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The Contribution of Nitrous Oxide Emissions from Irish Agriculture To Global Warming

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Declaration

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Mohamed Abdalla

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Abstract

Results from this thesis concern the calculation of annual fluxes and emission factors of the greenhouse gas nitrous oxide from two agricultural soils in Co. Carlow, Ireland.
For a cut and grazed pasture in 2004, the annual emission was calculated as 2.4 ± 0.3 kg N_2O-N ha^{-1}, or in terms of global warming potential, 200 kg CO_2-C equivalents ha^{-1}. In contrast an arable field in which spring barley was grown and managed under two tillage regimes (reduced and conventional) gave an annual emission of nitrous oxide for 2004 of 0.6 ± 0.1 and 1.4 ± 0.1 kg N_2O-N ha^{-1} or 50 and 118 kg CO_2-C equivalents ha^{-1}.

Emission factors were also derived from the field measurements where an emission factor of 0.83 ± 0.15% was calculated for the cut and grazed pasture. This is less than 70% of the IPCC default emission factor for applied nitrogen fertilizer. It is also lower than the other published data for Irish grasslands. Reasons for the relatively low annual emissions and emission factor are discussed in terms of limiting rainfall and soil type.

A small plot trial was established on the arable field to investigate the efficacy of reduced tillage and reduced N fertilizer on seasonal fluxes and emission factors of N_2O. Emission factors ranging from 0.42 ± 0.41 to 0.65 ± 0.14 % were calculated for two consecutive seasons. Reduced tillage had no effect on N_2O emissions. However, by reducing the applied nitrogen fertilizer by 50 % compared to the normal field rate, N_2O emissions could be reduced by 57 % but with little effect of 16% on grain yield. This was consistent over the two years of measurements.

Laboratory experiments were also carried out investigating the effect of organic carbon, N fertilizer, temperature and moisture on denitrification of the grassland soil using the acetylene inhibition technique. Here the activation energy and Q_{10} of denitrification of the grassland soil was calculated as 47 kJmol^{-1} and 5.8 respectively. An overall EF of 0.67% for denitrification was also calculated, which is comparable to field results. It is likely therefore that all of the N_2O emitted from the grassland soil rose from denitrification.

A combined study for all field data revealed the same response of both soils with regards to N_2O fluxes as a function of applied fertilizer and soil nitrate. Here an overall EF of 0.61 ± 0.08 % was calculated.

Comparisons of measured and modeled fluxes were carried out using the process based model, DNDC. Excellent agreement was found for both the arable field and, when adjusting the soil organic carbon inputs, the cut and grazed pasture.

Abbreviations

EF	Emission factor
GHG	Greenhouse gases
N_2O	Nitrous oxide
WFPS	Water filled pore space
CAN	Calcium ammonium nitrate
SWC	Soil water content
C	Conventional tillage
L	Low till
N_1	Field fertilizer rates (140 or 159 kg N ha^{-1})
N_2	Medium fertilizer rates (70 or 79 kg N ha^{-1})
N_3	Control plots (zero fertilizer)
SMC	Soil moisture content
DNDC	DeNitrification DeComposition
N	Nitrogen
DF	Degree of freedom
ANOVA	Analysis of variance
IPCC	International Panel on Climate Change
GW	Global warming
SOC	Soil organic carbon
SAR	Second assessment report
TAR	Third assessment report
ARF	Adjusted radiative forcing
IRF	Instantaneous radiative forcing
DOC	Dissolved organic carbon

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Chapter 1: General introduction

1.1 Background

Agricultural practice is assumed to be one of the major sources of greenhouse gas emissions, particularly for nitrous oxide (N_2O), and accounts for approximately one-fifth of the annual increase in radiative forcing (IPCC, 1996). A recent review on sources of N_2O emissions reported that agricultural land is the most important (de Araujo, *et al.,* 2006), contributing approximately 52% (Mosier, *et al.,* 1998; Kroeze *et al.,* 1999), or 46% (Olivier *et al.,* 1998) of the global anthropogenic N_2O flux. This is equivalent to a global warming potential (GWP) of about 1.0 Pg C y^{-1} (Robertson, 2004).

The major part of this global flux is the N_2O produced in soils as an intermediate during nitrification and denitrification (Hutchinson and Davidson, 1993). Primary reasons for enhanced N_2O emission from cultivated soils are increased N inputs by mineral fertilizers, animal wastes and biological N fixation (IPCC, 1996). The emission of N_2O increases when agricultural lands and forests are fertilized or manured (Mosier *et al.*, 1991; Castro *et al.*, 1994b; Bouwman, 1995; Nevison *et al.*, 1996).

Currently, the dependency of N_2O emissions from agriculture on regional differences or managements is not well known (Freibauer and Kaltschmitt, 2000). However, the Irish Environmental Protection Agency (EPA, 2005) revealed that agriculture is the largest source of nitrous oxide emissions in Ireland, accounting for approximately 80% of all emissions of this greenhouse gas, mainly from the breakdown of nitrogenous fertilisers in the soil. N_2O emissions of 1.8 - 4.92% of applied fertilizer were reported at the Teagasc Research Centre at Johnstown Castle, Wexford, for a grazed pasture, where total N applied was 303 and 493 kg N ha^{-1} respectively (Hyde *et al.*, 2005).

The aims of this PhD study were to measure and model N_2O emissions from Irish arable and grassland soils and to understand the key processes that govern these emissions.

Moreover, the study attempted to refine the standard empirical approach for annual N_2O emission reporting and to discuss the possible impact of the results of this study on emission assessment and on strategies for future mitigation. Hence, this dissertation is organized into seven Chapters. Chapter 1 is a general introduction to this study, Chapters 2, 3 and 4 focus on two years of experimental work on N_2O emissions from grassland and arable sites. Chapter 5 investigates soil denitrification and its response to environmental factors, Chapter 6 discusses modelling of N_2O emissions from both the arable and grassland sites using the DNDC model, and finally, Chapter 7 brings together and discusses common observations from all the separate experiments and suggests further future work.

1.2 N_2O in the atmosphere

Nitrous oxide is an important greenhouse gas in the atmosphere. Direct measurements of atmospheric N_2O, combined with historic ice-core data suggest that the global concentration of N_2O has increased from approximately 275 to 314 ppb over the past 150 years, with a steady linear increase of 0.7 ppb per year occurring over the last forty years (Machida *et al.*, 1995; Hansen and Sato, 2000). Agriculture is known to be a considerable source of this N_2O release (Kroeze *et al.*, 1999) as illustrated in Table 1.1.

Table 1.1: Anthropogenic global emissions of N_2O

Reference	Mosier *et al.*, (1998) and Kroeze *et al.*, (1999)	Olivier *et al.*, (1998)
Year base	1994 (Tg N y^{-1})	1990 (Tg N y^{-1})
Agricultural land	4.2 (52%)	1.9 (46%)
Burning biomass	0.5 (6%)	0.5 (12%)
Industrial sources	1.3 (16%)	0.7 (17%)
Cattle	2.1 (26%)	1.0 (25%)
Total (anthropogenic)	8.1 (100%)	4.1 (100%)

Source: de Araujo, *et al.,* (2005) based on TAR-WGI, (2001) Emissions of this gas into the atmosphere are of concern worldwide because of the role of N_2O in global warming (Houghton *et al.*, 1990), and in the destruction of the ozone layer (Crutzen, 1976). Although both the present day concentration and the annual rate of increase for N_2O are considerably less than those calculated for the two other major greenhouse gases (GHGs), carbon dioxide (356,000 ppbv; 1,600 ppbv y^{-1}) and methane (1745 ppbv; 7 ppbv y^{-1}), on a molecule for molecule basis N_2O has a radiative force approximately 200 to 300 times that of carbon dioxide (CO_2), and an atmospheric life time of about 150 years compared with a radiative force approximately 20 times that of carbon dioxide and atmospheric life time of 12 years for methane (Houghton *et al.*, 2001).

The release of N_2O to the atmosphere is increasing at an annual rate of 0.3% (Prinn *et al.*, 1990; Khalil and Rasmussen, 1992a). Coupled with its role as a stratospheric ozone sink, the contribution of N_2O to global warming in terms of radiative forcing has been estimated to be approximately 6% of all greenhouse gases in the atmosphere (Houghton *et al.*, 1996; Houghton *et al.*, 2001).

According to Houghton *et al.* (1996) the European climate in the 21st century is likely to be warmer, with drier summers, wetter winters, and more variable patterns of rainfall and temperature. The major cause of this climate change is the increase in the atmospheric concentration of greenhouse gases, particularly carbon dioxide, nitrous oxide and methane (CH_4). Emissions of N_2O to the atmosphere also result in impacts on human health, visibility, crop damage, and regional acidification and eutrophication (Brink *et al.*, 2000), while releases to land result in eutrophication to both fresh and coastal waters.

Climate change from greenhouse gas emissions has been at the forefront of current research in the past decade (IPCC, 1995; Seki and Christ, 1995). The aim of these efforts was defined at the Earth Summit in Rio de Janeiro as achieving: 'stabilization of greenhouse gas concentrations in the atmosphere at a level that prevents dangerous anthropogenic interference with the climatic system' (UNEP, 1997). Recent studies estimated the aggregated monetary damage due to climate change at 1.5 - 2% of world gross domestic product (GDP) and 2 – 9% of national gross national product (GNP) for developing countries for a two-fold increase in atmospheric CO_2 concentration from the pre-industrial level (Fankhauser and Tol, 1996).

1.3 Global warming

Many scientists believe that global warming is a consequence of the increase in the concentration of greenhouse gases in the atmosphere. The main conclusion achieved by the International Panel on Climate Change (IPCC, 2001a) is that global temperatures have increased over the past 50 years, greenhouse gases acting as a blanket that retains solar heat in the atmosphere (El-Fadel *et al.,* 2001). This creates higher global temperatures, or what is commonly known as global warming. According to the IPCC (1994), there are two types of radiative forcing: adjusted (ARF) and instantaneous (IRF). The adjusted RF is the change of net total (IR + Visible + UV) radiation flux at the tropopause level due to GHG. The instantaneous RF is considered when the initial stratospheric temperature is also fixed (IPCC, 1990, 1994). The value of radiative forcing strongly depends on thermo-dynamical processes in the troposphere. For instance, the radiative forcing caused by the changes in the stratospheric ozone concentration decreases approximately by a factor of 2 due to tropospheric temperature adjustment (Forster *et al.,* 1997).

Global warming potential is widely used for the estimation of the influence of greenhouse gases and other atmospheric radiatively active substances on the global climate (Hansen *et al.,* 1981; Shine *et al.,* 1995; Granier and Karol, 1997; Forster *et al.,* 1997; Myhre *et al.,* 1998 and Christidis *et al.,* 1997). It is suspected of triggering adverse environmental consequences including the flooding of coastal zones and desertification (El-Fadel *et al.,* 2001). Many signs of global warming are evident today. The global temperature is approximately 0.5°C warmer than it was 100 years ago and expected to be 3°C warmer in 2100. Snow and ice-cover have decreased this century, deep ocean temperatures have increased and global sea levels have risen by 100 – 200 mm. Moreover, changes in distribution of disease-bearing organisms and in extreme weather conditions e.g drought and flood are expected (Collins, 2001).

