmospheric concentrations of the greenhouse gases carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) in air trapped within the ice cores and from recent atmospheric measurements (IPCC, 2007).

In New Zealand agriculture is the dominant industry where GHG emissions from agriculture contribute over 50% of the nation's emissions, thus N_2O emissions form a considerable part of New Zealand's total GHG emissions (Figure 2.2) (de Klein and Ledgard, 2005; IPCC, 2007). The intensification of the dairy industry is a major reason for the increase in N_2O emissions in New Zealand (de Klein and Ledgard, 2005). Over the last 20 years New Zealand dairy production has risen 77 %, from three million dairy cattle in 1989 to six million dairy cattle in 2009 (Ministry for Primary Industries, 2013). Intensification has resulted in a wider range of dairy production systems, where systems have been evolving from the traditional all grass system to systems where a portion of the feed is imported, either as supplements or grazing off farm (Hedley et al., 2006). However, increasing N inputs from imported feeds in conjunction with substantial fertiliser inputs of N have become a growing concern with regards to N_2O emissions (Robertson and Vitousek, 2009).

New Zealand has signed up to the Kyoto Protocol and therefore has an obligation to aim to reduce GHG emissions to 1990 levels. Therefore, in order to reduce future total GHG emissions there is a need to find ways to mitigate agricultural emissions in order to reduce the effects of agriculture on global atmospheric pollution and climate change.

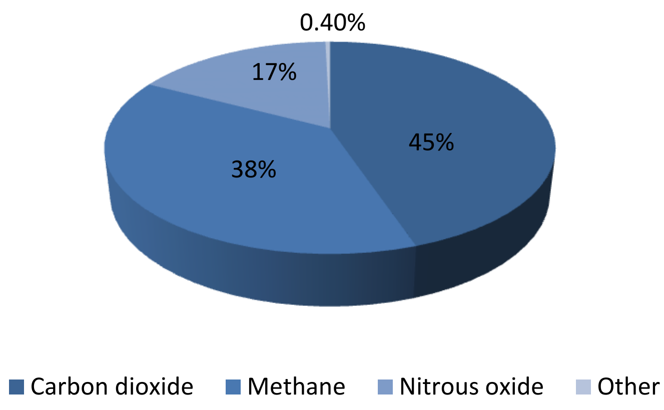

Figure 2-2. Relative contribution (CO_2 equivalent) of the three main greenhouse gasses to New Zealand's GHG inventory in 2001. Adapted from de Klein and Ledgard (2005).

2.1.1 Sources of nitrous oxide in agricultural soils

Human and animal waste and management

The main source of N_2O in grazed systems is excreta deposited by grazing animals or applied as effluent collected in the milking shed or winter housing systems. Because ruminants utilize relatively little of the N in their feed approximately 75-90% of their dietary N re-enters the system as manure and urine (de Klein et al., 2008). The amount of N excreted per animal will influence the amount of N_2O emitted from animal wastes (Oenema et al., 2005). For example, urine patches from dairy cattle are considered a major source of N_2O. This is because large amounts of N are deposited back onto small areas of pasture, which usually exceed plant requirements in the surrounding area. Nitrogen in cattle urine can be returned to pasture a rates ranging between 400-1200 kg N ha^{-1} (Fraser et al., 1994). The type of animal farmed, the intensity of production and farm management practises will affect the amount of N_2O produced from the farming system. Globally, it is expected that livestock numbers could increase by 40% between 2000 and 2030 (Food-Agriculture-Association, 2001). Coupled with a probable increase in N excreted per individual it is likely that N_2O emissions associated with animal wastes will continue to increase in the near future.

An increase in land application of biosolids in New Zealand may also be a contributing source of N_2O to the atmosphere. The end uses of biosolids can range from fertiliser or soil conditioner for pasture, crops, forests or reclamation, agriculture, horticulture, landscaping and nurseries (Clapp et al., 1994). Further research is required to determine the extent to which N_2O is emitted from these soils.

Synthetic fertiliser

Synthetic N fertiliser is essential to modern agriculture. Used to improve pasture growth during spring and autumn, N_2O emissions generally occur after initial application prior to uptake by plants (Mosier et al., 1998). Previous review have observed the N_2O emission factor associated with N fertiliser application to range from 0.1 to 2.0% of N applied, although emissions have been as high as 12%. Variation in the amount of N_2O emitted from N fertiliser applications is dependent on factors including agricultural practices, the rate of N applied, climatic conditions and soil properties (Cole et al., 1997; de Klein et al., 2001).

Cultivated histosols

Histosols are characterised by their high organic matter content. It is estimated that N_2O emissions resulting from the cultivation of these organic rich soils is 2 – 15 kg N_2O-N ha^{-1} y^{-1} of cultivated histosols (Mosier et al., 1998). Cultivation of histosols is thought to enhance the emission of N_2O through the mineralisation of N rich organic materials thereby promoting microbial activity in the soil. Cultivation further promotes soil aeration and this coupled with substrate supply can enhance nitrification in the soil and therefore N_2O emissions (Del Grosso et al., 2006; Nol et al., 2008).

Indirect emissions

Synthetic fertilizer and manure N input can give rise to indirect N_2O emissions. These can occur through NH_3 volatilization or NO_3^- leaching/runoff. Volatilisation and subsequent re-deposition of N in the form of NH_3 and NO_x may undergo further nitrification and denitrification to produce N_2O in locations downwind of the original source (Brumme and Beese, 1992). Schimel et al. (1986) has reported that approximately 20% of manure N applied to soils is volatized as NH_3 soon after application. Upon entry into these waterways, N lost as NO_3^- can further enhance biogenic production of N_2O as it undergoes nitrification and denitrification processes. However, there is limited data regarding N_2O emissions associated with N leaching and surface runoff, in particular in New Zealand and more research in this area is required (Mosier et al., 1998).

2.1.2 Processes involved in nitrous oxide production

Understanding the N cycle in agricultural systems is fundamental in order to understand the release of N_2O from agricultural soils. Denitrification and to a lesser extent, nitrification and nitrifier-denitrification are the main processes responsible for the production of N_2O in soils (Figure 2.3). Abiotic mechanisms including chemodenitrifiation can also produce N_2O emissions (de Klein et al., 2001).

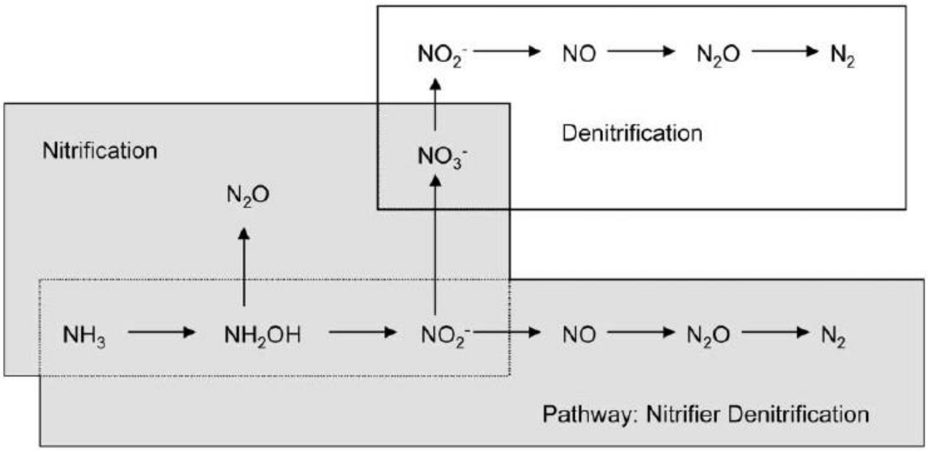

Figure 2-3. Summary of the transformations of mineral N in the cycling of soil N (Wrage et al., 2001).

Nitrification

Nitrification is an aerobic process in which NH_4^+ is oxidised to NO_2^- (equation 1) and then NO_2^- is further oxidised to NO_3^- (equation 2) (de Klein et al., 2001). This 2-step process involves two main groups of microorganisms. The first reaction is carried out by NH_3 oxidising bacteria including *Nitrosomonas* and *Nitrospira* and the second by NO_2^- oxidising bacteria including *Nitrobactor* (McLaren and Cameron, 1996). Under acidic conditions, archaea and heterotrophic fungi may also perform this process. This process typically occurs rapidly and as a result NO_2^- rarely accumulates in the soil (Di et al., 2010; Wrage et al., 2001).

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ + \text{energy} \qquad \text{(Eqn. 2.1)}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- + \text{energy} \qquad \text{(Eqn. 2.2)}$$

Nitrous oxide can be produced as a by-product of the intermediate products during nitrification. This is the result of the dissociation of hydroxylamine (NH_2OH) and NO_2^- (Figure 2.3) (Wrage et al., 2001). A range of soil and environmental factors affects both the rate of nitrification and the production of N_2O associated with this process. These can include pH, substrate supply, O_2 and moisture (Bremner, 1997; Haynes, 1986).

Denitrification

Denitrification is the anaerobic stepwise reduction of NO_3^- to N_2 (Figure 2.3) (Wrage et al., 2001). Predominantly carried out by heterotrophic bacteria including *Pseudemonas, Bacicillus* and others, denitrification involves a series of intermediate pathways that with reductase enzymes catalysing a particular sequence (Equation 2.3) (Sherlock, 1992; Wrage et al., 2001).

$$NO_3^- \xrightarrow{\text{Nitrate reductase}} NO_2^- \xrightarrow{\text{Nitrite reductase}} NO \xrightarrow{\text{Nitric oxide reductase}} N_2O \xrightarrow{\text{Nitrous oxide reductase}} N_2 \qquad \text{(Eqn. 2.3)}$$

Nitric oxide (NO) and N_2O are obligate intermediates in denitrification. Incomplete denitrification can occur when NO and N_2O are lost to the atmosphere before they can be reduced. Similar to nitrification, the soil environment influences the rate of denitrification and the products produced. It is widely accepted that pH, C substrate, O_2 and NO_3^- concentrations are influential factors controlling denitrification in soil (Haynes, 1986; Oenema et al., 2005).

Nitrifier-denitrification

Nitrifier-denitrification is the process in which the oxidation of NH_3 to NO_2^- is followed by the reduction of NO_2^- to N_2O and N_2 (Figure 2.3) and until recently this process was not considered to be of significant importance (Wrage et al., 2001). Poth and Focht (1985) suggest that nitrifier-denitrification occurs in response to limited oxygen (O_2) levels, toxic levels of NO_2^- and to decrease competition for O_2 by removing the substrate required by NO_2^- oxidisers. The production of N_2O during nitrifier-denitrification is thought to be increased when moisture levels are insufficient for denitrification (Kool et al., 2011) although the exact mechanisms behind these processes are not yet well understood.

2.1.3 Factors influencing nitrous oxide emissions

A number of primary factors including temperature, pH, substrates supply, O_2 and C affect nitrification and denitrification. However, these are often regulated by secondary factors such as soil texture and moisture levels (Figure 2.4). Because of these diverse and interacting factors, N_2O flux exhibits large spatial and temporal variability. This can often make quantifying total N_2O emissions from agricultural systems difficult (de Klein, 2001; Smith et al., 1998).

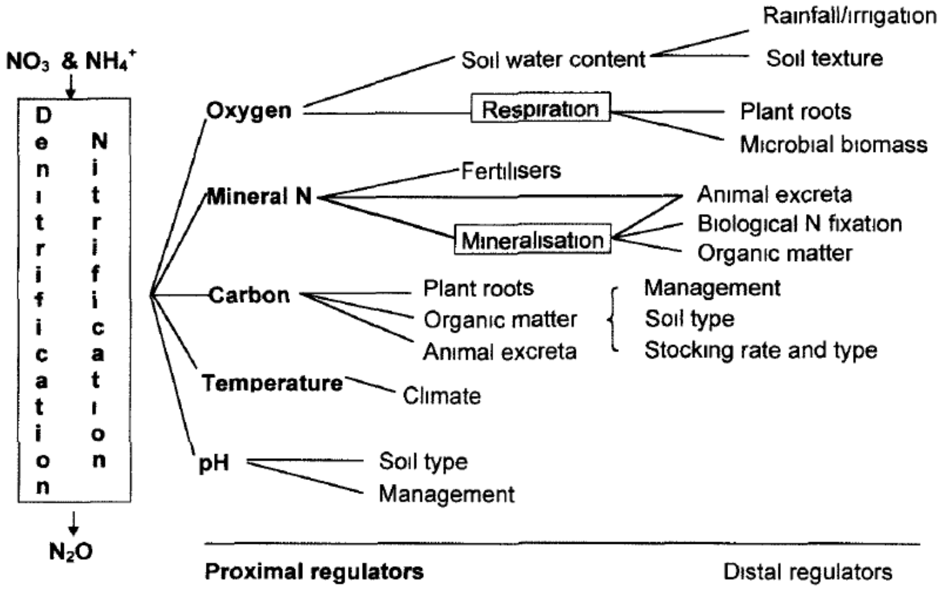

Figure 2-4. Systematic diagram illustrating the factors influencing N_2O emissions in agricultural soils (de Klein, 2001).