1.4 Kyoto Protocol

Following the Kyoto protocol, Annex 1 countries are now committed to reducing their overall emissions of greenhouse gases by at least 5% below 1990 levels in the commitment period 2008 - 2012 (IPCC, 1997). This is probably the beginning of a process to reduce emissions even further in the near future. At present, under IPCC protocols, the removal of greenhouse gases by sinks are limited to direct human-induced land use change and forest activities limited to afforestation, reforestation and deforestation since 1990, measured as variable changes in stocks in each commitment period.

In order to provide an estimate of current rates and assess change in N_2O emissions, one of the obligations of signatory states to the United Nations Framework Convention of Climate Change (UNFCCC) is to establish a national emission inventory that fully reports all anthropogenic sources of greenhouse gases, using comparable methodologies. To this end, protocols have been developed by the IPCC, which provide a methodology for calculating emissions using defined emission factors. For this purpose, agricultural N_2O emissions are assumed to be derived from three principal sources (IPCC, 1997):

1. Direct emissions from soil nitrogen (N), denoted here as ‘soil’ e.g. applied fertilizers in both manures and artificial (chemically fixed N) forms, N deposited by grazing animals, mineralization of crop residues, biological N fixation and the cultivation of high organic content soils.

2. Emissions from animal waste management systems, denoted here as’ animals’.

3. Indirect emissions from N lost to the agricultural system, e.g. through leaching, runoff or atmospheric deposition.

1.5 Emission factors evaluation

The increased used of N fertilizers has resulted in greater quantities of N being cycled through agricultural systems, which, in turn has increased N_2O emissions from soils (Smith *et al.*, 1997). These emissions can be as a direct result of N fertilizer application. The IPCC default emission factor (EF), of 1.25%, for N fertilizer applied, i.e N fertilizer induced N_2O, is adopted from the work of Bouwman (1996), who summarized a range of data and concluded that the annual N_2O emissions from cultivated soils were decisively influenced by N supply. This has led to the production of simple predictive equations based solely on fertilizer application rate for agricultural sources. Bouwman's equation calculates default emissions in the absence of national sampling programmes, where the annual flux of N_2O-N from agricultural soil, is 1 + 0.0125 * N- application rate (kg N ha^{-1}), 1 kg N_2O-N representing background emissions and 0.0125 being the conversion coefficient relative to fertilizer application. Further refinements are possible given the uncertainty regression coefficient of 0.0125 ± 0.01 (mean ± standard error). In addition to an emission factor for fertilizer application, the IPCC has produced default values for other direct and indirect emission sources (IPCC, 1997; IPCC, 2000a), as illustrated in Table 1.2.

In a follow up study of 846 published measurements of N_2O flux from agricultural soils, Bouwman *et al.* (2002) assessed the influence of a number of factors on N_2O emissions. Whilst N-fertilizer application was still the dominant influence, the type of fertilizer used was also a significant determinant. Interestingly, the duration and intensity of field measurements of N_2O emission influenced the extent of the effect observed, longer measurement periods (> 1 year) increasing the fertilization effect whilst programmes of intensive measurement (> 1 per day) produce lower emissions than less intensive programmes (2 - 3 per week). N_2O emissions due to urea fertilizer applications can be as high as following application of nitrate or ammonium-based fertilizer (de Klein *et al.*, 2001). However, the highest N_2O emissions were measured following the application of calcium ammonium nitrate. In general, when soil conditions favoured denitrification, nitrate fertilizers caused higher emissions, whereas in warm, dry conditions emissions following applications of urea or ammonium-based fertilizers were higher (Smith *et al.*, 1997; Bouwman, 1996).

A recent study of N_2O emission rates in organic and conventional dairy crop rotations in five European countries (Austria, Denmark, Finland, Italy and UK), showed that across the two systems and the five locations, there was a significant relationship between total N and N_2O emissions at crop rotation levels. The study indicated that 1.6 ± 0.2% (mean ± standard error) of total N inputs were lost as N_2O gas, while there were background emissions of 1.4 ± 0.3 kg N_2O-N $ha^{-1}y^{-1}$. This suggested that N input is a significant determinant for N_2O emission from agricultural soils (Petersen et al., 2005).

According to Dobbie and Smith (2003), N_2O emissions from intensively managed grassland ranged from 1 - 3% of the applied N. These higher N_2O emissions from grassland were observed earlier by Smith *et al.* (1998) who studied the effect of temperature, water content and N fertilization on N_2O. They concluded that grazed grassland had higher N_2O emissions than grassland cut for conservation, which in turn had higher emissions than cereal crops.

On the other hand, a review by Eichner (1990); Mosier and Klemedtsson (1994) showed 0.3 - 2.1% of the N fertilizer applied to corn was emitted to the atmosphere in the form of N_2O. They reported that N_2O emissions rates for corn were higher than the rate for other grains and grasses; at least for soils predominantly composed of sand and clay. Grains and grasses typically emit about 0.2 - 1.5% of fertilizer nitrogen as N_2O, compared to 0.3 - 2.1% for corn (Mosier and Klemedtsson, 1994; Eichner, 1990). Moreover, Eichner,

(1990) reported that the total N_2O emissions per acre from cornfields are four times higher than the total emissions from soybean fields. Furthermore, Matthews (1994) estimated a mean loss of 1.3% of the fertilizer applied to corn as N_2O-N emitted to the atmosphere, while Mosier *et al.* (1986) found that 1.5% of the fertilizer N applied to corn was lost as N_2O-N compared with 0.4% for barley.

A later N_2O model (Mummey *et al.,* 1998) predicts that conventionally tilled corn fields have lower total N_2O emissions than do conventionally tilled fields of sorghum, soybean, cotton, peanuts, tobacco, vegetable row crops, wheat, oats, rice and barley (only sunflower fields have lower emissions). However, Kaiser *et al.* (1998) found that N_2O emissions from fertilized wheat, barley, beet, and rape fields in Germany represented 1 - 8% of fertilizer N applied. Groffman *et al.* (2000) suggested that differences in such factors as soil type, freezing and thawing events might be important determinants of N_2O emissions than crop type. In several studies on both pastoral and arable land (Table 1.4), direct annual N_2O emissions were found to be ranging from <0.1 to about 7% of the N fertilizer applied.

In contrast to these results, Smil (1999) suggested that N_2O release from denitrification of synthetic fertilizer does not cause a major threat to the integrity of the global environment. He reported that emissions of N_2O account for < 0.5 - 5% of initially applied fertilizer nitrogen. Because N_2O from synthetic fertilizers accounts for less than 10% of all emissions of the gas and because N_2O is currently responsible for less than 10% of the global greenhouse gas effect, even the most liberal estimate must ascribe less than 1% of global warming effect to N_2O release from application of synthetic fertilizer.

1.6 Important microbial processes of N_2O in soils

Nitrogen is one of the most important mineral elements that affect world's ecosystems. Nitrogen is available to plants only in the form of two minerals: ammonium (NH_4^+) and nitrate (NO_3^-). Though Earth's atmosphere is almost 80% nitrogen, it is mostly in the form of nitrogen gas (N_2), which is unavailable to plants.

Table 1.2: Default values and uncertainty ranges of IPCC emission factors for N_2O production from agricultural soils

Name	Used for	Estimated parameter	Default value and uncertainty range
EF_1	IPCC direct	Fraction of N released as N_2O	1.25% ± 1%
EF_2	IPCC direct	N_2O emitted from cultivated organic soils	8 kg N ha^{-1} y^{-1} temperate, 16 tropical (no range given)
EF_3	IPCC direct	Fraction of N from deposited manure (pasture, range, paddock), not applied	2% (range 0.5% -3%)
EF_4	IPCC indirect	Fraction of N from atmospheric deposition released as N_2O	1% (range 0.2% -2%)
EF_5	IPCC indirect	Fraction of leached N released as N_2O	2.5% (range 0.2% -12%)
EF_6	IPCC indirect	Fraction of N from human sewage release as N_2O	1% (range 0.2% -12%)

Sources: (IPCC, 1997; IPCC, 2000)

Nitrogen enters ecosystems via two natural pathways, the relative importance of which varies greatly from ecosystem to ecosystem. The first, atmospheric deposition, account for approximately 5 - 10% of the usable nitrogen that enters most ecosystems. In this process, NH_4^+ and NO_3^- are added to soil by being dissolved in rain or by settling as parts of fine dust or other particulates. The other pathway for nitrogen to enter ecosystems is via nitrogen fixation. Only certain prokaryotes can fix nitrogen- that is, convert N_2 into minerals that can be used to synthesize nitrogenous organic compounds such as amino acids. Nitrogen is fixed in terrestrial ecosystems by free-living (non-symbiotic) soil bacteria as well as by symbiotic bacteria in the root nodules of legumes and certain other plants. Some cyano-bacteria fix nitrogen in aquatic ecosystems. In addition to these natural sources of usable nitrogen, industrial fixation of nitrogen for fertilizer makes a major contribution to the pool of nitrogenous minerals in terrestrial and aquatic ecosystems (Campbell *et al.*, 1999).

In soil, the largest fraction of N is in organic compounds, unavailable to plants. By mineralization processes performed by microbes, a series of reactions break the organic molecules into ammonium and nitrate. Simultaneously, N immobilization occurs (the transformation of inorganic into organic N forms), and the net effect of mineralization and immobilization will determine the amount of N available for vegetation growth in natural environments (Brady and Weil, 1999).

One of the environmental problems related to nitrogen compounds is the increased emissions of N_2O and other N oxide gases, which have adverse consequences on the environment. Soils are important sources of atmospheric N_2O emissions. Soil microbes can transform inorganic N forms into nitrous oxide by a wide range of processes, of which the most important are nitrification and denitrification processes. Aerobic and anaerobic zones in soils, combined with soil chemical characteristics, define which processes are predominant (Davidson, 1991).

The most widely used conceptual model of trace N gas flux from soils is the "hole in the pipe" model proposed by Firestone and Davidson (1989), Figure 1.1. This model suggests that trace N gas production in soil is regulated at three levels (Stark *et al.*, 2002). The first level is the gross rate of nitrification and denitrification combined. The second level is the "size of the holes in the pipe", which represents the factors that control partitioning of N among the end products like NO_3^-, temperature and pH. The third level is transport processes in which water filled pore space plays a major role.

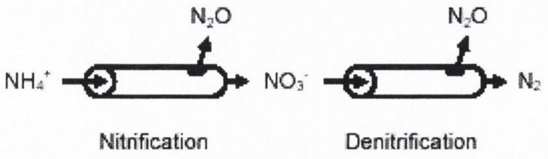

Figure 1.1: "Hole-in-the-pipe" conceptual model of N_2O gas production in soil. Modified from Firestone and Davidson (1989).