Temperature

Nitrous oxide flux has been observed to vary at different temperatures (Haynes, 1986; Sahrawat, 2008). Direct linear relationships between N_2O production and seasonal temperature changes are evident in many soils, particularly in temperate climates (Skiba and Smith, 2000). The optimum temperature for nitrifying bacteria ranges between 25 – 30°C, although this will vary between climatic regions. A significant reduction in nitrification occurs when temperatures decrease to around 5°C (Malhi and McGill, 1982; Myers, 1975). The rate of denitrification has been observed to increase with increasing temperature up to 30°C, but can also occur at a wide range of temperatures between 2 – 67°C (Malhi et al., 1990; Sherlock, 1992). (Smith et al., 2008) demonstrated that minimum and maximum flux of N_2O occurred at different times of the day and closely followed the soil temperature pattern. Here N_2O flux was observed to increase with an increasing surface temperature from 14 – 18°C. Additionally, temperature may also indirectly affect N_2O flux by disrupting O_2 solubility and diffusion in soil (Skiba and Smith, 2000).

Soil pH

Soil pH affects both nitrification and denitrification in the soil where it has been proven to influence the rate at which these processes occur and the product ratio of the gasses involved (Haynes, 1986; Šimek and Cooper, 2002). Rapid denitrification occurs when the soil pH is high (pH 7.0 to 8.0) and slows under acidic conditions (pH <5.0). Neutral and alkaline conditions favour N_2 production while acidic are conducive to the formation of N_2O (Wrage et al., 2001). This is reflected in the findings of Koskinen and Keeney (1982) who observed an increase in the N_2O:N_2 ratio at pH values of 4.6 and 5.2 compared to samples collected at pH 6.9 where N_2 was the dominant gas present. This may be because of the high sensitivity of the N_2O reductase enzyme to pH. The optimum pH for nitrification is within the range of 4.5 - 7.5. An increase in the presence aluminium (Al) ions at low pH levels can have a negative effect on the survival of nitrifying bacteria thus slowing the rate of nitrification. However, such conditions are unlikely to occur in agricultural soils due to the limiting effect low pH can have on plant growth, thus generally resulting in applications of lime to raise the soil pH (Šimek and Cooper, 2002). Additionally, the effect of pH may be indirect and influence the availability of soil constituents such as organic C and N mineralisation which become less available in acidic conditions (Šimek and Cooper, 2002).

Substrate supply

The availability of mineral N as a substrate for nitrification and denitrification is an essential element controlling N_2O flux (Mosier, 1994). The application of mineral N fertilisers rapidly increases N_2O emissions provided other soil conditions are optimal (Cameron et al., 2013). Similar results have been observed following the application of excreta and urine from grazing animals (Skiba and Smith, 2000). Evidence suggests that increases in nitrification and denitrification rates and subsequently N_2O losses associated with mineral N applications peak around 10-15 days after deposition. Therefore N_2O losses can be relatively short lived and near background levels obtained when the substrate is depleted (Yamulki et al., 1998). When NO_3^- levels are low, a delay in the reduction of N_2O to N_2 can occur, increasing N_2O loss to the atmosphere (Bremner, 1997). However, abundant levels of NO_3^- may also increase the rate at which N is lost as N_2O (Wrage et al., 2001). This is thought to occur because NO_3^- is preferred over N_2O as an electron acceptor and has been demonstrated by Gaskell et al. (1981) who showed that NO_3^- inhibited the reduction of N_2O to N_2 when present at high concentrations.

The accessibility of C to denitrifying bacteria strongly influences the rate of denitrification. Increasing the C availability enhances the energy and electron supply to denitrifiers while, also increasing O_2 consumption. Denitrification rates are positively correlated with the total C content of soil and to a greater extent the water soluble organic carbon in anaerobic conditions (Sherlock, 1992). Decreasing C availability is likely to increase the N_2O:N_2 ratio. This associated with the occurrence of partial denitrification resulting in the release of intermediate gasses N_2O and NO (Haynes, 1986; Sherlock, 1992).

Moisture and aeration

Soil moisture dynamics largely determine the biogeochemical environment for microbes, affecting the availability of dissolved nutrients and microbe activity (Haynes, 1986). High water contents stimulate denitrification and thus enforce the production of N_2O. Higher N_2O losses have been observed during winter and spring when the WFPS is above field capacity (Oenema et al., 2005).

Davidson (1991) developed a model that demonstrated the relationship between the water filled pore space (WFPS) of the soil and N trace gas emissions which showed that maximum N_2O loss occurs at a WFPS of 60%. Although Dobbie et al. (1999) has observed maximum loss to occur when WFPS is between 80-85%. Knowles (1982) found that the ratio of N_2O:N_2 produced is strongly influenced by the presence of O_2 due to the inhibition of nitrous oxide reductase. Here, it was observed that while the overall rate of denitrification was reduced when O_2 was present, the portion of N_2O released increased. Soil texture and farm management may also indirectly affect N_2O emissions. For example, the trampling effect of animals can result in soil compaction thereby limiting water infiltration and creating conditions favourable to denitrification (Sherlock, 1992).

2.2 Evaluation of nitrous oxide sampling methods

Nitrous oxide emissions are most commonly determined by enclosing the atmosphere above the soil and measuring the increase in headspace N_2O concentration over time (closed chamber method). This method is commonly employed because it is relatively cost efficient and straightforward, and it allows for process-based studies of N_2O emission from the soil (de Klein et al., 2001). Closed chamber sampling has been employed in studies in a range of environments. Lysimeters are commonly used in field studies to measure N_2O flux over time, where water troughs at the base of the chamber ensure that a gas tight seal is formed between the chamber and outside atmosphere (Di and Cameron, 2002c; Zaman et al., 2008). Laboratory incubation studies are also common, where soil is placed into jars and gas tight lids are used to collect samples (Azam et al., 2002; Wrage et al., 2005). This creates an controlled environment, where such studies have proven to be invaluable in establishing the effects of variables such as temperature, mineral N supply and soil water content on N_2O fluxes (Mosier et al., 1996). While less common, soil columns in the lab have also been used in certain instances (Clough and Kelliher, 2005). This method of sampling measures N_2O emission over a relatively small area, which due to large special variability in N_2O emissions, can hamper the extrapolation to field scale. It is suggested that this can be overcome by increasing the number and size of the flux chambers used (Mosier et al., 1996).

Variation in the availability of resources and the aims of the various studies has resulted in a wide range of materials and designs for sampling N_2O emissions using the closed chamber method. The chambers used are typically circular and can be made from a range of materials including PVC, metal insulated with polystyrene foam, and stainless steel (Ambus et al., 2007; Clough and Kelliher, 2005). They can range in height from 10 – 45 cm although most fall between 10 – 15 cm. Similarly, there is significant variation in sampling intervals used in individual studies. Dependant on the nature of the study, samples may be taken at intervals of 15, 20, 30, 40, 60 and 120 minutes to determine N_2O fluxes (Clough and Kelliher, 2005; Collins et al., 2011; Di and Cameron, 2002c). Alternate methods of

N_2O may also include micrometeorological methods, which involve measurements of N_2O in the atmosphere at two or more points above the soil surface, in combination with meteorological measurements or the employment of isotope techniques (Mosier et al., 1996).

Part B

2.3 Lignite

Lignite is a low-rank coal, which comprises of inorganic and organic materials. The inorganic fractions typically consist of clay minerals, carbonates, quartz and sulphides while the organic fraction originates from plant residues (Kabe et al., 2004). The formation of lignite is a process that occurs over several hundred million years. It involves the physical and chemical decomposition and alteration of plant residues via bacterial action under waterlogged and anoxic conditions. Plant material is first transformed into peat deposits, which upon on-going sedimentation become coalified as a result of pressure and temperature from the overlying sediment (Kabe et al., 2004; Senn and Kingman, 1973). The structure of lignite is still under discussion and research in this field has not been extensively undertaken. Figure 2.5 illustrates one possible structure of lignite and indicates how this can change depending on rank (degree of coalification) (Fakoussa and Hofrichter, 1999).

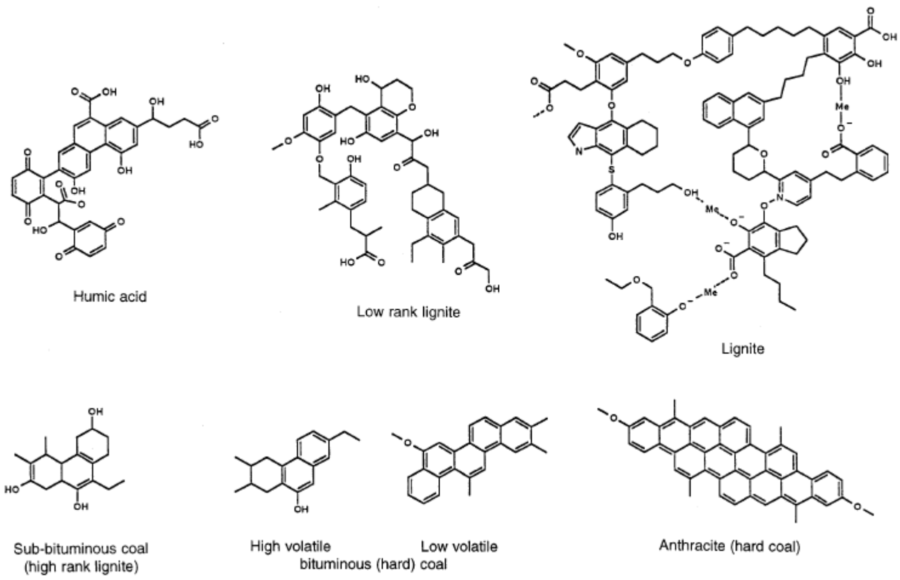

Figure 2-5. Examples of molecular structure for different ranked coals. Note that there is no simple formula for any of these coals, each of which contains a suite of molecules of varying molecular weights.

The general structure contains a range of aromatic rings, ester or ether linkages, alkylene bridges and humic materials, particularly humic acids. As the coal matures a corresponding increase in carbon can be observed, likewise a decrease in O_2. The elemental composition of lignite can vary significantly between samples of varying origin although it is usually consist of approximately 70% C, 25% O and 8-5% H (Table 2.1) (Hue and Adams, 1984; Kwiatkowska et al., 2008). The presence of sulphur in the form of pyrite (FeS_2) is also common in lignite. The amount of sulphur present can range from < 0.2% to >10% (Table 2.1) (Yani and Zhang, 2010). When exposed to O_2, pyrite can be oxidised to form ferrous, sulphate and hydrogen ions which may affect the biogeochemistry of the surrounding environment (Pugh et al., 1984). The type of lignite used as an amendment may therefore determine its success.

Table 2-1. Physiochemical properties for a range of lignite's varying in origin and rank.

	Moisture %	Volatile matter %	Fixed C %	C %	H %	N %	O %	S %	Reference
Canadian coal	7.3	31.8	38.2	72.6	4.5	1.1	21.0	0.4	(Goodarzi, 2002)
Canadian lignite	17.17	-	-	53.9	3.5	0.8	15.9	0.67	(MacPhee et al., 2006)
Greek lignite 1	18.8	47.7	39.2	55.0	5.3	1.9	24.1	0.6	(Vamvuka et al., 2003)
Greek lignite 2	-	66.2	33.7	55.1	5.7	2.7	34.5	1.8	(Pentari et al., 2009)
Greek lignite 3	-	56.9	43.0	65.8	5.0	1.5	25.0	2.5	(Pentari et al., 2009)
Greek lignite 4	-	-	-	56.7	4.2	2.4	33.0	3.7	(Kalaitzidis et al., 2006)
Turkish lignite	20.0	26.0	-	62.5	5.7	1.8	28.8	1.9	(Pehlivan and Arslan, 2006)
Spanish lignite	2.6	37.8	54.7	63.0	4.2	0.5	20.4	0.5	(Gómez-Serrano et al., 2004)
Spanish leonardite	4.2	38.3	51.8	53.9	3.4	0.5	31.8	5.3	(Gómez-Serrano et al., 2004)
Australian lignite 1	-	-	-	72.7	5.9	5.0	20.7	0.2	(Fei et al., 2006)
Australian lignite 2	-	-	-	67.6	5.0	6.0	26.2	-	(Nakajima et al., 2005)
Malaysia lignite	37.4	-	-	58.0	4.1	1.92	24.1	0.65	(Azmi et al., 2006)
Czech republic lignite	37.8	-	-	72.9	5.8	-	-	2.13	(Jochová et al., 2004)

Oxidation of lignite could further increase its effectiveness as an amendment by increasing the presence of functional groups able to partake in ion exchange (Dick et al., 2002; Martínez and

Escobar, 1995). If incorporated into soil natural wreathing agents including O_2, CO_2, H_2O and biota could increase the functional group content over time however, there is no current data indicating the rate and extent to which this could occur. Martínez and Escobar (1995) indicate that as weathering proceeds, there is a stong corresponding change in humic sustance concentrations and an associated decline in aliphatic structures (Table 2.2).

Table 2-2. Chemical data indicating the effect of weathering on sample moisture, humic acid and carboxylic acid content for a range of coals varying in rank.

	Moisture (%)	Humic acids (wt%)	Carboxylic acids (meq. g)
Fresh bituminous coal	1.7	0	0
Weathered bituminous coal	17.8	23	0.90
Fresh subbituminous	8.0	0	0.04
Weathered subbituminous	17.8	30	1.32
Fresh subbituminous	7.9	0	0.15
Weathered subbituminous	17.6	73	1.54
Peat	49.3	60	0.74
Peat	26.7	1	0.24

2.4 Persistance in soil

Lignite in its basic or modified form is a carbonaceous material relatively resistant to microbial decomposition thus it is likely to remain in the soil for a long time. This gives it an advantage over other organic amendments, which are readily decomposed (Pusz, 2007; Zein El-Abedine and Hosny, 1982). The incorporation of organic C into hydrophobic domains where it becomes physically protected from rapid decomposition has been proposed as one potential explanation for its persistence in soil (Spaccini et al., 2002). The long-term persistence of lignite in soil was evident in a pot trial where 140 g of lignite per pot was added to the lignite treatments. Results indicated that the pots amended with lignite had a higher C and N content than the control pots seven years after initial application (Kwiatkowska et al., 2008). Continued reductions in Cd concentrations in the leaf tissue of a variety of plant species two years after amendment with lignite also implies that lignite may remain in the soil for a minimum two year period (Vermes and Kadar, 2002). Following the field application of basic and modified lignite in granular form, cracking and breakdown of the modified lignite appeared to be more pronounced than the un-modified treatments implying that modified lignite may be more susceptible to breakdown and decomposition (Zein El-Abedine and Hosny, 1982). The translocation of lignite, in particular finer fragments, downwards in the soil profile may cause losses of lignite from the soil surface thus reducing its effect as a soil amendment. However, complete removal from the root zone is not expected (Zein El-Abedine and Hosny, 1982) and leaching experiments have proven the infiltration into aqueous environments to be negligible (Pekar, 2009).

2.5 Aditional benefits

2.5.1 Cd mitigation

Cadmium is a toxic heavy metal that is accumulating in New Zealand pasturelands due to repeated applications of contaminated phosphate fertilisers. The entry of Cd from the soil into pasture plants, vegetables and consequently the human diet poses a risk to human health where levels exceed the maximum Cd residue levels for human consumption (Loganathan et al., 2003; Robinson et al., 2009).

Recent research has demonstrated that the addition of lignite to pasture soils in New Zealand caused a significant reduction in Cd accumulation by perennial ryegrass (*Lolium perenne* L.). Results indicated that Cd became less phytoavaialble in treatments amended with lignite concentrations of 1 mg/kg although long term effects have not yet been determined (Simmler et al., 2013). Vermes and Kadar (2002) also found that when added to contaminated soils at a rate of 40 t/ha, lignite application reduced tissue concentrations of Cd by approximately half. The successful removal of Cd from aqueous solution using lignite has also been proven (Pehlivan and Arslan, 2006; Pentari et al., 2009).

2.5.2 Plant growth and soil fertility

The majority of published research on the effects of humic substances on soil fertility and plant production has used humic acid derivatives from oxidised lignite opposed to raw lignite and field research on the response of crops to lignite applications is scarce. It is proposed that humic substances could directly improve plant growth through the uptake and transport of humic substances into plant tissues (Nardi et al., 2002) or indirectly by positively affecting soil physical properties (aggregation, moisture content, aeration and solubilisation of nutrients) (Tahir et al., 2011). The results of various studies on the effect lignite may have on plant production are summarised in Table 2.3.

Table 2-3. Various effects of lignite derived humic acids (HA), lignite and lignite fly ash on plant growth.

Author (s)	Study	Results
(Tahir et al., 2011)	Lignite derived humic acid effect on growth of wheat (*Triticum aestivum* L.) plants.	60 mg kg $^{-1}$ HA increased wheat height and shoot dry weight by 10% and 25% respectively compared to control.
(Richards et al., 1986)	Effect of particle size distribution in pinebark:sand:brown coal potting mixes on moisture and plant growth.	Brown coal increased tomato (*Lycopersicon esculentum* Mill.) shoot dry weight from 5.35-6.29 g. Attributed to increased CEC.
(Fu-sheng et al., 2002)	Effect of peat and weathered coal on *Pinus sylvestris* seedlings.	5 and 8% weathered coal increased seedling growth by 321 and 107% and root length by 37 22% respectively.
(Jones et al., 2007)	Effect of lignite HA on phosphorus and micronutrient availability and wheat yield.	No significant differences were found in nutrient uptake, shoot biomass or gain yield between HA treatment and control
(Wang et al., 1995)	HA and phosphorus availability in wheat (field trial).	Humic acid treated plots increased both P uptake and yields by 25%.
(Duval et al., 1998)	Leonardite as a crop growth enhancer for turnip (*Brassica rapa* L.) and mustard greens (*Brassica hirta* L.).	400 lbs./acre leonardite had no difference on the turnip and mustard greens growth parameters studied.
(Lau and Wong, 2001)	Fly ash amended manure compost	Weathered coal fly ash at 5% resulted in higher seed germination rate and root length of lettuce (*Lactuca sativa* L.)
(Sikka and Kansal, 1995)	Lignite fly ash and the yield and nutrient composition of rice (*Oryza sativa* L.) and wheat.	2–4% fly ash significantly increased N, S, Ca, Na and Fe content of rice plants.

2.5.3 Nitrate leaching

Currently no studies have investigated N lost via leaching where lignite has been applied as a soil amendment. However, there is evidence that similar carbonaceous materials such as biochar have successfully reduced N loss. When compared to the control, Alfisol and Vertisol soils treated with biochar significantly reduced (55 - 65% and 87 - 94%) NH_4^+-N leached during the second leaching event. Here it was also observed that NO_3^- concentrations declined in the second leaching event indicating that carbonaceous material could be more effective long term (Singh et al., 2010). Similarly, in another study cumulative mineral N (NO_3^- and NH_4^+) results were significantly lower from biochar-amended columns compared to the controls. Here biochar reduced mineral N in leachate from fertiliser treated soils by approximately 44% (Angst et al., 2013).

Part C

2.6 Biosolids

Biosolids are essentially the solid by-product of wastewater treatment plants. This treated and processed sludge can be safely and sustainably recycled and applied as a fertiliser or amendment to improve and maintain productive soils (Knowles et al., 2011). Biosolids waste which enters wastewater systems originates from a range of sources including urban, industrial and commercial areas however, in developed countries increasing regulations are being imposed to limit the amount of toxic waste able to enter these systems. The characteristics of biosolids are primarily functions of their source with the extent of treatment, process modes and methods of stabilisation being subsequent determinants of their final properties and ultimately their use or disposal (Mantovi et al., 2005). Treatment and processing of biosolids may include pre-treatment, thickening, conditioning, stabilisation, dewatering, drying, disinfection and utilisation (Clapp et al., 1994; Oleszkiewicz and Mavinic, 2002). The degree of treatment for biosolids will depend on the planned end use. This is because there are differing regulations for the use of biosolids in an agricultural system than biosolids disposed of in a landfill. This is due to risks associated to biosolids in each situation as determined by possible exposure pathways to the adverse components of biosolids. For instance, the disposal of biosolids to landfill has far fewer possible exposure pathways than the use of biosolids in an agricultural system (Chaney, 1990; Clapp et al., 1994). Therefore, classes of biosolids have been introduced where a high class (treated to a high degree) of biosolids is required when planned for use in an agricultural system, but a lower class can be used when biosolids are planned to be disposed of in a landfill (Epstein, 2003).

2.7 Land application

New Zealand produces approximately 240,000 t of dry sludge solids per year. With increasing pressure from regulations there is the potential for the beneficial use of biosolids to become a mainstream practice if it can be proven to be environmentally friendly, economically viable and socially acceptable (Wang et al., 2008). Currently in New Zealand end uses and disposal of biosolids rank in the following order: land reclamation (116,380 t) > landfill (79,440 t) > other beneficial uses (36,817 t) > ponding (875 t) > forest application (600 t) (Bradley, 2008). Research has indicated that when managed correctly, land application of the biosolids can improve site productivity by increasing soil organic matter content, physical properties and fertility (Smith, 2009).

2.7.1 Soil physio-chemical properties

Dependant on soil properties there is potential for biosolids application to benefit the physical properties of the soil by improving soil porosity, strength and aeration and chemical properties including CEC and pH (Ojeda et al., 2003). Biosolids, when applied at a rate of 80 Mg ha^{-1} improved the structure of a highly degraded carbonated soil one year after waste application by a small decrease in particle bulk density and an increase in water retention (Illera et al., 1999). García-Orenes et al. (2005) concluded that when applied to degraded soils biosolids significantly increased the organic carbon, carbohydrates and aggregate stability percentage, resulting in a decrease of the bulk density of both soils. The high organic matter content of biosolids has also been observed to increase soil water retention however; results in the literature have been conflicting. Cameron *et al.* (1997) stated that biosolids increased the macroporosity of a sandy loam from 11 to 19% and the saturated hydraulic conductivity (K_{sat}) from 39 to 57 mm/hr. Although Reneau, *et al.* (1989) reported reductions in infiltration rate impeded by the dissolution of OM. Lindsay and Logan (1998) have suggested that the effects of biosolids application on soil physical properties persisted for up to four years. Relatively high application rates of biosolids increased CEC thus helping retain nutrients within the rooting zone due to additional cation binding sites. Such responses are however dependant on the ratio of biosolids to soil (Singh and Agrawal, 2008). Stadelmann and Furrer (1985) found that the concomitant effect of increased OM in the soil resulted in an increase in soil CEC from 17.2 $cmol_c$/kg to 23.7 $cmol_c$/kg from the application of 5 t/ha biosolids over a seven year period. Literature indicates that biosolids can increase or decrease soil pH depending on the type applied. Changes in pH have been correlated with the calcium carbonate content and acid production during biosolids decomposition (Singh and Agrawal, 2008). Soil pH consideration is especially important due to its effect on the availability of plant nutrients and heavy metals (McLaren and Cameron, 1996).

2.7.2 Soil microbes

The addition of biosolids to soil stimulates microbial activity by increasing nutrient pools and carbon substrates. The extent and effect to which biosolids achieve this is not completely understood but several trials have investigated certain aspects. Singh and Agrawal (2008) found biosolids amendments caused enhancements in enzyme and microbial activities which increased over a 2 - 3 week period before reaching an optimum level, and was discovered to have a high correlation with C:N ratios. This was in agreement with Haynes et al. (2009) who concluded that the constituents of biosolids would ultimately only have a positive effect on soil microbial activity.