1.6.1 Nitrification

Nitrification is a two-stage oxidation process in which ammonia is oxidized to nitrite (NO_2^-) and the nitrite to nitrate (NO_3^-) producing N_2O as a by-product (Troeh and Thompson, 2005):

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

$2NO_2^- + O_2 \rightarrow 2NO_3^- + \text{energy}$

Nitrification rates are high when NH_4^+ is readily available (Robertson and Vitousek, 1981), but the concentrations of other nutrients generally have little effect (Robertson, 1982b, 1984; Christensen and MacAller, 1985). However, the soil microbial population may adapt to a wide variety of field conditions. Nitrification is generally lower at low pH, low O_2, low soil moisture content, and high litter C/N ratios (Rosswall, 1982; Robertson, 1982a; Bramley and White, 1990). According to Vitousek and Matson, (1988) most tropical forests have high rates of nitrification and mineralization, but Marrs *et al.* (1988) reported that net mineralization and nitrification were inhibited by exceptionally high soil water contents in Montane tropical forests of Costa Rica.

A variety of processes affect the concentration of NH_4^+ in the soil solution, including uptake by plants, immobilization by microbes, and fixation in clay minerals. Some of the remaining NH_4^+ may undergo nitrification, in which the oxidation of NH_4^+ to NO_3^- is coupled to the fixation of carbon by chemoautotrophic bacteria in the genera *Nitrosomonas* and *Nitrobacter* (Meyer, 1994). In some cases, organic N is also oxidized by heterotrophic nitrification, producing NO_3^- (Schimel *et al.,* 1984; Duggin *et al.,* 1991). Nitrate may be taken up by the plants and microbes or lost from the ecosystem in runoff waters or in emissions of N-containing gases. Nitrate taken up by soil microbes (mobilization) is reduced to NH_4^+ by nitrate reductase and used in microbial growth (Davidson *et al.,* 1990; DeLuca and Keeney 1993; Downs *et al.,* 1996). At any time the extractable quantities of NH_4^+ and NO_3^- in the soil represent the net result of all of these processes. A low concentration of NH_4^+ is not necessarily an indication of low mineralising rates, because it can also indicate rapid nitrification or plant uptake (Rosswall 1982; Davidson *et al.,* 1990).

A large amount of effort has been directed toward understanding the control of nitrification following disturbances, such as forest harvest or fire (Vitousek and Melillo, 1979; Vitousek, 1982). When vegetation is removed, soil temperature and moisture contents are generally higher, and rapid ammonification increases the availability of NH_4^+. Subsequently, nitrification may be so rapid that the uptake by re-growing vegetation and immobilization by soil microbes are insufficient to prevent large losses of NO_3^- in stream water following disturbance. However, not all disturbed soils show large losses of NO_3^-. In pine forests in the south eastern United States, microbial immobilization in harvest debris accounted for 83% of the uptake of the ^{15}N that was applied as experimental tracer following forest harvest (Vitousek and Matson, 1984). Microbial immobilization also retards the loss of nitrate following burning of tall grass prairie (Seastedt and Hayes, 1988).

1.6.2 Denitrification

Denitrification is a microbial process in which heterotrophic facultative bacteria reduce NO_3^- to N_2O and N_2 gases under anaerobic conditions (Tiedje, 1982). This process takes place under conditions where O_2 supply (the respiratory electron acceptor) is limited (Simek *et al.,* 2002). Here several abiotic reactions, respiratory NO_3^- reduction by microbes, and non-respiratory N_2O production, would all be termed denitrification. It is the only process capable of producing and consuming N_2O and NO. Hence this bacterial process plays a central role in global N trace gas dynamics (Firestone and Davidson, 1989). The reaction sequence of denitrification may be simplified as follows:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Denitrification is mainly regulated by soil moisture, availability of organic carbon substrate and soil nitrate concentration (Tiedje, 1982). Other factors, which have a bearing on this process, are soil pH, temperature and soil particle distribution. These factors in turn are influenced by soil topography, climate, vegetation type, geology and the pattern of organic C production and decomposition. Moreover, in agro-ecosystems, soil management affects one or more of controlling factors of denitrification (Khalil *et al.,* 2002), which can either enhance or retard denitrification rates.

The capacity to denitrify is widely spread among a number of taxonomic and physiological groups of bacteria (Tiedje, 1988). However, only a few genera seem to be numerically dominant in soil, marine freshwater and sediment environments. *Pseudomonas* species capable of denitrification are dominant in many environments, with *Alcaligenes* species commonly comprising the second most numerous denitrifying populations (Tiedje, 1988). Denitrification is the major process that returns N_2 to the atmosphere, completing the global biogeochemical cycle of nitrogen (Bowden, 1986).

For a long time, denitrification was thought to occur only in flooded anoxic soils, and its importance in upland ecosystems was overlooked. Later, soil scientists have shown that oxygen diffusion to the centre of soil aggregates is so slow that anoxic micro-sites are common, even in well-drained soils (Tiedje *et al.,* 1984; Sexstone *et al.,* 1985a). Thus, denitrification is widespread in terrestrial ecosystems, especially those in which organic carbon and nitrate is readily available in the soil (Burford and Bremner, 1975; Carter *et al.,* 1995; Wagner *et al.,* 1996). According to Davidson and Swank (1987), addition of NO_3^- stimulated denitrification in forest soils of Western North Carolina, and the addition of organic carbon stimulated denitrification in the mineral soil. Rainfall generally increases the rate of denitrification, because the diffusion of oxygen is slower in wet soils (Sexstone *et al.,* 1985b; Smith and Tiedje 1979; Rudza *et al.,* 1991; Schlesinger and Peterjohn, 1991).

The relative importance of denitrification as a source of NO, N_2O and N_2 varies depending upon environmental conditions (Firestone and Davidson, 1989; Bonin *et al.*, 1989). In Germany, well-drained soils with near-neutral pH produced NO only from nitrification, whereas in acid anoxic soils, NO was produced from denitrification (Remde and Conrad, 1991). In studies of a semi desert ecosystem, Mummey *et al.* (1994) found that nitrification accounted for 61 - 98% of the N_2O produced in moist soils, but denitrification was the predominant reaction in saturated conditions (Skiba *et al.*, 1993). Typically, in denitrification, the production of N_2O dwarfs the production of NO, so the total (nitrification plus denitrification) and proportional loss of NO from soils declines with increasing moisture content, while the flux of N_2O increases (Potter *et al.*, 1996). Matson and Vitousek, (1987) found a direct relation between N_2O production and nitrogen mineralization in comparisons of various tropical forests, implying that nitrification was the source of N_2O, whereas in the wet soils of the Amazon rainforest, N_2O appeared to be formed mostly from denitrification (Livingston *et al.*, 1988; Keller *et al.*, 1988).

Field measurements of denitrification are usually based on the observation that acetylene blocks the conversion of the intermediate denitrification product, N_2O, to the final product N_2 (Yoshinari and Knowles, 1976; Bruton and Beauchamp, 1984; Tiedje *et al.*, 1989). Thus, following application of acetylene to laboratory soil or field plots, the sole product of denitrification is N_2O, which is easy to measure with gas chromatography against its background concentration of about 320 ppb in the atmosphere. The incubation must be short, because acetylene also blocks nitrification and the rate measured during a long-term incubation will be affected by a decline in the pool of NO_3^- that is available for denitrification (Davidson *et al.*, 1986). Denitrification can also be estimated by the application of $^{15}NO_3^-$ to field plots and by measurements of the release of ^{15}N gases or the decline in $^{15}NO_3^-$ remaining in the soil (Parkin, 1985; Mosier *et al.*, 1986; Remde and Conrad, 1991). Short-term incubation studies using $^{15}NO_3^-$ also show promise for understanding the role of denitrification in the production of N_2O and N_2 (Spier *et al.*, 1995).

1.7 The Global N_2O budget

Although N_2O ranks second to N_2 as an atmospheric nitrogen species, its global budget is still not quantified. An annual increase of 0.7 ppbv has been estimated to reflect an imbalance between sources and sinks of approximately 3 to 5 Tg N y^{-1} (Mosier *et al.*, 1998a). There are two methodologies to estimate the global N_2O budget. One involves a "bottom-up" approach, the other uses "top-down" constraints. The bottom–up approach consists in summing up individual contributions from various sources and requires an up-scaling of local flux measurements to the global scale. In contrast, "top-down" constraints on total N_2O sources can be inferred, e.g., from the sum of global sink strengths and the rate of increase. Measurements of N_2O mixing ratios at single locations can easily be extrapolated to the global scale, so that the increase in the global N_2O burden is the best known parameter of the N_2O budget. The sink strength can be calculated from photochemical models of the stratosphere (Minschwaner *et al.,* 1993).

Recent estimates from "bottom-up" studies (Kroeze *et al.,* 1999; Mosier *et al.,* 1998a) coincide with the "top-down" constraints and show that the global N_2O budget can be closed. Previous studies missed some of the impact of agriculture (especially livestock) on the global nitrogen cycle, so that in the Second IPCC Assessment Report (SAR) the best estimate of the total added source was 10% short of the source implied by the sum of sinks and annual trends (Table 1.3).

1.8 N_2O sources

1.8.1 Indirect N_2O sources

Indirect N_2O emissions can be substantial, in some cases equalling or exceeding direct N_2O emissions (Mosier *et al.*, 1998a). However, though relatively little is known about indirect N_2O emissions from atmospheric deposition, there is a strong relationship between chronic deposition of atmospheric N onto soils, nitrification and increased N_2O

emissions (Brumme and Beese, 1992; McDonald *et al.,* 1997; Butterbach-Bhal *et al.,* 1997).

Earlier studies by Mosier *et al.* (1988a) suggested that N_2O emissions from N deposited from the atmosphere are approximately 0.2 - 1.6% of the nitrogen fertilizer applied. However, more recent studies indicate higher N_2O emission rates. Mosier *et al.* (1999) found annual N_2O emissions from a short grass steppe of about 2% of annual N input estimated from wet and dry deposition, while Skiba *et al.* (1998a) measured N_2O emissions from atmospheric N deposition of 0.2 to 15% of N deposited, depending on the distance from the N source. Van der Gon and Bleeker (2005) reported that indirect N_2O emissions due to deposition are underestimated in current global N_2O budgets. They calculated indirect N_2O emissions of at least 20% higher than the IPCC default value.

Nitrogen lost through leaching and runoff enters ground and surface waters, riparian zones, rivers and eventually the oceans (Mosier *et al.,* 1998a). Early estimates of the offsite N_2O evolution rate were based on very little data. To account for N_2O emissions off-site and after the on-site sampling period, Eichner (1990) and the IPCC (1990) doubled the measured on-site N_2O emissions. Eichner's doubling essentially was guess work, whilst the IPCC's is based on two studies, by Ronen *et al.* (1988) and Conrad *et al.* (1983). Later, the IPCC (1997) reported that 2.5% of the on-site N is emitted as N_2O-N, 1.5% in ground water and surface run off, 0.75% in rivers and 0.25% in coastal areas. Moreover, Kroeze and Seitzinger (1998) modelled N inputs to rivers and estuaries and related N_2O emissions, world wide from the year 1990 to 2050. Their model indicates that 4 - 5% of the leached N emitted as N_2O-N. This amount increases as systems become increasingly saturated with N. They concluded that 4 - 5% N_2O-N evolution is reasonable compared with the IPCC (1997) recommended value (2.5%), because studies prior to theirs tended to have incomplete representation of N_2O from aquatic systems.

Table 1.3: Estimates of global N_2O budget (Tg N y^{-1}) from different sources (adapted from the IPCC, 2001).

References	Mosier *et al.* (1998) Kroeze *et al.* (1999)		Olivier *et al.* (1998)		SAR[a]		TAR[b]
Base year	1994	range	1990	range	1980s	range	1990s
Source							
Oceans	3.0	1-5	3.6	2.8-5.7	3.0	1-5	
Atmosphere NH_3 oxid.	0.6	0.3-1.2	0.6	0.3-1.2			
Tropical soils							
Wet forest	3.0	2.2-3.7			3.0	2.2-3.7	
Dry savannahs	1.0	0.5-2.2			1.0	0.5-2.0	
Temperate soils							
Forests	1.0	0.1-2.0			1.0	0.5-2.3	
Grasslands	1.0	0.5-2.0			1.0		
All soils			6.6	3.3-9.9			
Natural sub-total	9.6	4.6-15.9	10.8	6.4-16.8	9.0		
Agricultural soils	4.2	0.6-14.8	1.9	0.7-4.3	3.5	1.8-5.3	
Biomass burning	0.5	0.2-1.0	0.5	0.2-0.8	0.5	0.2-1.0	
Industrial sources	1.3	0.7-1.8	0.7	0.2-1.1	1.3	0.7-1.8	
Cattle and feedlots	2.1	0.6-3.1	1.0	0.2-2.0	0.4	0.2-0.5	
Anthropogen-ic sub-total	8.1	2.1-20.7	4.1	1.3-7.7	5.7		6.9[c]
Total sources	17.7	6.7-36.6	14.9	7.7-24.5	14.7	10-17	
Imbalance (trend)	3.9	3.1-4.7			3.9	3.1-4.7	3.8
Total sink Stratospheric	12.3	9-16			12.3	9-16	12.6
Implied total source	16.2				16.2		16.4

[a] Second IPCC Assessment Report (Houghton *et al.*, 1996)

[b] Third IPCC Assessment Report (Parther *et al.*, 2001)

[c] IPCC Special Report on emissions scenarios (Nakicenovic *et al.*, 2000)

The third indirect N_2O source is that from rivers and estuaries following the discharge of sewage. N_2O emissions following land application of sewage are included in the direct emissions, while N_2O emissions directly from sewage treatment plants are assumed to be negligible. The 1996 IPCC default value for sewage discharge to rivers and estuaries is 1%; this is very uncertain and needs further investigation (de Klein *et al.,* 2001).

1.8.2 Direct emissions

Soil emissions of N_2O from nitrification and denitrification are thought to compose the largest global source of N_2O with the contribution from agricultural systems accounting for a quarter of all global emissions (Mosier *et al.,* 1998a). Both nitrification and denitrification in soils produce N_2O and these emissions are strongly dependent on vegetation type and land management. The highest N_2O production during nitrification and denitrification has been reported for fertilised *Lolium perenne* dominated grassland in moist temperate environments (Christensen, 1983 and Clayton *et al.,* 1997). Particularly large emissions of N_2O have been reported from tropical soils (Matson *et al.*, 1990; Bouwman *et al.* 1993). Furthermore, conversion of tropical forests to cultivated land and pastures results in greater N_2O emissions (Matson *et al.*, 1990; Keller and Reiners, 1994). The increase in N_2O emissions from disturbed and fertilized soils systems is due to higher rates of nitrification which makes NO_3^- available to denitrifying bacteria.

The downward leaching of fertilizer nitrate also has the potential to stimulate denitrification in ground waters. Ronen *et al.* (1988), suggests that ground water may be an important source of N_2O to the atmosphere (up to 1×10^{12} g N y^{-1}). The oceans appear to be a source of N_2O to the atmosphere as a result of nitrification in the deep sea (Cohen and Gordon, 1979; Oudot *et al.,* 1990). In many areas seawater is super-saturated in N_2O with respect to the atmosphere. Specifically, the water of the northwest Indian Ocean, a local zone of upwelling, may account for 20% of the total flux of N_2O from the oceans to the atmosphere (Law and Owens, 1990). Based on the belief that the N_2O super-saturation of the sea water is widespread, calculated emissions from the ocean dominated the earliest global estimates of N_2O sources (Liss and Slater, 1974). When more extensive sampling showed that the areas of super-saturation were limited, these workers substantially lowered their estimate of N_2O production in marine ecosystems (Hahn, 1981, Liss, 1983; Butler *et al*., 1989). The most extensive survey of ocean water suggests a flux of about 4 x 10^{12} g N y^{-1}, emitted as N_2O-N to the atmosphere (Nevison *et al.*, 1995). A large portion of this may derive from coastal waters (Bange *et al*., 1996).

Relatively small emissions of N_2O result from the combustion of fossil fuels or biomass (Muzio and Kramlich, 1988; Linak *et al.,* 1990; Andreae, 1991; Cofer *et al.,* 1991; Khalil and Rasmussen, 1992a; Bergers *et al.,* 1993). The annual global N_2O emission from vehicle exhausts is estimated to be about 1 - 4% of the total atmospheric N_2O (Becker *et al*., 2000). The industrial production of nylon (Thiemens and Trogler, 1991) and other chemicals result in a significant flux of N_2O to the atmosphere (1.3 x 10^{12} g N y^{-1}). Disposal of human sewage may also represent a large source of N_2O in the atmosphere (Kaplan *et al.,* 1978).

1.9 N_2O sinks

The only significant sink for N_2O is stratospheric destruction, which consumes about 12 x 10^{12} g NO_2-N per year (Minschwander *et al*., 1993). Few soils and oceans have been proposed as N_2O sinks (Ryden, 1981; Cicerone, 1989; Donoso *et al.,* 1993), but the global sink in soil is unknown and probably very small (Blackmer and Bremner, 1976; Conrad, 1994). Moreover, oceans and coastal waters are largely in equilibrium with the atmosphere or supersaturated with N_2O (Bange *et al.,* 1996), so that a sink- if it exists- is likely to be small.

1.10 N_2O inventories

1.10.1 N_2O emissions from grassland and arable sites

Grassland is one of the major terrestrial ecosystems, covering about 25% of the global terrestrial area (Tieszen and Delting, 1983). Nitrogen losses in air (Freibauer and

Kaltschmitt, 2000) and to ground water by leaching are higher in intensively managed grasslands than in arable crops (Hack-ten Broeke, *et al.*, 1999). The emission of N_2O from grazed pasture contributes about 30% of the total global warming potential (Denmead *et al.,* 2000). This is due to nitrogen provided by fertilizers, fixed by legumes and voided by animals. Mosier *et al.* (1998) studied the effect of long-term and short-term N fertilization on a Colorado short grass steppe where it was found that N fertilizer enhanced N_2O emissions as much as 14 years after fertilization stopped. Such results imply that fertilizer stimulates N_2O emissions at a rate of 0.5% g N_2O-N g^{-1}N fertilizer (see section 1.5).

1.10.2 N_2O emissions from animal manures

Animal excreta deposited on pasture during grazing and application of manure or slurry by farmers represents a major source of N_2O emissions. Urine patches contain extremely high but localized concentrations of plant available N. These concentrations greatly exceed the uptake capacity of the grass, therefore urine patches are especially susceptible to ammonia volatilization, denitrification and leaching (Whitehead, 1995). According to the New Zealand Climate Change Office (2003), over 80% of direct and indirect N_2O emissions in New Zealand are due to depositions of animal excreta during grazing. These N_2O emissions from animal excreta largely occur from cattle urine patches deposited under wet soil conditions in autumn and winter (Ledgard *et al.*, 1996; de Klein, *et al.*, 2003, 2004). The strategic use of a feed pad on dairy farms could restrict the amount of excreta N returned to pasture during this time of the year, and thus reduce N_2O emissions and other environmental losses (de Klein *et al.*, 2005).

The IPCC (1996) estimated N_2O emissions from pasture and animal grazing as 28% of global anthropogenic N_2O emissions. High emissions of N_2O have been obtained from pig manure which contains a much higher total N than cattle manure (Petersen *et al.*, 1998). Moreover, dairy farming is the largest source of N_2O and CH_4 emissions and therefore has a large potential for the production of greenhouse gases (Gugele *et al.*, 2002). In The Netherlands, dairy farming contributes to 55% of the N losses (Van

Bruchem, 1999) hence, burning of animal wastes (Van der Hoek, 2001) and application of animal manure (Berges and Crutzen, 1996) increase the emissions of N containing compounds.

Organic and mineral fertilizers are the key variables in regulating trace gas emissions from soils (IPCC, 1996; Mosier *et al.*, 1998; Dobbie and Smith, 2003). In a study from four European countries (Denmark, Finland, Italy and UK), emissions of N_2O from organic crop rotation, in which only manure was used as N fertilizer, were significantly lower compared with N_2O emissions from conventional rotation where manure was mixed with fertilizer (Petersen *et al.*, 2005).

1.10.3 N_2O emissions from leguminous crops

Legumes can have both direct and indirect effect on N_2O emissions. The indirect effect is by increasing the amount of N cycling through the plant-soil system, which can be nitrified or denitrified to N_2O in the same way as fertilizer N. Emissions of N_2O from biologically fixed N is probably less than from fertilizer N (Velthof *et al.*, 1998). Legumes can increase N_2O emissions by a factor of 2 or 3 (Duxbury *et al.*, 1982). Globally, estimated N_2O emissions from fields of cultivated leguminous crops are in the range of 23 to 315 Gg N_2O-N y^{-1} (Eichner, 1990).

Legume crops could have a direct effect on N_2O emission if they provide significant rhizobial denitrification (Steele, 1983). However a recent study considered N_2O emission directly from rhizobial denitrification to be slightly greater than the background emission from agricultural crops and much lower than those predicted by using 1996 IPCC methodology (Rochette and Janzen, 2005).