2.7.3 Nutrient availability and plant growth

When managed correctly, the application of biosolids can increase crop production resulting from an increase in nutrient supply (Sigua et al., 2005; Wang et al., 2004). Singh and Agrawal (2008) indicated that biosolids were a great source of micro and macronutrients and when applied to soil served as a great source for plant nutrients such as N, P, calcium (Ca) and magnesium (Mg) while organic constituents as in organic matter act as a soil conditioner. The positive effect on plant growth following biosolids application is essentially due to the readily available N found in biosolids, as N is the most limiting nutrient for optimising plant growth (Taiz and Zeiger, 2002). A 30% increase in tall fescue (*Festuca aruninaceous* Schreb.) yield was observed by Boswell (1975) following the application of 5.6 Mt/ha dry weight over a two year period. Magdoff and Amadon (1980) found that biosolids applied to supply 50, 100 and 200 kg N/ha/yr significantly increased corn (*Zea mays* L.) yield. However, while a study by Miah et al. (1999) also observed an increase in the grain yield of barley (*Hordeum vulgare* L.), results also showed elevated concentrations of heavy metals in biosolids treated plants compared to the control. This could have implications for the long-term land applications of biosolids.

2.8 Contaminants

While biosolids can improve soil fertility, the many trace elements associated with biosolids also raise concern in regard to their long residence time in soil and effects on human health if they become present in the food chain. Trace elements may include arsenic (As), Cd, Cu, lead (Pb), mercury (Hg), nickel (Ni), selenium (Se) and Zn (Singh and Agrawal, 2008). McBride (2004) found that the application of biosolids to agricultural land increased elemental concentrations of Cd, chromium (Cr), Cu and Ni in relation to alternative farms in the region with a positive correlation occurring between the application rates and loading concentrations. Singh and Agrawal (2008) identified that excessive applications of biosolids increased bioavailability of HMs in soils but low doses e.g. 80 t/ ha dry wt/ yr did not cause significant increases in concentrations. Further research is needed to determine the long-term effects biosolids may have on soil properties and the role soil organic matter pH and redox potential on the availability of these elements. Additional issues which have raised concern in relation to the land application of biosolids include nutrient leaching, organic contaminants, the presence of pathogens including bacteria, viruses, protozoa and fungi, odour and public perception, a more in depth description on these contaminants can be found in Lu et al. (2012).

Chapter 3

Materials and Methods

3.1 Lysimeter setup

Eighteen undisturbed monolith lysimeters (70 cm depth, 50 cm diameter) of a free draining Lismore stony silt loam were sourced from Lincoln University's dryland farm in Mid-Canterbury, New Zealand (43°39'05.82"S 172°19'41.47" E). The lysimeters were collected according to the method described by Cameron et al. (1992) and were installed at the Lincoln University field trench lysimeter facility (43°38'53.48"S 172°28'07.58" E). Each lysimeter consisted of a steel cylindrical casing, which was pushed into the soil to collect the undisturbed soil monolith. Once the casing had reached the desired depth (70 cm), the soil monolith was then cut at the base with a cutting plate, secured on the lysimeter casing and lifted out of the collection site. The lysimeters were then installed with the surface of the lysimeter at the same level as that of the surrounding soil surface and the space surrounding the lysimeters casings backfilled with soil to the same level as the surface of the lysimeters and the surrounding field. The lysimeters were thus exposed to the climatic conditions as the soil and pasture in the surrounding field. The lysimeters were installed with nine lysimeters either side of the trench. Stainless steel gas rings of a diameter 50 cm were then attached to the top of each lysimeter to provide a water trough to assist with gas collection. Leachate from drainage tubes was collected at the base of each lysimeter in ten litre containers (Figure 3.1). The properties of the soil and treatments are presented in Table 3.1.

Table 3-1. Soil chemical properties for the Lismore stony silt loam, New Vale lignite and biosolids. Values in brackets represent the standard error of the mean (n = 3). Concentrations are on a dry weight basis. Adapted from Gough (2012).

	Lismore stony silt loam*	New Vale lignite*	Biosolids**
Moisture (%)	n.d	38	53
pH (H_2O)	6.31	4.5	4.1
CEC (meq/100g)	13.5 (0.2)	44.8	n.d
Base saturation (%)	93.6 (2.1)	95.2	n.d
C (%)	4.3 (0.1)	57.2 (0.2)	28.0 (0.2)
N (%)	0.37 (0.01)	0.8 (0.01)	2.7 (0.2)
NO_3^- (mg/kg)	5	< 1	867
NH_4^+ (mg/kg)	1.2	22	7
P (mg/kg)	991.2 (21)	57.6 (0.2)	4683 (0.03)
S (mg/kg)	486.7 (5)	6539 (35)	6972 (2)
Ca (mg/kg)	5392.4 (216)	17502 (119)	9818 (43)
Mg (mg/kg)	1637.6 (68)	2815 (11)	2204 (176)
K (mg/kg)	2330.3 (102)	219 (2)	4330 (17)
Cd (mg/kg)	0.17 (0.001)	0.06 (0.007)	2.8 (67)
Zn (mg/kg)	80.5 (3)	9 (1)	878 (13)
Cu (mg/kg)	7.3 (0.1)	2 (0)	561 (33)
Fe (mg/kg)	18186.0 (450)	12981 (145)	n.d
B (mg/kg)	7.0 (0.2)	36.3 (0.1)	n.d
Li (mg/kg)	31.1 (0.3)	n.d	n.d

* Gough (2012).

** Knowles et al. (2011)

Figure 3-1. Lysimeter trench (lysimeters 1-18) prior to N_2O gas collection.

3.2 Soil amendments

Lignite

Solid Energy New Zealand Ltd. provided powdered lignite. The powder was sourced from an open cast mine in Southland, New Zealand (46°08’23.80”S 168°54’11.62”E). The powder was produced using a crusher with an air swept classifier. Upon being crushed the material was blown over a partition by a fan. This enabled the desired particle size to pass over the partition while larger particles are returned to the crusher (Simmler, 2012).

Biosolids

Partially treated biosolids were collected from the Kiakoura regional treatment works, Kaikoura, New Zealand (42°21’50.04”S 173°41’19.68”E). Approximately 160 kg of biosolids were sampled from the sewage treatment plant storage pile with sampling occurring at eight locations across the pile to obtain a representative sample. The biosolids were prepared by homogenising the biosolids in a concrete mixer before being passed through a 20 mm sieve. The biosolids application rate of 30 t/ha was equivalent to the rate recommended to rebuild a degraded soil.

Urea

Balance agri-nutrients N-Rich-Urea, 46-0-0-0 (N-P-K-S) manufactured at the ammonia-urea plant Kapuni, New Zealand was used in this experiment. The N application rate of 200 kg/ha was equivalent to the maximum N in urea form that can be applied per hectare under New Zealand regulations.

3.3 Experimental design

Six treatments, each with three replicates, were allocated to the lysimeters in a randomised design. The six treatments and rates of application are given in Table 3.2.

Table 3-2. Treatments and rates of application in the lysimeter experiment.

Treatment	Initial application per lysimeter	Second application per lysimeter	Rate of application
Control	-	-	
Control + lignite	400 g (L)	-	20 t/ha
Biosolids	600 g (B)	600 g (B)	30 t/ha biosolids or
Biosolids + lignite	600 g (B) + 400 g (L)	600 g (B) + 400 g (L)	400 kg N/ha
Urea	8 g (U)	8 g (U)	400 kg/ha urea or
Urea + lignite	8 g (U) + 400 g (L)	8 g (U)	200 kg N/ha

Where: (L) = Lignite, (B) = Biosolids, (U) = Urea

3.4 Treatment applications

Initial application

Each treatment had the top 0.1 m of soil removed from the lysimeter. The soil was then incorporated with the applicable treatment for approximately two minutes in a concrete mixer to create a homogenised treatment application initiating the agricultural practice of conventional tillage. Control treatments were handled in the same manner with no additional treatment added. All treatments were homogenised and applied on the 16 May 2012. Mixer was cleaned between each sample to avoid contamination. Aside from the treatments, no fertiliser was applied to the lysimeters.

Secondary application

Italian ryegrass (*Lolium multiflorum* Lam.) was applied to each lysimeter at a rate of 2 g. The seed was hand sown by broadcasting the seed evenly across the lysimeter surface and lightly hand pressing it into the soil. Good grass cover was established.

The treatments were applied to the surface of the lysimeters on the 8 May 2013. The biosolids was mixed by hand with 1 L of water for approximately two minutes to form well mixed slurry as this is how biosolids would typically be applied in field conditions. The slurry was applied to each the lysimeter by applying it evenly across the lysimeter surface (Figure 3.2). Following application, a further 1 L of water was applied across the surface of the lysimeter to wash the any treatments that remained on the ryegrass into the soil. This process was repeated for the biosolids (with lignite) and urea (with and without lignite) treatments. The control (with and without lignite) were handled in the same manner with no additional treatments added.

Figure 3-2. Homogenising of biosolids and lignite prior to application (Left), Treatment application (middle) and evenly distributing treatment across the lysimeter surface (right).

3.5 Gas sampling- collection and analysis

Nitrous oxide gas collection

A standard closed chamber method similar to that described by Hutchinson and Mosier (1981) was used to determine N_2O emissions from the treated lysimeters. This same method has been used to provide N_2O emissions data for the New Zealand national inventory. Sampling was carried out over a four week period starting 7 May 2013, in which samples were collected every day for the seven days and every second or third day for the remaining weeks. An initial gas sample was taken prior to treatment application on 6 May 2013. Gas collection occurred between 12.30 pm and 2.30 pm. The gas chamber was constructed from a metal cylinder, insulated on the outside with 2.5 mm thick polystyrene foam to avoid heating from the atmosphere in the chamber during sampling. The gas ring mounted on the monolith lysimeters formed a U-shaped water trough around the lysimeter to which the chamber was fitted to during sampling to create an airtight seal (Figure 3.3). Each chamber was created with two holes in the top, one with a cut down 30 mL plastic vial screw lid, the other a rubber septum in which to insert the sampling needle and valve. At each sampling time, the chamber was placed on top of the lysimeter for a period of 60 minutes, and three samples (25 mL), 20 minutes apart were collected. Samples were collected in a 6 mL exetainer with a septum in the lid which had been evacuated prior to sampling. Samples were taken by attaching the exetainer to the needle located on the gas chamber. The syringe was then also inserted into the septum of the exetainer and an initial 60 mL sample of gas drawn from the chamber and discarded to flush any ambient air out of the chamber. Following the subsequent collection of 25 mL gas, the exetainer was removed from the chamber needle and the syringe contents compressed into the exetainer (Figure 3.3). Samples collected during the 20 and 40 minute periods had an additional 60 mL drawn out and pumped three times to mix the chamber air before the final 25 mL sample was collected. The air temperature was recorded prior to sampling followed by measurements of the chamber air temperature at 20, 40 and 60 minutes.

Figure 3-3. Lysimeters with and without gas collection chamber (left). Collection of gas samples (middle) and gas sampling syringe and needle setup (right).

Measurement of nitrous oxide

Immediately prior to analysis, gas samples were brought to ambient atmospheric pressure. Nitrous oxide concentration was determined using gas chromatography (GC) (SRI 8610 gas chromatograph; SRI Instruments, CA, USA) fitted with a ^{63}Ni electron capture detector (ECD), and linked to an autosampler (Gilson 222 XL; Gilson Inc., WI, USA). PeakSimple (SRI Instruments, CA, USA) was the software used to control and monitor the ECD.

Calculation of nitrous oxide flux

The following equations derived from Muller (1995) were used to calculate the N_2O flux (g N_2O-N ha/day) from the concentration (µL/L) given after GC analysis:

Equation A, when: $(C_1\text{-}C_0)/(C_2\text{-}C_1) \leq 1$

$$: ([(C_2 - C_1)\ V_C\ P] / [G_C\ (T_K + T_{°C})])\ /A_C\ C_{ha}/t_2\ C_D\ M_{N2}$$

Equation B, when: $(C_1\text{-}C_0)/(C_2\text{-}C_1) > 1$

$$: [(V_C\ (C_1\text{-}C_0)^2/(2C_1 - C_2 - C_0)]\ \ln[\ (C_1\text{-}C_0)/(C_2\text{-}C_1)]\ P/\ [G_C\ (T_K + T_{°C})]/A_C\ C_{ha}/t_1\ C_D\ M_{n2}$$

where:

C_0, C_1, C_2	= N_2O concentration [µL L^{-1}] at times t_0, t_1, t_2 respectively
P	= atmospheric pressure [atm] = 1
V	= chamber volume [m^3]
R	= gas constant [L atm K^{-1} mol^{-1}] = 0.08205746
T_K	= absolute temperature at 0^oC [K] = 273.15
T_{oC}	= air temperature [^oC]
A	= soil surface area [m^2]
t_2	= total cover period [min]
t_1	= $t_2/2$ [min]
t_0	= 0 minutes, start of cover period [min]
M_{N2}	= molecular weight of N_2O-N [g mol^{-1}] = 28.01344
C_D	= minutes per day [min] = 1440

If Equation B > 2 it was assumed that, some artefact had occurred during sample collection so that C_2 had to be disregarded. To calculate the flux under these conditions Equation A was slightly modified using C_1 instead of C_2.