Table 1.4: Annual N_2O emissions from pastoral and arable land (adapted from de Klein, et al., 2001)

System	Soil type	N input ($kgNha^{-1}y^{-1}$)	Emission[a] Factor	Reference
Pasture				
Ryegrass pasture	Sandy loam	350 (4 x 87.5)	0.7	Kaiser *et al.*, 1998
Ryegrass pasture	Sandy loam	340 (4 x 85)	0.5	Kaiser *et al.*, 1998
Grass/clover Spray irrigated	Sandy loam	400 (2x200)	0.7	Khan, 1999
Grass/clover Flood irrigated	Sandy loam	400 (2x200)	1.0	Khan, 1999
Grassland	Sandy loam	78 (2x39)	1.9	Mogge *et al.*, 1999
grass/clover pasture (grazed)	Coarse silt	250 + 60	1.3	Williams *et al.*, 1999
Grass	Peat soil	120-200	2.8-8.3	Regina *et al.*, 2004
Ryegrass	Clay loam	303-493	0.7-4.9	Hyde *et al.*, 2005
Arable				
Wheat		100	0.49	Smith *et al.*, 1998
Spring barley	Sandy caly loam	120	0.17	Smith *et al.*, 1998
Winter wheat		180	0.67	Smith *et al.*, 1998
Potatoes		140	0.86	Smith *et al.*, 1998
Potatoes	Loam	170	1.8	Smith *et al.*, 1998
Wheat	Silt loam	111	1.6	Ruser *et al.*, 2001
Potato	Silt loam	220	3.7	Ruser *et al.*, 2001
Maize	Loam	34-291	2-7	McSwiney *et al.*, 2005

[a] The Emission factor is calculated as a percentage of total N input

1.11 Main factors affecting N_2O flux from soil

All forms of nitrogen input to agricultural soils, such as mineral fertilizer, organic manures, biological nitrogen fixation, green manures or post-harvest crop residues, represent the main contributory factor to N_2O emissions. However, the amount of N_2O released to the atmosphere also depends on a complex interaction between soil properties, climatic factors and agricultural practices, the main soil factors being NH_4^+ and NO_3^- concentration (Ball *et al.,* 1997; Castaldi and Smith, 1998; Senevirante and Van Holm, 1998), soil aeration status and soil water content (Carran *et al.,* 1995; Teira-Esmatges *et al.,* 1998 and MacKenzie *et al.,* 1998), microbial activity (Ineson *et al.,* 1998; Kaiser *et al.,* 1998) and finally, soil pH and soil temperature (Mahmood *et al.,* 1998). Due to the complexity of interactions, one single factor may not always correlate with N_2O flux.

1.11.1 Nitrogen fertilizer

To meet the needs of human dietary requirements, the use of synthetic nitrogen fertilizers in agriculture has increased worldwide (Howarth *et al*., 2002). N fertilizer has a direct influence on N_2O production by provision of N for both nitrification and denitrification (Baggs *et al*., 2004). In a study by Flessa *et al.* (2002) the mean background N_2O-N emission from sites with no N input was 0.5 kg ha^{-1} y^{-1} while, the annual N_2O-N emissions from fertilized soils ranged from 1.3 to 16.8 kg $ha^{-1}y^{-1}$. Dobbie *et al.* (1999) summarized data on N_2O emissions from fertilized soil in Scotland and concluded that the emission factor for grassland and potato crops may be higher than the IPCC default value of 1.25%, depending on the distribution and total amount of precipitation. Moreover, in a German field experiment, Kaiser *et al.* (1998) found that relative N_2O emission from applied N fertilizer ranged between 0.7 and 4.1%. But MacKenzie *et al.* (1998) suggested in Quebec, Canada, that about 1.0 - 1.6% of the added N under maize was emitted as N_2O. However, to have an accurate N_2O predictor from fertilized fields, Kaiser and Ruser (2000) proposed long-term nitrogen in/out balance (see section 1.5).

1.11.2 Soil moisture

Soil moisture affects the N_2O emission rate by reducing the volume of gas in the soil, restricting O_2 supply and by dissolving the applied fertilizer. The moisture and aeration status of a soil is closely related to its physical properties, as determined mainly by soil texture, mineralogy, stoniness, organic matter content and structure and by rainfall/irrigation regime and the crop or vegetation cover. Plants consume oxygen by root respiration and use water thereby decreasing the amount of water held in the pore spaces. Fluctuations in the water filled pore space in turn influence the rate of N_2O diffusion in the soil, the amount of N_2O dissolved in the soil water, the rate of N_2O production by soil micro-organisms, the rate of reduction of N_2O to N_2 by soil micro-organisms and the amplitude in the diurnal change in temperature that occurs at any given depth in the soil (Blackmer *et al.*, 1982). Hence, soil moisture content may influence the rate of N_2O emissions (Choudhary *et al.,* 2002). The lowest emissions occur when soil moisture content is low during the summer period. This strong correlation between N_2O emissions and soil moisture content (SMC) suggests that the high rainfall in winter and early spring together with soil properties, such as drainage characteristics are important in the assessment of N_2O emission (Choudhary *et al.,* 2002). On grassland, rainfall, particularly around the time of N application was the main driving factor for N_2O during the growing season (Dobbie and Smith, 2003). According to Vinther (1984) and Rudaz *et al.* (1999), seasonal changes in soil moisture have strong influences on the N_2/N_2O ratio. Furthermore, McSwiney and Robertson (2005) found that for a continuous maize cropping system, soil water content and soil N availability were co-required for high N_2O emissions. Similar results have been demonstrated earlier in forest and grassland systems (Abassi and Adams, 2000; Maddok *et al.,* 2001; Ball *et al.,* 2002; Maljanen *et al.,* 2002).

Soil moisture primarily and positively regulates the spatial and seasonal variability of N_2O emissions (Wang *et al.*, 2005). In an experiment by Dobbie and Smith (2001), the relationship between N_2O emissions and water filled pore space (WFPS) was highly significant. The flux from arable soil was 30 times greater at 80% WFPS than at 60%, while the corresponding flux from the grassland soil was about 12 times greater than its counterpart at 60% WFPS. Similar results were found by Keller and Reiners (1994), where N_2O emissions increased logarithmically between 52 and 85% WFPS. As WFPS increases, diffusion of oxygen into soil aggregates will decrease causing an increase in N_2O production by denitrification (Dobbie and Smith, 2001).

Water stimulates denitrification by temporarily reducing the oxygen diffusion into the soil as well as by increasing the solubility of organic carbon and nitrate (Bowden and Bormann, 1986). Prolonged waterlogging can limit denitrification if it also restricts nitrification which produces nitrate for denitrification. Later studies, both in the tropics (Veldkamp *et al.,* 1998) and in temperate climates (Dobbie *et al.,* 1999) suggest that maximum N_2O emissions occur at WFPS of 80 - 85%. Further support for the importance of this higher range comes from the work of Ruser *et al.* (1998), which indicated that the highest fluxes were induced by the loss of macro-pores due to compaction, which increased WPFS to a mean value of 85%. This suggests that a much wetter and greater degree of anaerobicity is required to produce maximum N_2O emissions.

1.11.3 Soil temperature

Temperature affects N_2O emissions by either increasing the emission rate of microbial activity, (for which the Q_{10} is the way of quantifying the increase), or due to freeze/thawing events. Rates of nitrification and denitrification increase with increasing temperature, hence, microbial activity is highly temperature dependent (Addiscott, 1983; Scott *et al.*, 1986). The difference in N_2O emissions from winter to summer indicates that temperature is a controlling variable. During winter N_2O emissions are positively correlated with temperature. Direct linear relationships between N_2O emission and seasonal and diurnal temperature changes have been shown for many soils in temperate climates (Addiscott, 1983; Scott *et al.,* 1986). According to Flessa *et al.* (2002) 89% of diurnal variability in N_2O emissions release from decomposing grass mulch could be explained by changes in temperature. The diurnal pattern in N_2O production from arable soils was studied by Skiba *et al.* (1996), using micrometeorological techniques. The N_2O emission was found to be strongly temperature dependent with the best predictor being soil temperature at 12 cm depth. Whereas, Christensen (1983) observed a diurnal pattern in N_2O production from grassland soils treated with slurry and ammonium nitrate fertilizer, with strong correlation between N_2O emission and temperature at 2.5-5 cm. Furthermore, Baggs *et al.* (2001) reported that the strong relationship between topsoil temperature and N_2O emissions suggests that most of this gas was released from the top 5 cm of soil.

Brams *et al.* (1990) observed that warmer soil temperatures were not sufficient to enhance the emission of N_2O, but were necessary to allow the soil microbial population to respond to other perturbations such as fertilization or rainfall, and particularly a combination of the two. In agricultural soils in Scotland, it has been shown that if soil WFPS or mineral N content are limiting, there may not be a clear relationship with temperature. However, when only those data points where the other factors are non-limiting are considered, there is evidence of a very steep response to temperature, with Q_{10} values of up to 8 (Dobbie *et al.,* 1999). In tropical natural soils, where seasonal variations in temperature are much smaller, evidence of diurnal variations is mixed. For example, in the close canopy of a Terra Firme forest in Brazil, no diurnal variations in N_2O emissions were observed (Matson *et al.,* 1990), but in a semi-deciduous forest in Venezuela daytime fluxes were typically 50% larger than night time fluxes. However, in a nearby savannah diurnal temperature changes did not affect N_2O emissions (Sanhueza *et al.,* 1990). Moreover, the N_2/N_2O ratio was also found to increase with soil temperature (Bailey, 1976; McKeeney *et al.,* 1979).

On the other hand high winter N_2O emissions were observed during soil freezing/ thawing phenomena such as physical disruption of soil organic matter, release of readily degradable carbon compounds from dead soil microbes (Christensen and Tiedje, 1990) or due to the increase of N_2O/N ratio (Van Bochove et al., 2000).

1.11.4 Crop residue

Incorporation of crop residues and other organic materials into soils is one of the most important agricultural practices that can affect N_2O emissions through changing of C/N ratio. The flux depends on the amount of amendment introduced and its chemical composition (Reinertsen *et al.,* 1984; Aulakh *et al.,* 1991), the increase in respiration induced, and soil factors such as water content, temperature and aeration (Scott *et al.,* 1986). This was also observed by Baggs *et al.* (2000), who found that higher N_2O was emitted followig incorporation of residues with low C/N ratios, such as those of legumes or horticultural crops, than after cereal straw incorporation. In earlier experiment carried by Aulakh *et al.* (1984), the incorporation of wheat straw residues doubled gaseous N losses over a growing season (9 kg N_2O-N ha^{-1} y^{-1}) compared to those from bare soil. Emissions after rotary tillage of lettuce residues were greater than after rotary tillage of bare soil. Most of this N_2O was emitted during the first two weeks after incorporation. This is probably a reflection of rapid microbial decomposition (Shen, *et al.,* 1989), possible creation of anaerobic micro-sites resulting from microbial respiration and placement of residues (Tiedje *et al.,* 1984; Thomson *et al.,* 1997) and the increased C supply and substrate for nitrification and denitrification (De Catanzaro and Beauchamp, 1985).

Stimulation of denitrification N_2 and N_2O production under anaerobic conditions by wheat straw and other organic materials has been reported (McKenny *et al.,* 1993; Ragab *et al.,* 1994; Avalakki *et al.,* 1995; Lessard *et al.,* 1996). Nitrous oxide produced near the surface would probably diffuse out of the soil in the atmosphere, whereas N_2O produced after deeper cultivations may take longer to diffuse from the soil providing more opportunity for reduction to N_2 before reaching the atmosphere (Arah *et al.,* 1991). The method of incorporation affected the magnitude and pattern of N_2O emissions, presumably by varying the supply of organic C and N to microorganisms, and changing the soil moisture/aeration status around the incorporated material (Aulakh *et al.,* 1991).