3.6 Leachate- collection and analysis

Drainage leachate was collected four times following the second treatment application. Prior to analysis, the volume of leachate was measured and recorded during each sampling. A 100 mL sample was taken mid flow for analysis. Each sample was vacuum filtered with a water aspiration apparatus through 0.45 µm cellulose acetate filter membrane. Leachate was analysed using the KCl extraction method to determine NH_4-N and NO_3-N using Flow Injection Analyser (FIA) (FOSS FIAstar 5000 triple channel with SoFIA software version 1.30; Foss Tecator, Hoganas, Sweden).

3.7 Climate and irrigation

Located in the field, lysimeters were exposed to the elements characteristic of the Canterbury region. Simulated rainfall was applied (if necessary) to all lysimeters to supplement a shortage of natural rainfall and to simulate typical irrigation practice on local farms. The irrigation system was controlled through a remote computerised irrigation programme. The rainfall, irrigation, and air temperature data is presented in Figure 3.4.

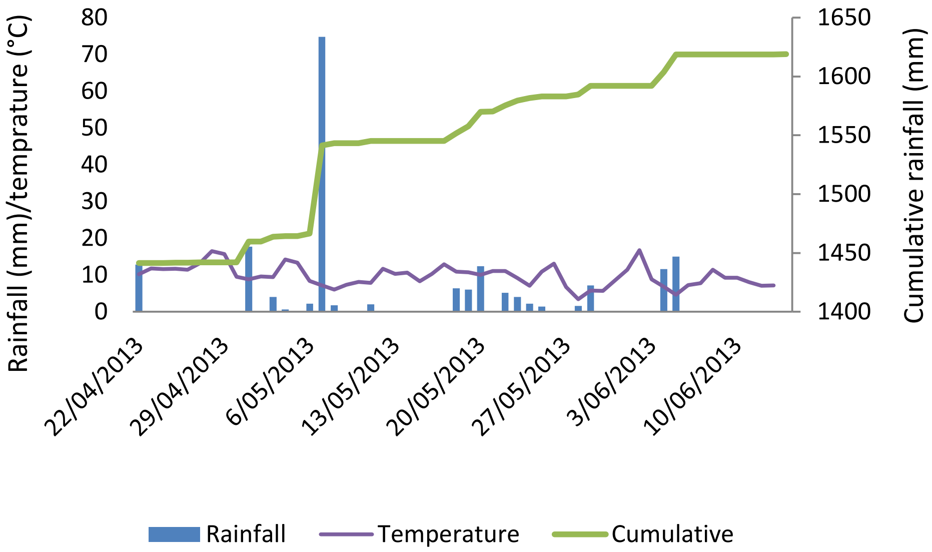

Figure 3-4. Rainfall and temperature data for 18 lysimeters over the duration of N_2O sampling.

3.8 Soil moisture and temperature

The average soil water content of 0-15 cm depth was measured using a Hydrosence moisture probe (15 cm) (Campbell Scientific, Utah, USA). Soil temperature was recorded using a 107-L temperature sensor (Campbell Scientific, Utah, USA) to measure the soil temperature at 7.5 cm depth. A data logger (CR23X, Campbell Scientific, Utah, USA) was used to collect soil moisture and temperature information every ten minutes during the N_2O measurement periods. Hourly and daily averages were also recorded throughout the experiment. Both moisture and temperature probes were installed on 29 May 2013 causing some disruption to the soil.

3.9 Soil collection and analysis

Soil samples were collected at the end of the N_2O sampling period, as to avoid disturbing the soil upon removal. Two samples were collected from each lysimeter using a 7.5 cm soil corer and placed into re-sealable bags. Samples were then weighed out for analysis with the remaining soil air dried for 48 h at 25°C.

Ammonium and nitrate

Field moist soil (4 g) was weighed into 50 mL centrifuge tubes, to which 40 mL of 2M KCl was added. Samples were then place in an over end shaker for 1 h before being centrifuged at 2000 rpm for 10 minutes and filtered through MicroScience MS 5AS 52 mm Ashless filter paper. These were then frozen prior to analysis by Flow Injection Analyser (FIA) (FOSS FIAstar 5000 triple channel with SoFIA software version 1.30; Foss Tecator, Hoganas, Sweden).

Total soil nitrogen and carbon

The C and N content of the soil was determined using an Elementar vario MAX CN element analyser. Pseudo-total element concentrations were measured in acid digests using ICP-OES. Half a gram of soil was digested in 5 mL HNO_3 / 1 mL H_2O_2 (Merck Soil pH hydrogen peroxide 30%). The digest was diluted with Milli Q (Barnstead, EASYpure RF, 18.3 MΩ-cm) to a volume of 25 mL and filtered with a Whatman 52 filter paper (pore size 7 µm).

Soil pH

Air dried soil was broken up using a mortar and pestle and passed through a 2 mm nylon sieve to remove large aggregates and stones. Following this (10 ± 0.05 g) was weighed into a 70 mL plastic vial to which 25 mL of deionised water was added. Samples were mixed and left to settle overnight prior to pH measurement using a pH meter (S20 SevenEasy™ pH; Mettler-Toledo, Switzerland). Soil pH data were transformed into hydrogen ion (H^+) concentration via Equation 3.1 to calculate means. This was then converted back to pH values.

$$pH = -\log[H^+] \qquad \text{(Eqn. 3.1)}$$

Soil moisture content

Field moist soil (approximately 10-20 g) was weighed into a metal dish and allowed to dry for 24 h at 105°C. Samples were removed from the oven and placed in a desiccator. Once cool samples were re-weighed and the moisture content determined by Equation 3.1

$$(\text{moist weight} - \text{dry weight} * 100)/\text{dry weight} \qquad \text{(Eqn. 3.2)}$$

3.10 Statistical analysis

Statistical analysis of N_2O flux was carried out using Minitab 16.0 with a 1-way ANOVA used to determine treatment effects and interactions. Soil moisture content, and soil data was also analysed using a 1-way ANOVA to determine treatment effects and interactions. The post hoc test used to identify significantly different groups of data was Fischer's method. Standard errors displayed on graphs were calculated using the square root of the standard deviation divided by the number of samples.

Chapter 4

Results

4.1 Nitrous oxide flux

Daily fluxes of N_2O over time

Figure 4.1 shows that from day 2 the urea + lignite treatment maintained the highest emissions out of all treatments peaking at 36 g N_2O-N/ha 12 days after application. Emissions initially peaked 7 days after treatment application where the highest N_2O flux from treatments occurred in the following order: urea + lignite > urea > biosolids > biosolids + lignite > lignite and control treatments. A higher secondary peak occurred 12 days after treatment application where N_2O flux from treatments occurred in the following order: Urea + lignite > biosolids > urea > biosolids + lignite > lignite and control treatments (Figure 4.1). These peaks are consistent with the application of water to each lysimeter on day 6 followed by a significant rainfall event (Figure 3.4). After day 12, emissions from the urea + lignite, urea, biosolids and biosolids + lignite treatments decreased to concentrations similar to those obtained prior to treatment application with the exception of two small peaks at days 20 and 25. Emissions from both the control and lignite remained below < 2 g N_2O-N ha/day for the duration of the N_2O collection period and there was no significant difference between the two treatments (Figure 4.1).

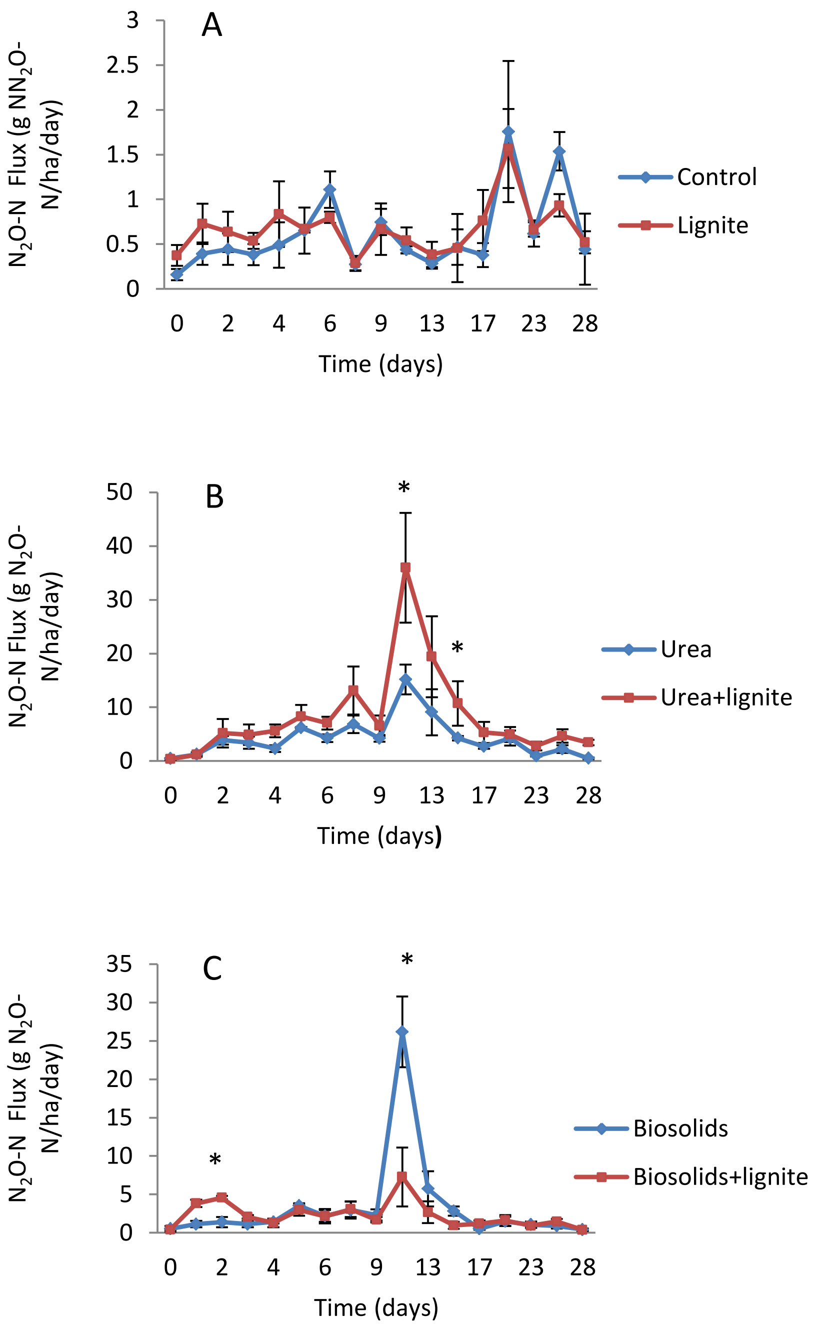

Figure 4-1. Daily N_2O fluxes (g N_2O-N ha/day) over time showing (A) flux between control and lignite treatments (B) urea and urea + lignite treatments and (C) biosolids and biosolids + lignite treatments over a 28 day period. Error bars are standard error of the mean (n = 3). Asterisks denote significant differences (p<0.05) .

Cummulative N_2O-N

The mean cumulative N_2O emissions across treatments ranged from the equivalent of 20 to 250 g N_2O-N/ha (Figure 4.2). The urea + lignite had the highest emissions of N_2O of 243 g N_2O-N/ha. This was significantly higher ($P < 0.002$) than any of the other treatments over the 28-day study. Surprisingly, results showed that amendment with lignite significantly increased N_2O emissions by 93% when N was applied as urea. In contrast to this lignite amendment, reduced N_2O emissions by

40% when N was applied as biosolids however this relationship was not significant (Figure 4.2). Figure 4.1 shows that highest losses occurred 12 days after treatments were applied. The urea treatment had the second highest cumulative N_2O-N emission with an average of 125 g N_2O-N/ha lost however, this was not significantly different from the biosolids and biosolids + lignite treatments. The control and lignite treatments had the lowest N_2O emissions (< 25 g N_2O-N/ha) over 28 days and were not significantly different from each other or the soils amended with biosolids and biosolids + lignite (Figure 4.2).

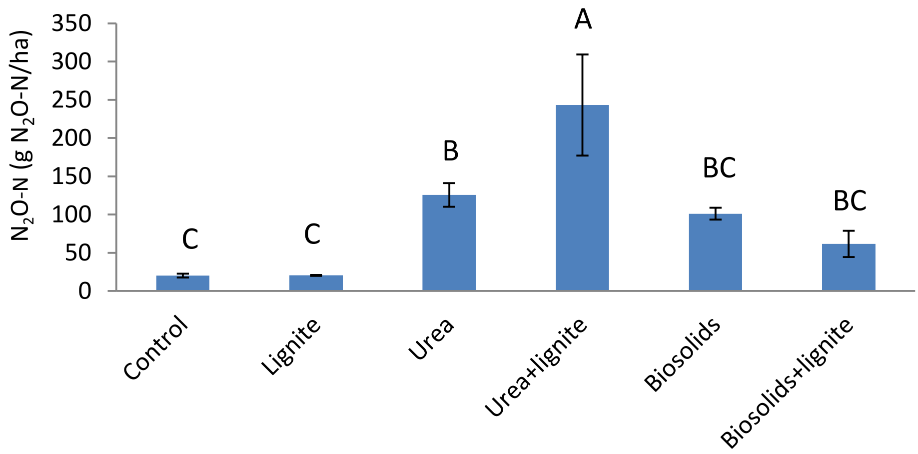

Figure 4-2. Average cumulative N_2O loss (g N_2O-N/ha/day) over 28 days. Means that do not share a letter are significantly different. Error bars are standard error of the mean (n = 3).

4.2 Nitrogen leaching

N leached over time

The N leached was predominantly in the form of NO_3^- with little NH_4^+ detected in the leachate due to the positive charge that is associated with the NH_4^+ ion. Figure 4.3 shows that the urea and urea + lignite treatments maintained the highest N loss out of all treatments peaking at 1.8 and 1.5 g N/lysimeter, equivalent to 94 and 79 kg/ha 28 days after application. This was significantly higher than all other treatments where N loss did not exceed 0.1 g N/lysimeter, equivalent to 2 kg N/ha over the 39 day period. The majority of N leached from the biosolids and biosolids + lignite treatments at the start of the 39-day period, peaking 3 days after application.

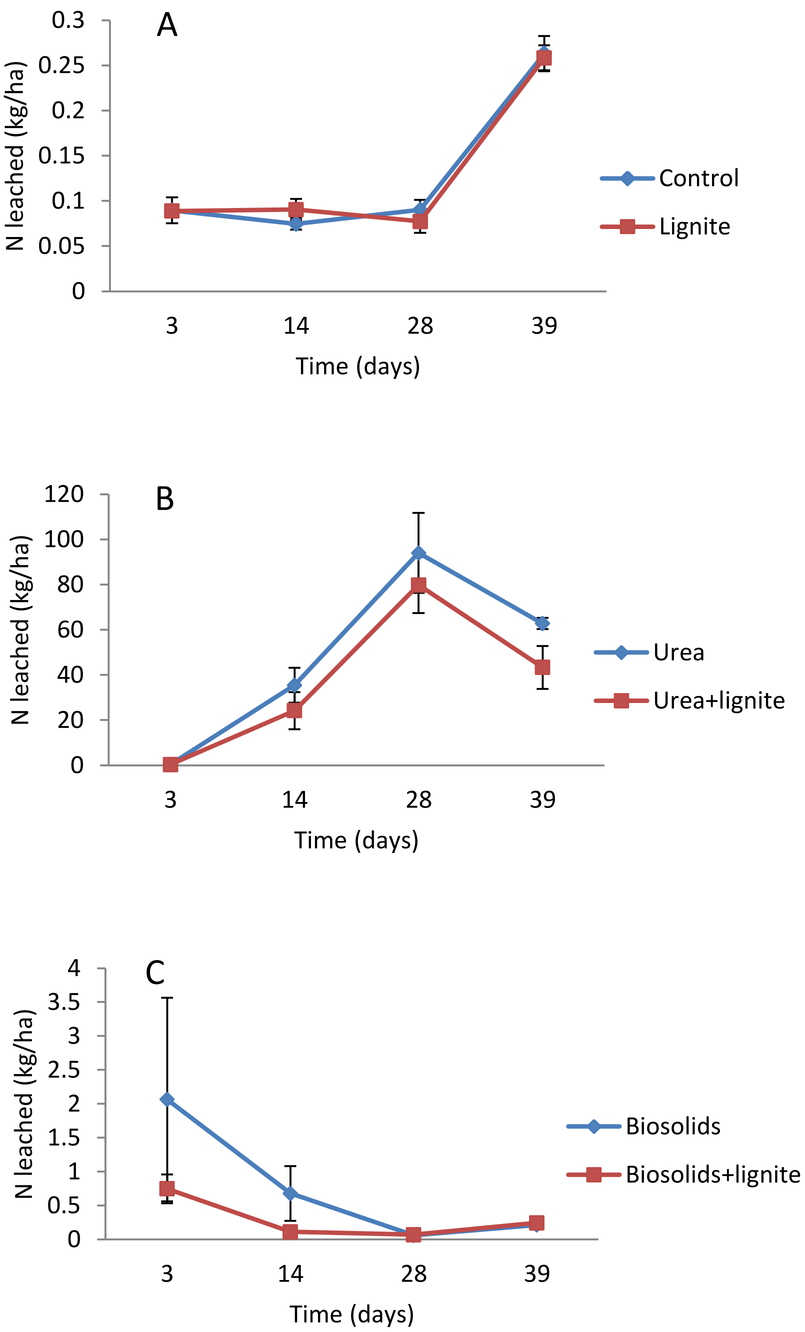

Figure 4-3. Mineral N leached (kg/ha) over time between (A) Control and lignite treatments (B) urea and urea + lignite treatments and (C) biosolids and biosolids + lignite treatments over a 39 day period. Error bars are standard error of the mean (n = 3).

Cumulative N leached

The mean cumulative N leached ranged from 0.01 to 3.9 g N/lysimeter, equivalent to 0.5 to 193 kg N/ha (Figure 4.4). The highest loss of N was from the soil treated with urea at 193 kg N/ha. This was significantly higher ($p < 0.05$) than all other treatments over the 39 day period. A positive result was obtained from the soils amended with lignite, which with the exception of the control treatments, reduce N leaching compared to their counterparts. Results showed that soil amendment with lignite significantly ($P < 0.05$) reduced N leaching by 23% when urea was applied (Figure 4.4). Given the short duration of this study (39 days), over a longer period a significantly different relationship may develop between the biosolids and biosolids + lignite treatments. The control and lignite treatments leached less than 0.5 kg N/ha over 39 days, and were not significantly different from each other or the soils amended with biosolids and biosolids + lignite (Figure 4.4). Because of the higher quantities of N lost via leaching on a per ha basis results have been presented in kg/ha opposed to g/ha which were used for N_2O flux.

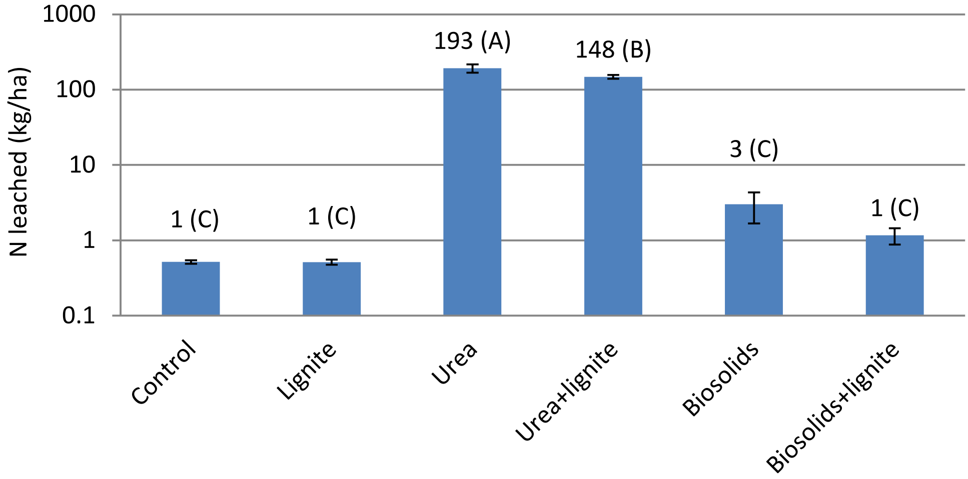

Figure 4-4. Average cumulative mineral N loss (kg/ha) over 39 days. Means that do not share a letter are significantly different. Error bars are standard error of the mean (n = 3).

4.3 Mass balance

Cumulative N_2O emissions in this trial were low from all treatments (< 0.25 kg/ha) over 28 days in comparison to other studies (Tables 4.1 & 5.1). Most of the N that was applied leached in 39 days from the soils amended with urea. A smaller total mass of N was recovered in the leachate from the biosolids amended soils.

Table 4-1. Mass balance of N in the soil during the period of the trial.

	N applied (kg/ha)	N leached (kg/ha)	N_2O-N (kg/ha)	Emission factor (%)
Control	-	0.5 (0.028) ^{NS}	0.02 (0.002) ^{NS}	0.01
Lignite	-	0.5 (0.042) ^{NS}	0.02 (0.001) ^{NS}	0.01
Urea	200	192.5 (24.7) *	0.13 (0.016) *	0.06
Urea + lignite	200	147.6 (8.82) *	0.24 (0.066) *	0.12
Biosolids	400	3.0 (1.33) ^{NS}	0.10 (0.008) ^{NS}	0.05
Biosolids + lignite	400	1.2 (0.28) ^{NS}	0.06 (0.017) ^{NS}	0.03

Where: (NS) = no significant difference between treatments and (*) = significant difference.

4.4 Soil measurments

The biosolids + lignite treatment had the highest soil C and N concentrations at 8.9 and 0.54% respectively, which were significantly higher than all the other treatments (Table 4.2). The increase in C compared to the other treatments can be explained by the second application of lignite (400 g) that was applied with biosolids + lignite treatment prior to sampling. The significantly higher N concentrations may be explained by the surface application of the biosolids amendments. There was little variation in the concentration of NH_4^+ and NO_3^- concentrations between treatments. The lignite amended soils appeared to have higher concentrations of NH_4^+ and NO_3^- compared to their counterpart treatments however, this was not significant for any of the treatments (Table 4.2). Soil temperature varied over the 28-day sampling period, but little variation between treatments occurred. Results from the Hydrosense moisture probes show that the average soil moisture content between treatments ranged from 22 to 34%. Over the duration of the 28-day trial the soil moisture content remained below 40% at the time gas sampling was undertaken.

Table 4-2. Variation in soil temperature at 7.5 cm over 39 days and average soil moisture content at 15 cm. Average soil carbon and nitrogen (%), NH_4^+ and NO_3^- (mg/g soil) and pH across the six lysimeter treatments taken post sampling. Means that do not share a letter are significantly different. Brackets are standard error of the mean (n = 3).

	Control	Lignite	Urea	Urea + lignite	Biosolids	Biosolids + lignite
C (%)	4.2 (0.087) ^{C}	5.4 (0.030) ^{B}	4.3 (0.058) ^{C}	5.8 (0.432) ^{B}	4.9 (0.065) ^{BC}	8.9 (0.746) ^{A}
N (%)	0.39 (0.012) ^{C}	0.40 (0.006) ^{C}	0.40 (0.006) ^{C}	0.40 (0.013) ^{C}	0.44 (0.020) ^{A}	0.54 (0.447) ^{B}
NH_4^+ (mg/g soil)	13.8 (0.167) ^{A}	14.5 (0.667) ^{A}	14.6 (1.194) ^{A}	17.6 (2.627) ^{A}	15.8 (1.053) ^{A}	17.0 (2.044) ^{A}
NO_3^- (mg/g soil)	6.7 (0.036) ^{C}	6.9 (0.323) ^{C}	8.3 (0.374) ^{AB}	8.7 (0.762) ^{A}	6.8 (0.199) ^{C}	7.5 (0.297) ^{BC}
pH	6.0 ^{A}	6.2 ^{A}	6.0 ^{AB}	5.9 ^{AB}	6.1 ^{A}	5.6 ^{B}
Temperature (°C)	3 - 11	4 - 13	5 - 13	3 - 12	4 - 12	3 - 12
Soil moisture (%)	34	32	26	22	27	28

Chapter 5

Discussion

5.1 Effect of lignite amendment on N loss

5.1.1 Nitrous oxide

A soil amendment equivalent to 20 t/ha of lignite significantly exacerbates N_2O emissions from soil treated with urea fertiliser. This was unexpected as it was hypothesised that lignite could reduce the inorganic N pool available in the soil for N_2O producing mechanisms. However, the low concentration of N_2O emitted in this trial indicates that N lost in the form of N_2O may be negligible in free draining, low fertile soils.