There is evidence that increasing C availability decreases the N_2O fraction (Firestone, 1982). Since organic matter in soils is represented by plant debris, crop species have a significant influence on N_2O emissions (Kaiser *et al.,* 1998). This was also observed by Drury *et al.* (1991), who found that concentrations of biomass carbon (C) and organic carbon in the soil are highly correlated with denitrification activity. According to Choudhary *et al.* (2001) total N_2O emission during the winter increased with the decreasing dry matter-to-N-content ratio of plant residues incorporated into the soil by ploughing.

1.11.5 Soil ploughing

Soil ploughing changes soil organic matter and soil aeration and consequently affect N_2O emissions. No-Tillage (NT) farming has been promoted as an agricultural practice that is reducing soil erosion and enhancing agricultural sustainability concomitant with mitigating greenhouse gas emissions (Cole *et al.*, 1997; Paustian *et al.*, 1997; Schilesinger, 1999). However, longer term (> 10 years) of NT adoption is required before it can be suggested as a mitigation strategy appropriate for the three major biogenic GHGs (CO_2, N_2O and CH_4). True mitigation is only possible if the overall impact of NT reduces the total net global warming potential for these greenhouse gases (Six *et al.*, 2004).

Ploughing increases the rate of N_2O production from nitrification, denitrification and total denitrification (Estavillo *et al.,* 2002). Here it has been noted that soil nitrate content of unfertilised plots may be higher in the ploughed treatments than the unploughed treatments at all depths. That suggests that ploughing may promote soil organic N mineralization. Estavillo *et al.* (2002), reported that soil ammonium content was at a low and similar value in all treatments as a result of highly efficient nitrification which converted ammonium to nitrate however, the highest N_2O production rates were obtained from ploughed treatments, which had been fertilized. On the contrary Colbourn, (1988) reported that denitrification in an undrained ploughed soil was one-fifth of that in a drained, direct-drilled soil. Hence, tillage restricted denitrification to a greater extent than did drainage. The explanation given was that lack of disturbance in the reduced tillage soil led to a reduction in large pores, an increase in soil aggregation and a reduction in soil aeration, therefore producing higher rates of denitrification.

Intensive tillage practices impact the nitrogen cycle through loss of organic matter and deterioration of soil structure, which could influence the extent of N_2O emissions (Saggar *et al.,* 2001; Shepherd *et al.,* 2001). It is known that soil disturbance through cultivation decreases N_2O fluxes due to better aeration, while the amount of fertilizer applied into cultivated soil increase the potential emissions of N_2O (Shepherd, 1992). Mosier *et al.*

(1997) found that changing cultivated soils back to grasslands eventually (8 - 50 years) led to N_2O emissions similar to those of native soils of the same texture and parent material. Moreover, the conservation practices, aimed at reducing harmful effects of extensive conventional practices, contributed to N_2O emissions through improved soil conditions. Hence increasing soil organic content favours emission of N_2O (Mosier *et al.,* 1997).

Soil compaction also increases N_2O emissions by increasing the WFPS and increasing the likelihood of anaerobic soil conditions and denitrification, which are particular problems in moist, temperate climates (Douglas and Crawford, 1993; Hansen *et al.,* 1993). Soil physical conditions, particularly near the surface, are also important mainly through their influence on soil aeration (Arah *et al.,* 1991). Avoiding soil compaction and improving soil structure can reduce nitrous oxide emissions (Beauchamp, 1997). A complex interaction between WFPS and soil compaction influences microbial activity and nitrogen losses by denitrification (Torbert and Wood, 1992).

The compaction of wet soil by tractor traffic increases nitrogen loss by denitrification 3 - 4 fold and may decrease crop yield by 25% (Bakken *et al.*, 1987). Hence, stimulation of N_2O emissions by compaction is associated with adverse soil physical conditions and corresponds with adverse conditions for crop growth (Ball and Ritchie, 1999). Here the restricted crop growth increases the emissions by reducing uptake of available nitrogen and water (Bakken *et al.*, 1987). However loosening of a heavily compacted soil improves crop growth and soil aeration and may not consistently lead to a lowering in cumulative emissions (Ball and Ritchie 1999).

1.11.6 Soil pH

Soil pH influences N_2O emissions by affecting nitrification and denitrification processes. It has been called the master variable of the soil, since it influences many physical, chemical and biological properties and processes in soil (Brady and Weil, 1999). It therefore has a clear influence on denitrification rate and the distribution of gaseous end products. According to Bouwman (1990), soil pH influences both nitrification and denitrification rates as well as the N_2/N_2O ratio. Knowles (1981) found that the optimal pH range for denitrification is 7 - 8. With a further drop of pH below 6 the rate of denitrification tends to decrease (Eaton and Patriquin, 1989). However, at pH above 7, N_2 is a much more important denitrification product than nitrous oxide (Simek *et al.*, 2002).

N_2O may be the dominant gas evolved in acid infertile forest soils (Mellilo *et al.*, 1983; Eaton and Patriquin, 1989). This could be due to the great sensitivity of the nitrous oxide reductase enzyme to low pH or proton activity (Knowles, 1982). In another study by Simek *et al.* (2002), acid soil gave the highest potential for denitrification. They concluded that if short-term determination of denitrification is performed, the largest denitrifying enzyme activity will be found at or near natural soil pH. Furthermore, Goodroad and Keeney (1984a) reported that nitrification increase with increase in soil pH over the range 4.7 - 6.7, when temperature ranged from 10 to 30°C and water content from 10 to 30%.

1.12 Modelling N_2O

Different modelling approaches of varying complexity are used to predict N_2O emissions. At the complex end are the mechanistic models that consider all the proximal factors acting on N_2O production processes. Models of medium complexity have been developed with the objective of simulating the terrestrial ecosystem carbon and nitrogen biochemistry like DNDC (DeNitrification DeComposition), CENTURY, ExpertN and NASA-Ames model. These models include similar components (soil physics, decomposition, plant growth and N transformations), but in some cases use different algorithms for these processes. The simulated N_2O fluxes using these models were within a factor of 2 of the observed annual fluxes, but even when models produced similar N_2O fluxes they often produced very different estimate of gaseous N loss as nitric oxide (NO), dinitrogen (N_2) and ammonia (NH_3) (Frolking *et al.*, 1998). Here application of the model is hampered by the nature and the amount of input data required. At the simple end of the model-complexity spectrum are the highly empirical N_2O flux models based on statistical analysis e.g Conen et al. (2000); Freibauer and Kaltschmitt, (2003); Roenaldt et al. (2005).

The DNDC model (Li *et al.*, 1992) is a process oriented simulation model of C and N biochemistry in agricultural ecosystems, developed to assess N_2O, NO, N_2, NH_3 and CO_2 emissions from agricultural soils. The model has reasonable data requirement and is suitable for simulation at appropriate temporal and spatial scales. The rainfall driven process-based model DNDC (Li *et al.*, 1992) was originally written for USA conditions. It has been used for simulation at a regional scale for the United States (Li *et al.*, 1996) and China (Li *et al.*, 2001).

The DNDC model contains 4 main sub-models (Li *et al.*, 1992; Li, 2000):

The soil climate sub-model calculates hourly and daily soil temperature and moisture fluxes in one dimension. The soil is divided into different horizontal layers, water fluxes and heat flows between which are determined by soil texture and the gradients of soil moisture potential (for water fluxes) and soil temperature (for heat flows).

The crop growth sub-model simulates crop biomass accumulation and partitioning based on thermal degree-days and daily N and water uptake. If N or water stress occurs, crop growth will be depressed. The decomposition sub-model calculates the decomposition, nitrification, NH_3 volatilisation and CO_2 production on a daily time-step. Decomposition can occur in 3 decomposition pools: decomposable residue, microbial biomass and humads, each of which has labile and resistant components. The effect of soil properties such as soil temperature, clay fraction and water content is modelled using reduction factors that constrain decomposition rate from the maximum in non-optimum conditions.

The denitrification sub-model tracks the sequential biochemical reduction from nitrate (NO_3) to NO_2^-, NO, N_2O and N_2 based on soil redox potential and dissolved organic carbon (DOC) concentration. Soil factor such as pH and temperature are taken into account. The growth and death of denitrifier populations are simulated, which enable consumption of C, NO_3^-, NO_2^-, NO and N_2O. A comparison between estimated N_2O fluxes using the DNDC-model and measured values is shown in table 1.5.

1.13 Mitigation options

Nitrous oxide release from nitrification and denitrification are closely linked to other N transformations and loss processes, such as nitrate leaching and ammonia volatilisation (Whitehead, 1995). As a result, management options to reduce one loss process could potentially enhance other environmental problems (de Klein *et al.,* 2001). Moreover, options that may reduce direct emissions of N_2O, but potentially increase nitrate leaching or ammonia volatilisation, could also enhance the indirect emissions of N_2O. Therefore, mitigation option for reducing N_2O emissions should consider the nitrogen cycle of agricultural systems as whole, and aim to increase the N efficiency of these systems (Jarvis *et al.,* 1996).

Several options are available for reducing N_2O emissions from agriculture. Direct soil emissions can be mitigated by *reducing N input* to the soils, e.g. by a more efficient use of N in agriculture (Hendriks *et al.,* 1998; Mosier *et al.,* 1998a). *Replacing synthetic fertilizer by manure* can reduce N_2O emissions, but efficient use of manure is required (Hendriks *et al.,* 1998). *Low nitrogen feed* assumes changes in the composition of feed such that the N content decreases. This reduces N excreted emissions of N_2O (Brink, 2000). *Restrictions on the timing of fertilizer application* will reduce N_2O from soil as well as from nitrogen leaching and maximize N uptake by plants (IPCC, 2001a; Cole *et al.,* 1997). This option requires longer manure storage and greater capacities (AEA Technology Environment, 1998b). *Restricting grazing* in dairy farming systems reduced N_2O emissions (Velthof *et al.,* 1998). This was also noted by de Klein *et al.* (2006) in grazed pasture field, in New Zealand, who found that restrictions of an autumn grazing reduced direct and indirect on-farm N_2O emissions by 7 - 11% (de Klein *et al*., 2005). Fertilizer type has been considered as an option for mitigation of N_2O emissions, especially the use of slow-release fertilizers (Mosier *et al*., 1994). They suggested that the controlled supply of substrate provided for denitrifiers by slow-release fertilizers could substantially limit N_2O emissions. Furthermore, management practices like adoption of no-tillage practices generally increase N_2O emissions compared with conventional tillage, particularly in relatively dry areas (Mummey *et al.,* 1998). The same results were found by Baggs *et al.* (2003) who suggested that emissions of N_2O were 2 to 7 times higher from fertilized zero-till treatments than from fertilized conventional-till treatments.