Nitrous oxide flux can increase exponentially with increasing WFPS, mineral N and temperature and decline when any of these variables fall below a critical value (Dobbie et al., 1999). The soil type used in this trial and water application rate may have contributed to the low cumulative N_2O emissions when compared to other studies (Table 5.1). The Lismore soil had a high stone content, low organic matter and is characterised as a well aerated free draining soil (Cox, 1978). As a result, anaerobic conditions required for denitrification and subsequently N_2O production could have been insufficient in this trial. Pratt et al. (1980) presented data that gave an approximate ratio of leaching loss of 5:1 for a silt loam soil compared to a clay loam soil. The high water flow and concentration of N present in the leachate of the urea treated soils indicates that N rapidly leached through the soil profile, particularly between days 14 and 28 (Figure 4.3). Because the availability of NH_4^+ and NO_3^- influences denitrification (Cameron et al., 2013; Yamulki et al., 1998), rapid microbial conversion and leaching of NO_3^- may have reduced the potential for denitrification to occur. The low soil temperatures (< 12°C) during this study may also have been a contributing factor to the low N_2O flux. Thomson et al. (2012) found that the denitrification rate increased 10 fold in a grassland soil when soil temperatures increased from 10 to 20°C.

In this trial N_2O emissions peaked 12 days after N was applied before steadily declining to background concentrations. This is consistent with work by Yamulki et al. (1998) who found that the rate of nitrification and denitrification associated with mineral N caused a peak in N_2O flux 10 - 15 days after N was applied to pasture. Higher emissions were observed following rainfall events. Peak emissions occurred after occurred after the application of 1 L of water on day 7 and coincided with an increase in daily temperature over this period. It is likely the increase in anaerobic conditions following these events would have caused an increase in microbial activity, therefore increasing the conversion of NO_3^--N to N_2O through denitrification (McLaren and Cameron, 1996).

Biochar, a similar carbonaceous material, has also been explored as a potential amendment to reduce N_2O flux from agricultural soils and is an interesting comparison. Similar to this trial, Clough et al. (2010) found that the addition of biochar to a Wakanui silt loam soil under laboratory conditions, exacerbated N_2O flux when bovine urine was applied. However, after 55d there was no significant difference in cumulative N_2O between treatments. The mechanisms behind this were not fully understood, it was suggested that the higher N_2O flux may have been a consequence of greater 'leakage' from the nitrification process either by a reaction of NO_2^- or compounds in the nitrification pathway which are precursors such as hydroxylamine.

In contrast, under field conditions, biochar amendment has reduced N_2O flux. Taghizadeh-Toosi et al. (2011) found that a soil amendment equivalent to 30 t/ha biochar, significantly reduced N_2O flux from ruminant urine patches by > 50%. Similarly, Angst et al. (2013) found that with the exception of manure treatments, biochar significantly reduced N_2O emissions from N fertiliser and slurry treated soils compared to their un-amended counterparts. Fertiliser, slurry and manure amended soils emitted 1.7, 2.8 and 0.6% of the total N added compared to biochar amended soil which emitted 0.7, 1.0 and 0.3% respectively. It was suggested that the suppression of N_2O flux from biochar amended soils was likely due to a number of factors (pH, increased O_2 diffusion) but the sorptive properties of biochar reducing NH_4^+ availability was considered the most probable cause.

No significant difference in N_2O flux was observed between the control, lignite and biosolids (with and without lignite) treatments. A similar trial by Angst et al. (2013) found that over 55 days, N_2O emissions from manure and manure + biochar were also low compared to the N fertiliser treatments. This was attributed to relatively low levels of immediately available N in the manure and the high C content, conducive to microbial immobilisation of N and subsequently a decrease in N_2O emission. Due to the high organic N and C content of the biosolids in this trial, similar mechanisms may be responsible for the low N_2O flux observed in the biosolids amended soil. Had the trial been extended until the mineralisation of biosolids N was more complete, a significant difference may have emerged between treatments. There is evidence that the addition of lignite to cattle feedlot manure could reduce N_2O emissions compared to its un-amended counterparts (Kagimbo et al., 2012). However, this information does not come from a scientific paper, and no reference has been made to the significance of the reduction.

In contrast to the significant increase in N_2O flux found when urea was applied to lignite-amended soils, lignite had no effect on the N_2O flux between the biosolids treatments. The addition of 400 g extra lignite (equivalent to 20 t/ha) to the biosolids treatment, could possibly account for this trend, as could the homogenising of biosolids and lignite together prior to application on the soil surface. Alternatively, variation in local microflora and fauna between treatments may be a contributing factor. Analysis of soil microbial biomass was not investigated in this trial but could provide insight into these differences in future studies.

Greenhouse experiments by Sikka and Kansal (1995) showed that soil amendment with 2–4% fly ash significantly increased N, sulphur (S), Ca, sodium (Na) and iron (Fe) content of rice plants. Pekar (2009) found lignite had a positive influence on maize production when added as an amendment to soils varying in quality. If lignite enhances plant uptake of N, this may reduce the amount of mineral N available to denitrifying bacteria in the soil and a subsequent reduction in N_2O. Pasture assimilation of N applied in this experiment may also been an influential factor in the low N_2O flux in this study. However, plant uptake of N was not investigated in this experiment due to the short duration of the study, low pasture growth in winter and the methods of N application that were employed, and therefore plant uptake of N cannot be verified at this stage.

Ammonia (NH_3) volatilisation was not measured in this study, but could also have been a source of N loss. Urea application results in a sharp increase in soil pH, which favours NH_3 volatilisation. Volatilisation of NH_3 is usually highest in the first few days following application and declines as nitrification processes become significant and soil pH drops (Cameron et al., 2013). The low soil temperature and pH of the soils in this trial (pH 5.6 – 6.2) are likely to have restricted the loss of N through this pathway. Similarly, we cannot account for N returned to the atmosphere as N_2 however given the low moisture content of the soil it is unlikely that soil conditions favouring complete denitrification would have occurred.

5.1.2 Nitrogen leaching

While the effect of lignite amendment on N leaching was not the original focus of this dissertation, analysis of the leachate showed interesting results. In contrast to its effect on N_2O emission, N leaching following the application of urea was significantly reduced when soils were amended with the equivalent of 20 t/ha lignite. The N collected in the leachate was predominantly in the form of NO_3^- indicating stimulation of *Nitrosommonas* and rapid oxidation by *Nitrobactor* bacteria, which convert NH_4^+ to NO_3^- according to Equations 2.1 and 2.2.

Lignite decreased N leaching from the urea treatment by 23%. No significant decrease was observed from the biosolids + lignite treatment. These results were similar to the 44% reduction in N leaching found by Angst et al. (2013) when biochar was incorporated in to soil columns treated with N fertiliser. This was attributed to biochar limiting the concentration of NH_4^+ available for nitrification.

Calculations show that the decrease in N leaching following urea application (equivalent to 200 kg N/ha) was proportional to the CEC of the lignite added:

Hydrolysis of 8 g urea (equivalent to 200kg N/ha) can form 0.266 M NH_4^+ in the soil:

$$(8 \text{ g urea}/60) \times 2 = 0.266 \text{ M } NH_4^+ \qquad \text{(Eqn. 5.1)}$$

Given the CEC of lignite is 44.8 $cmol_c$/kg, lignite could potentially retain 0.113 M NH_4^+ when 400 g (fresh weight) was applied (rate equivalent to 20 t/ha). Given the water content of lignite is 38%, lignite dry weight is equal to 252 g:

$$(0.252 \text{ g lignite} \times 44.8 \text{ cmol}_c/\text{kg})/100 = 0.113 \text{ M of -ve charge} \qquad \text{(Eqn. 5.2)}$$

Therefore, if all the lignite CEC were occupied by NH_4^+ we would expect that 0.154 M NH_4^+ remains available for nitrification followed by leaching:

$$0.226 - 0.113 = 0.154 \text{ M free } NH_4^+ \qquad \text{(Eqn. 5.3)}$$

Therefore, we should expect lignite to leach 58% of the urea only treatment, which represents a 42% reduction in N leached from the lignite amended soil:

$$(0.154/0.266) \times 100 = 54\% \text{ of the urea only treatment.} \qquad \text{(Eqn. 5.4)}$$

$$(0.113/0.226) \times 100 = 42\% \text{ reduction in N leached}$$

Our measurements showed just a 23% reduction in N leaching relative to the urea only treatment. The discrepancy may be due to the displacement of NH_4^+ by the major soil cations (Al^{3+}, K^+, Mg^{2+}, Ca^{2+}), which bind preferentially to CEC sites (Simmler, 2012).

The reduction in N leaching from lignite-amended soil provides evidence that marketed fertilisers such as black urea and humates could in fact mitigate N loss into waterways where it can become an environmental contaminant. This is important because trials investigating the effects of black urea have primarily focused on dollar return; therefore, research has focused on commercial aspects of farming rather than an environmental approach. For example, a trial investigating the effects of black urea compared to standard urea on the yield of a cotton (*Gossypium spp*) crop found black urea yielded significantly higher, producing on average 1.2 bales per ha more cotton. However, no reference is made to the amount of N retained in the soil over time, assimilated by the plant or lost through alternative pathways between treatments (Advanced Nutrients, n.d.).

The lack of effect of lignite on NO_3^- leaching from biosolids treatment may be due to the high NO_3^- concentration in the biosolids (Table 3.1). Nitrate would not be expected to bind to lignite and hence would leach freely. Further evidence for this comes from the pattern of NO_3^- leaching in the urea and biosolids treatments. In the urea treatment, the highest levels of N leached after 14 days which would be expected because the NH_4^+ generated by the urea has to undergo nitrification. In contrast, the N peak from the biosolids-amended soil occurred immediately, consistent with a high concentration of NO_3^- initially present in the biosolids.

Calculations show that the NO_3^- leached from the biosolids-amended soil was similar to the amount of NO_3^- added in the biosolids where NO_3^- present in the biosolids was equivalent to 2.8 kg NO_3^-/ha and 3.0 kg N/ha leached from the biosolids treatment in the experiment. The small discrepancy is explainable by the additional NO_3^- coming from the soil (the control leached 0.5 kg):

Assuming 53% water content, 600 g biosolids (rate equivalent to 30 t/ha) contains 282 g dry biosolids:

$$600 - (600 \times 0.53) = 282 \text{ g (dry weight)} \qquad \text{(Eqn. 5.5)}$$

Given that biosolids contained 867 mg/kg NO_3^- , there are 244 mg NO_3^- that would be freely available to leach from the biosolids amended soils:

$$0.282 \times 867 = 224 \text{ mg } NO_3^- = 55.2 \text{ mg N} \qquad \text{(Eqn. 5.6)}$$

55.2 mg of N is equivalent to 2.76 kg N/ha

One would expect that over the medium to long term, lignite would reduce NO_3^- leaching from biosolids by binding NH_4^+ that is formed from the mineralisation of organic N (Knowles et al., 2011). Since the main problem with NO_3^- leaching from biosolids occurs immediately following their application to soil (Robinson et al., 2011), lignite is unlikely to be an effective means of improving environmental outcomes from biosolids addition.