The use of *advanced fertilisation techniques* like using a nitrification inhibitor, placing fertilizer below ground, using foliar feed fertilizers or matching fertilizer type to seasonal conditions, can play a great role in reducing N_2O emissions (de Klein *et al.,* 2001). For example, Bronson *et al.* (1992) noted that the addition of nitrapyrin to urea fertilizer reduced cumulative N_2O losses from irrigated cornfields by about 50%. An alternative approach to mitigating N_2O emissions is to manipulate the end product of denitrification. The two main end products of denitrification are N_2O and N_2 (de Klein *et al.,* 2001). Therefore enhancing the conversion of N_2O to N_2 can reduce N_2O emissions. However, the ratio at which N_2O and N are produced during denitrification is very variable and depends on numerous soil and environmental factors. This hampers the development of mitigation options to reduce N_2O/N_2 ratio. Results from recent studies on the effects of soil pH on N_2O emissions found strong relative relationship between soil pH and the N_2O/N_2 ratio, and suggested that maintaining the soil pH at about 6.5 might help maintain a low mole fraction from denitrification (Wang and Rees, 1996; Ellis *et al.,* 1997; Yamulki and Jarvis, 1997; Stevens *et al.,* 1998a; Van der Weerden *et al.,* 1999).

Table 1.5: Comparisons between published N_2O emission data with DNDC model results for grass and arable land Adapted from De Vries et al. (2005).

Land use	Crop	Location	N_2O flux (kg N_2O-N ha^{-1} y^{-1})		Relative Difference (%)
			Measured	Modelled	
Grassland	Short grass prairie	Colorado, USA	0.14	0.25	79
	Grassland	Inner Mongolia, China	0.21-0.61	0.12 - 0.28	(-43) - (-54)
	Grassland	Berkshire, UK	2.92	3.80	30
	Pasture	Devon, UK	1.4-3.9	0.6 - 2.4	(-57) - (-38)
	Pasture, grazed	New Zealand	11	12	9
	Pasture, un-grazed	New Zealand	1.8	2	11
	Grassland	Cork, Ireland	11.6	15.4	33
Arable land	Wheat	Wu county, China	2.04 0.54	1.96 1.19	-4 120
	Maize	La selva, Cota Rica	3.85 1.11	3.42 1.14	-11 3
	Wheat	Ontario, canada	1.6	1.3	-19
	Onion	Mikasa, Japan	7.99	7.89	-1
	Carrot	Tsukuba, Japan	0.17	3.14	1747
	Single rice	Fengqiu, China	1.69	0.53	-69
	Summer rice, winter wheat	Nanjing, China	0.62	5.70	819
	Barley	Scheiern, Germany	4.2	5.7	36
	Potato-Maize, Organic soil	Scheiern, Germany	16	130	713

References: Li *et al.* (1992b); Li, (2000); Stange *et al.* (2000); Smith *et al.* (2002); Cai *et al.* (2003); Xu-Ri *et al.* (2003); Hsieh *et al.* (2005); Li *et al.* (2005); Velthof *et al.* (1996); Kammann *et al.* (1998); Kaiser *et al.* (1998); Anger *et al.* (2003) ; Hyde *et al.* (2005).

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Chapter 2: Emissions of N_2O from a cut and grazed pasture

2.1 Introduction

The majority of emissions of N_2O to the atmosphere arise from agricultural land, particularly grazed pastures. This is due to nitrogen provided by fertilizers, fixed by legumes and voided by animals. Globally emissions of N_2O from such grasslands contribute approximately 30% of the total global warming potential of the atmosphere (Denmead *et al.,* 2000).

In Europe grasslands are the major contributor to the exchange of greenhouse gases in the biosphere, with fluxes intimately linked to management practices. Here about 40% of the agricultural area is covered by permanent grassland used for livestock farming (FAO, 2004). The grasslands range from intensively fertilized pure grass swards to extensively managed grass-legume mixtures and semi-natural grasslands, which are often found in mountainous areas or on moist lowland soils (FAO, 2004).

In Ireland, agricultural land is dominated by grassland. The total land area of Ireland is 6.9 million hectares, of which 4.4 million hectares is used for agriculture, 4 million hectares of which is grassland (Teagasc, 2006; CSO Census of Agriculture, 2002). In 2000 the total area of grazed pasture (*Lolium/Trifolium* mixed sward) in Ireland was calculated as 2.2 million hectares, the total area of silage (*Lolium/Trifolium*) as 1.1 million hectares, hay meadows as 0.2 million hectares and rough grazing approximately 0.5 million hectares (Meade and Mullins, 2005). Therefore 80% of agricultural land is devoted to silage, hay and pasture, 11% to rough grazing, and 9% to crop production.

In 2004, the latest data published by the EPA, the Irish agricultural sector accounted for 20,000 kilotonnes of CO_2 equivalents, or 29% of total greenhouse gas emissions. Only greenhouse gas emissions from the combined energy industry in Ireland were comparable, calculated at 16,000 kilotonnes of CO_2 equivalents. However, few if any direct measurements of greenhouse gas emissions from the Irish agricultural sector are available. Instead the EPA use default values provided by the IPCC. In the case of nitrous oxide an emission factor of 1.25% is used. Here the total amount of fertilizer spread on agricultural land is calculated, 1.25% of which will be converted into nitrous oxide by soil micro flora. This emission factor is based upon a study by Bouwman, (1996) where data from 20 separate studies was used to calculate the emission factor of 1.25 ± 1%. Further refinements are possible given the uncertainty. In a follow-up study of 846 published measurements of N_2O flux from agricultural soils, Bouwman *et al.* (2002) assessed the influence of a number of factors on N_2O emissions. Whilst N-fertilizer application was still the dominant influence, the type of fertilizer used, the target crop, soil texture, drainage, pH and organic carbon content were also significant determinants. Ideally, recalculation of emission factors on a national scale should reflect the influence of such variables, particularly variations that exist between different land use or management schemes.

Results presented in this Chapter concern the measurement of N_2O from a cut and grazed *Lolium/Trifolium* pasture. The aim of this measurement program was to calculate a site specific emission factor and to calculate the total annual flux of N_2O from the soil. In addition measurements of soil temperature, moisture, soil nitrate, ammonium and total nitrogen were also taken, the aim of which being to determine the major influences on N_2O flux.

2.2 Materials and Methods

2.2.1 Experimental site

Two years of measurements of N_2O emissions were collected from a cut and grazed pasture at the Oak Park Research Centre, Carlow, Ireland. In the first year measurements were taken from October 2003 to November 2004, whereas in the second year measurements were taken from March 2005 - August 2005. The site had an elevation of 56m, a mean annual rainfall of 824 mm and a mean annual air temperature of 9.4° C. The soil is classified as sandy clay loam with a pH of 7.3 and a mean organic carbon and nitrogen content at 10cm of 44.1 and 4.4 g kg^{-1} dry soil respectively. The cut and grazed pasture has been permanent grassland for the past eighty years and was ploughed and reseeded in October 2001 with perennial ryegrass (*Lolium perenne* L., cv Cashel) at a density of 13.5 kg ha^{-1} and white clover (*Trifolium repens* L., cv Aran) at a density of 3.4 kg ha^{-1} (Figure 2.1).

Silage cutting for the pasture took place once in the first year, on the 15th of May 2004, and twice in the second year, on the 16th of May and 11th of July 2005. In the first year, nitrogen fertilizer was applied at a total rate of 200 kg N ha^{-1} y^{-1} divided in to two applications of 128 and 72 kg N ha^{-1} on the 2nd of April and 27th of May of 2004 respectively. Nitrogen fertilization rate in the second year was increased to 240 kg N ha^{-1} y^{-1}. This fertilizer was applied in three applications: on the 16th and 29th of March, 70 kg N ha^{-1} on each date was applied, whilst on the 20th of May 100 kg N ha^{-1} was applied. Separate areas of the field were kept unfertilized as control plots. Animal grazing was from July to November 2003, and then from July to November 2004 with stocking rate of 2 cattle ha^{-1}. Animals were excluded during the experimental period of 2005.

N_2O emissions from seven replicated chambers were measured on a weekly basis using the methodology of Smith *et al.*, (1995). Chambers consisted of two parts: a 52 x 52 x 15 cm high square collar inserted permanently in the soil over which a 50 x 50 x 30 cm high lid with a plastic septum could be sealed in place for gas sample collection

(Figure 2.2). Lids were placed on the collars and left for 1h before gas sampling, with an initial gas sample taken immediately after sealing of the lids.

2.2.2 Measurement of N_2O flux

Samples were taken using a 60 ml gas-tight syringe after flushing of the syringe to ensure adequate mixing of air within the chamber. All 60 ml of the sample was then injected into a 3ml gas-tight vial with a vent needle inserted into the top, and stored until analysis (Figure 2.3). Samples were taken as far as possible at the same time of day to minimize the effects of diurnal variation. The tightness of the static chamber was tested by checking the linearity of N_2O gas flux within the chamber.

Gas samples were measured within one month of collection at the Risø Research Centre in Denmark using a gas chromatograph (Shimadzu GC 14B, Kyoto, Japan) with electron capture detection. The closed flux chamber technique equation (Smith *et al.*, 1995; Baggs *et al.*, 2003) was used for calculating the daily flux of N_2O from each chamber.

$$\text{g } N_2O\text{-N ha}^{-1}\text{d}^{-1} = \frac{\text{Vol. (ml) x ppm change } (X\text{-}X_0) \text{ x 28 (g N) x 60 (mins.) x 24 (h) x } 10^8}{\text{Area (cm}^2\text{) x time closed (mins.) x 24000 (1 mole as ml) x } 10^6}$$

Emission factors (EFs) for N fertilizer were calculated by expressing the cumulative emissions from fertilized plots minus that of the control plots as a percentage of the total N applied after being adjusted for ammonia volatilisation.

$$EF = [(\text{Cumulative flux}_{\text{(fertilizer treatment)}} - \text{Cumulative flux}_{\text{(control)}})/ (\text{fertilizer applied x } k)] \text{ x } 100$$

Where k is 0.9 for synthetic N fertilizer (IPCC, 2001b).

Nitrous oxide emissions in term of global warming potential (GWP) were calculated using the equation of Watson *et al.*, (1996), where

$$GWP = CO_2 + CH_4 * 21 + N_2O * 310$$

Figure 2.1: The grassland field showing N_2O collection chambers in position.