The amount of N leached over 39 days was high in comparison to other studies (Table 5.1). Approximately, 74 and 96% of N applied as urea was recovered in the leachate collected from the urea and urea + lignite treatments over 39 days. This may be explained by several factors including soil type and the rate and timing of N application. In this trail the equivalent of 200 kg N/ha was applied in one application. This is not considered to be ‘best practice’ or an efficient use of N fertiliser. On the typical New Zealand dairy farms, split applications of N fertiliser are applied at a rate that typically does not exceed 50 kg N/ha per application. This has been observed to significantly reduce the risk of N leaching (Cameron et al., 2013). Nitrogen leaching is usually greatest during late autumn and winter when plant uptake of N is low (because of cooler conditions) and higher volumes of drainage occur from the soil (Cameron et al., 2013). Thus, the seasonal timing of this study and the two mass applications of water (2 L and 1 L) on days 1 and 6 may also have influenced the high amount of N in the leachate.

Finally, even though there was a difference in peak concentrations between the soils amended with lignite, the large error bars indicate large variability between replicate data sets for individual treatments. Large variability could have occurred due to the lysimeters being small and only three replicates representing each treatment. By being small, a minuscule incident can have a major impact on results. For example, a macropore may form in one lysimeter but not the rest in the same treatment and therefore that one lysimeter may drain faster, accelerating leaching. A greater number of replicates provide a more reliable average due to more figures being available to account for any misleading results.

Table 5-1. Comparative studies investigating N loss in the forms of N leached and N_2O emitted from grasslands.

	Study type	Soil type	Study duration	N applied (kg/ha)	N leached (kg/ha)	N_2O-N (kg/ha)	Emission factor (%)
(Zaman et al., 2008)	LFT	Sandy loam	3 months	150*	0.4	2.4	1.1
(Luo et al., 2007)	CCFT	Silt loam	3 months	50*	-	0.78	1.6
(Zaman et al., 2009)	CCFT	Silt loam	3 months	600**	-	3.4	0.4
Di and Cameron (2003)	LFT	Stony silt loam	8 months	1000**	-	27	2.2
(Di and Cameron, 2002a)	LFT	Stony silt loam	1 year	200+1000**	-	46	-
(Di and Cameron, 2002c)	LFT	Stony silt loam	1 years	200*	130	-	-
Monaghan et al. (2005)	PT	Clay loam	1 year	200*	46	-	-
(Sharpley and Syers, 1979)	MD	Silt loam	5 months	120*	2.8	-	-
(Gioacchini et al., 2002)	LFT	Sandy loam Clay loam	2 years	120*	103 9.8	-	-
(Di and Cameron, 2002a)	LFT	Stony silt loam	1 year	200*	7.9	-	-
Ledgard et al. (1996)	PT	Silt loam	1 year	200*	57		

Where: (LFT) = lysimeter field trial, (CCFT) = closed chamber field trial, (MD) = mole drainage and (PT) = plot trial.
* urea
** cow urine

5.2 Factors influencing N-fluxes in lignite amended soils

Effects of lignite amendment on the physical properties could be the main factor contributing to the increase in N_2O flux from soils fertilised with urea however, the mechanisms for this are unclear. If water is being retained by the lignite particles or lignite is coating soil aggregates, it could result in the formation of anaerobic microsites, which favour denitrification. Both nitrification and denitrification are coupled through a “common” NO_3^- pool. Because aerobic and anaerobic sites occur in close proximity to each other, NO_3^- formed in aerobic zones readily diffuses to anaerobic spots where it can undergo further reductions to form N_2O or N_2 (Russow et al., 2009).

The low organic matter content and texture of the Lismore soil used in this study are conducive to a low water holding capacity (WHC). It is therefore possible that the incorporation of lignite could have increased water retention and aggregation in the amended soil. Piccolo et al. (1996) studied the potential for coal-derived humic substances to improve the available WHC of a low fertile, Mediterranean soil. The field capacity and the available WHC were significantly ($p < 0.05$) higher when only 0.05 g/kg humic acids were applied to soil. When applied at an increased rate of 1.0 g/kg, available WHC increased 30% above the control. An increase in the WHC of a sandy soil was also observed by Richards et al. (1986) when lignite was added to pots in a glasshouse experiment. While the mechanisms were unclear, it was thought water was being retained in the porous structure of the lignite. Because no increase in plant available water was observed under the lignite treatment, it was assumed that the water was strongly held by the lignite particles. The consequences this could have for pasture growth therefore needs to be the subject of future research if lignite is to be used as an amendment for agricultural soils.

Alternatively, the presence of large quantities of hydrophobic substances in lignite could restrict water movement through the soil profile, and forming small anaerobic niches, which favour denitrification. Hydrophobicity in lignite can be associated with aliphatic constituents, wax residues and un-decomposed lignin type organic polymers (Gerke et al., 2001).

It is also possible that lignite provides a physical refuge for denitrifying microbes. Lignite particles may display similar properties to a soil aggregate, and therefore provide similar functions such as protection of organic matter, habitat for biota to colonise and reproduce and retention of soil nutrients (Atkinson et al., 2010; Lehmann et al., 2011). Lehmann et al. (2011) suggests that similar to soil aggregates, the preferential oxidation of the particle surface of carbonaceous materials relative to the interior could limit O_2 diffusion into the interior of the particle, and reducing redox potential. This change in redox potential may generate conditions favourable to denitrifying microorganisms and could perhaps account for the higher N_2O flux observed from soils amended with lignite in this experiment.

The decrease in N leaching from lignite-amended soils appears to be proportional to the CEC of the lignite in this experiment. It is possible that over time, natural weathering agents including O_2, water and soil biota could continue to increase the availability of functional groups able to participate in ion sorption in the soil, therefore making lignite a potential long term solution to mitigate N leaching associated with urea application (Dick et al., 2002). However, the effect of lignite on N leaching under grazed pasture warrants future investigation as N loading from cattle excreta could influence N retention. Vassileva et al. (2009) showed that as the concentration of NH_4^+ in solution increases the removal efficiency of lignite decreases due to saturation of exchange sites. Therefore, due to the high concentrations of N which can be returned to soil in cattle urine (400-1000 kg N/ha) from grazed pasture (Fraser et al., 1994), the equivalent of 20 t/ha lignite may not be sufficient to effectively reduce NO_3^- leaching, and could intensify N_2O emissions. Furthermore, the removal efficiency of lignite depends on the influence of specific surface area values and of the type of porous textures of these materials, which are very specific for different samples. Therefore, the range of lignite's available will require individual research.

Alternatively, part of the observed impact of lignite on N leaching could have been due to inhibition of the urease enzyme. Dong et al. (2009) investigated the effect of lignite-derived humic acids on ammonia-oxidising bacteria when urea was added to the soil. Results showed that the presence of humic acids delayed the release of NH_4^+ by 9 days compared to the urea only treatment, which also coincided with a delay in urease activity. The mechanisms behind this were not fully understood, it was suggested that lignite humic acids buffered the change in diversity and quantity of total bacteria caused by the application of urea to the soil through inhibition of the urease enzyme. Variation in microbial biomass between treatments was not a focus of this experiment therefore, while it is a possible mechanism for reduced nitrification, it cannot be confirmed at this stage.

The addition of substrates with high C:N ratios can inhibit mineralisation, especially in a soil with a low nutrient status (Kwiatkowska et al., 2008; Tahir et al., 2011). Kwiatkowska et al. (2008) found that seven years after application, soil amended with lignite had a higher C content, slightly higher N content and higher C/N ratio than the control soil. However, because lignite is comprised mainly of highly stable forms of C, the potential for immobilisation to explain decreased N leaching depends on the size of the labile fraction of C rather than the C:N ratio of the soil. Therefore, given the high stability of lignite in soil, it is unlikely that lignite had a great effect on immobilisation of N in this experiment. Piccolo et al. (2004) suggests that the process of hydrophobic protection may well prevent rapid microbial decomposition of the labile organic matter entering the soil with litter or plant residues when lignite is present.

5.3 Rates of application and practicality

Where farmers' may be able to reduce inputs of N fertiliser through improving N use efficiency, multiple benefits (economical, ecological and environmental) could be achieved. The use of lignite on a large scale is however in question as it could require significant processing before incorporation into the soil or combining it with another product such as biosolids or urea. Lignite in its natural state or with minimum additional treatment is preferred as a soil amendment as it reduces costs associated with additional handling and treatment processes.

Direct application can be cost effective, but this method is not 'user friendly' due to the fine dust like particles and the possibility of reduced stability in the soil. Therefore, possibilities of preparing easily applied granules using suitable binders have been investigated. Businova and Pekar (2007) have shown that it is possible to shape raw lignite into granules measuring 6 by 10 mm in diameter. The most effective binders were obtained using starches and molasses due to their biodegradability. Depending on the initial mass and/or coating used, release of the granules could be manipulated to occur in range from hours to months.

The economics and rationale of applying lignite to soil in an agricultural system is becoming more apparent with the ever increasing cost in urea fertilisers due to increasing costs of energy, therefore farmers are looking at ways to minimise costs while achieving the highest returns possible.

Calculations show that to eliminate NO_3^- leaching following a urea application, lignite would need to be applied at a rate of 118 kg for every kg of urea.

Given the mass of urea is 60:

$$((1 \text{ g urea}/60\ [M_r\ (NH_2)_2CO]\ ) \times 2\ [\text{each molecule can produce } 2 \text{ x } NH_4^+])$$

$$= 0.0333 \text{ mol N /g} \qquad \text{(Eqn. 5.7)}$$

Therefore, the lignite required to eliminate N leaching per g urea applied:

$$0.0333 / 0.000448 \text{ (M –ve charge per g)}$$

$$= 74.3 \text{ g (dry weight)}$$

$$= 118.0 \text{ g (fresh weight)} \qquad \text{(Eqn. 5.8)}$$

This would equate to 47 tonnes per hectare, which is agronomically feasible, but prohibitively expensive (ca \$14,160 per hectare @ \$300 per tonne). This would be reasonable for high-value land, such as agricultural land, where other benefits from the lignite could be realised. These would include reduced plant Cd uptake (Simmler et al., 2013), as well as benefits associated with organic matter in these highly tilled soils that are often low in organic carbon (Lal, 2002). These benefits may be offset by any increase in N_2O emissions from the lignite-amended soil. There are several unknowns in such a scenario. The bioavailability of NH_4^+ that is bound to lignite is unclear. This study did not test plant growth or N-uptake due to the aforementioned reasons. Lower rates of lignite addition may be acceptable if the crop can immediately assimilate the excess N. The persistence of lignite in soil under such management practices is unknown and should be the subject of future research.

Chapter 6
Conclusion and Recommendations

6.1 Conclusion

This experiment falsified the hypothesis that lignite would significantly reduce N_2O fluxes from soil. In unamended soil and soil amended with biosolids, lignite had no effect on N_2O emissions, while on soil that received urea; lignite caused a significant increase in N_2O emissions. Therefore, pastureland amended with lignite may emit more N_2O from urine patches or following urea fertilisation. Nevertheless, the rates of N_2O emissions in this experiment were small compared to other studies.

Lignite significantly reduced the NO_3^- leaching from soil following urea application. The decrease was directly proportional to the CEC of the lignite. Calculations show that to eliminate NO_3^- leaching following a urea application, lignite would need to be applied at a rate of 118 kg for every kg of urea, which could be economically feasible for high-value land.

Lignite did not reduce NO_3^- leaching from biosolids amended soils over the experimental period. This may be due to the high concentrations of NO_3^- in the biosolids, which are not retained by lignite. Therefore, lignite may not be an effective amendment to mitigate N loss from land application of biosolids.

6.2 Recommendations

- By necessity, the duration of this trial was short therefore longer term trials are needed to evaluate the full effects of lignite amendment on N_2O emissions and N leaching. This would allow for an evaluation of the effect seasonal variation has on N loss and how soil fertility and nutrient dynamics in the soil change over time. It would also allow for N to be applied at rates representative of the average New Zealand dairy farm.

- The current study did not encompass potential effects of plant interactions, plant cover or changes in the diversity and function of soil microbes. Future trials that include such interactions would help improve our understanding of the impact lignite has on the N cycle.

- Interaction effects of individual nutrients should be studied as these may influence the sorpitive ability of lignite and the availability of other nutrients in the soil.

- If lignite were used to minimise N loss from agricultural soils it would be important to determine how N loss is affected in a range of soil types amended with lignite. This trial only studied N loss from a stony silt loam soil with low organic matter content.

- Various application methods should be tested along with the appropriate aggregate size of lignite as this could potentially have an effect on the ability of lignite to persist in the soil and the adsorption of soil nutrients. Preparation, handling and transport may also limit the potential economical use of lignite; it would be beneficial to address these issues in future trials.

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