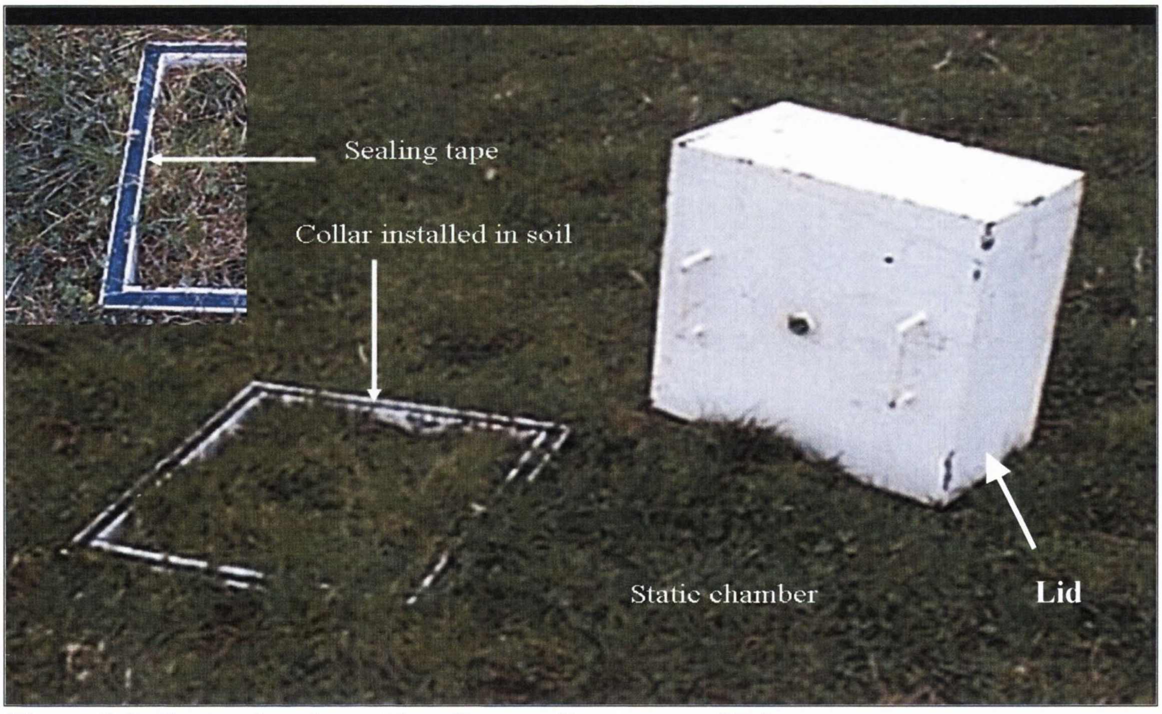

Figure 2.2: Static chamber with collar, sealing tape and lid

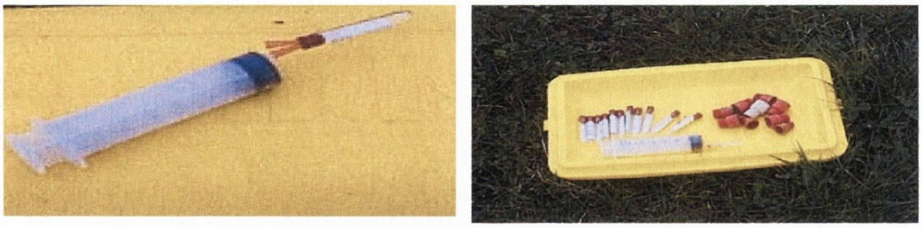

Figure 2.3: The 60 ml syringe, septum and vials used to measure N_2O flux

2.2.3 Soil temperature

Soil temperature at a depth of 10 cm was measured every half an hour by the Teagasc Research Centre weather station. Moreover, soil temperature from an area around each chamber, at the same depth was measured at each sampling occasion using a handheld digital thermometer.

2.2.4 Soil moisture and WFPS

Four soil samples were taken at a depth of 0 - 20 cm at every gas-sampling occasion. Samples were weighed, oven dried to constant mass at 105°C, and reweighed again. The dry weight and differences between fresh and dry weight were used to calculate the gravimetric soil water content (Choudhary *et al*., 2002):

$$SWC = (Dw/Sw) * 100$$

Where SWC is soil water content (%), Dw = difference between soil fresh and dry weight (g), Sw = stable soil dry weight (g).

Total porosity was calculated by: (1- (bulk density/particle size))* 100, where a fixed value of particle size of 2.65 cm^3 was used.

Volumetric soil water content was determined to calculate WFPS by dividing volumetric soil water by total porosity. Moreover, daily rainfall in (mm) was also recorded at the Teagasc Research Centre weather station

2.2.5 Nitrate and ammonium content of the soil

Four soil samples at a depth of 0 - 20 cm from the pasture field were taken every month (in the first year) and weekly after fertilizer application (in the second year). The concentration of nitrate and ammonium was measured colorimetrically using a Bran and Luebbe AutoAnalyzer (Bran and Luebbe, Norderstedt, Germany), based on the method of Armstrong *et al.*, (1976). Samples were homogenized manually and sieved through a 2 mm mesh. From each sample 20 g of fresh soil was taken and added to 100 ml of 2 M KCl and shaken for 1h on an automatic shaker. The extract was then filtered through Whatman No. 2 filter paper for the nitrate analysis, and filtered again through a cellulose acetate membrane with a pore size of 45 μm for the ammonium analysis.

2.2.6 Statistics

All statistical analyses were carried out using PRISM (GraphPad, San Diego, USA) and Data Desk (Data Description Inc. New York, USA) software packages. Flux data was checked for normal distribution and log transformed where appropriate. Both 1-way and 2-way analysis of variance were applied to the flux and soil N data, and a multiple regression carried out for N_2O flux vs soil nitrate, ammonium, moisture and soil temperature.

2.3 Results

2.3.1 Rainfall

Figure 2.4 illustrates the monthly rainfall experienced at the Teagasc Research Centre weather station in Oak Park for 2004 and 2005. This was situated approximately a quarter of a mile from the grassland field. A plot of the 30 year mean monthly rainfall is also included. What is apparent is that the 2004 and 2005 data sets differ significantly from the 30 y mean values if late winters, mid-summer and early autumn months are considered. For both years the February rainfall was approximately 30 % less than the 30 y mean value of 70 mm, whilst the October rainfall was approximately 48 % higher than the 30 y mean value of 80 mm. For 2004 August rainfall was double that of the 30 y mean value of 70 mm, as opposed to 2005 where a drought occurred over the late summer months resulting in an August rainfall of 40 mm.

2.3.2 Soil temperature

Figure 2.5 illustrates the mean monthly soil temperature measured at a depth of 10 cm at the Teagasc Research Centre weather station in Oak Park for 2004 and 2005. In March and July of 2005 the soil temperature was 2°C higher than for the same months in 2004.

2.3.3 Soil moisture and temperature at the grassland field

Figure 2.6 relates the weekly rainfall data collected at the Teagasc Research Centre weather station in Oak Park with direct measurements of soil moisture content taken from the grassland field on days that N_2O measurements were taken. As expected there is a close relationship between the two where limiting rainfall in the spring of 2004 and the summer of 2005 has resulted in a soil moisture content of 13 %, applicable to WFPS of approximately 23 %, as opposed to spring and autumn maximum soil moisture was 28 %, applicable to WFPS of 47 %. To put these values into perspective, the field capacity of the soil was measured as 43 ± 0.002 %, hence over the measuring period of 2004 to 2005, soil moisture content was reach or exceed the field capacity on few dates (Appendix 4).

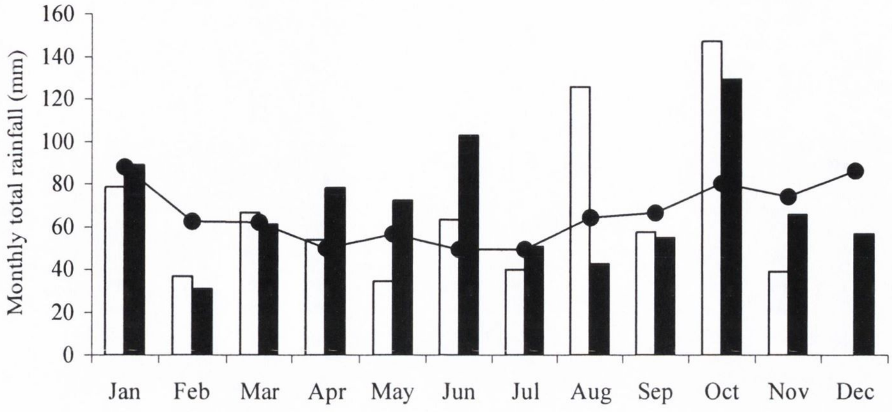

Figure 2.4: Monthly rainfalls for 2004/2005 at the Teagasc Oak Park Research Centre, Carlow. Symbols indicate rainfall in 2004 (□), 2005 (■) and the 30 year mean (●). Data kindly provided by John Hogan, Teagasc.

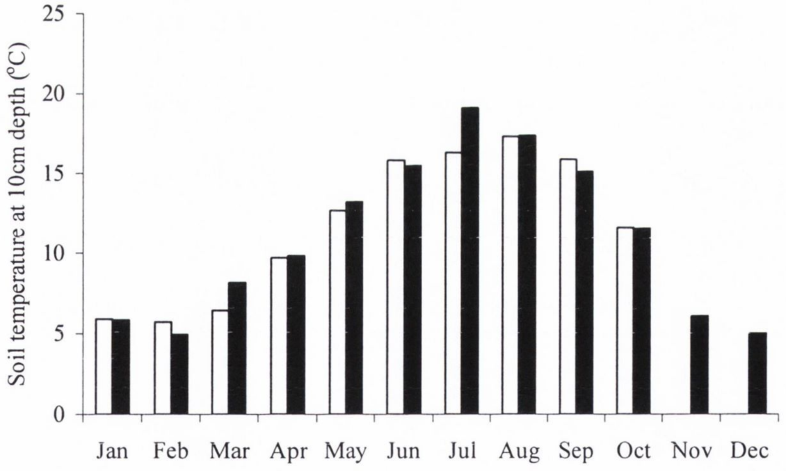

Figure 2.5: Monthly average soil temperatures for 2004/2005 at the Teagasc Oak Park Research Centre, Carlow. Symbols indicate soil temperature of 2004 (□) and 2005 (■). Data kindly provided by John Hogan, Teagasc.

Figure 2.7 compares field measurements of soil temperature made on days where N_2O sampling occurred, with the average weekly soil temperature data collected at the Oak Park Research Centre weather station. The close correlation between the two means that the continuous temperature data set from the weather station can be used to fill in missing data required for a multiple regression of N_2O flux with soil parameters.

Figure 2.8 relates field measurements of soil moisture content with field measurements of soil temperature, all values taken on days that N_2O sampling occurred over 2004 and 2005. Here a negative linear correlation between the two is observed, the equation for which accounting for 41% of the observed variation. As in the case of Figure 2.4, this correlation can therefore be used to estimate soil moisture content from the continuous data set of soil temperature.

2.3.4 Soil nitrate and ammonium content

Figures 2.9 and 2.10 illustrate the change in soil nitrate and ammonium for 2004 and 2005 in the control and fertilised plots with fertiliser application dates shown by arrows. Unfortunately in March of 2005 the control plots received the same amount of fertiliser as the fertilised plots, 140 kg N ha^{-1}. From this date however, the control plots received no extra fertiliser. Overall peak concentrations of soil ammonium were significantly higher than soil nitrate and were not related to times of fertilizer application, neither was there a marked difference between the concentration of soil ammonium recorded in the control and fertilised plots. However, in the case of soil nitrate, peak concentrations corresponded to fertilizer application with significant differences between control and fertilised plots. As such Figure 2.11 illustrates the change in the concentration of soil nitrate due to fertilizer application for 2004 where each point represents the difference between the fertilised and control plots. Here it can be seen that the applied nitrate remained in the soil for approximately six months.

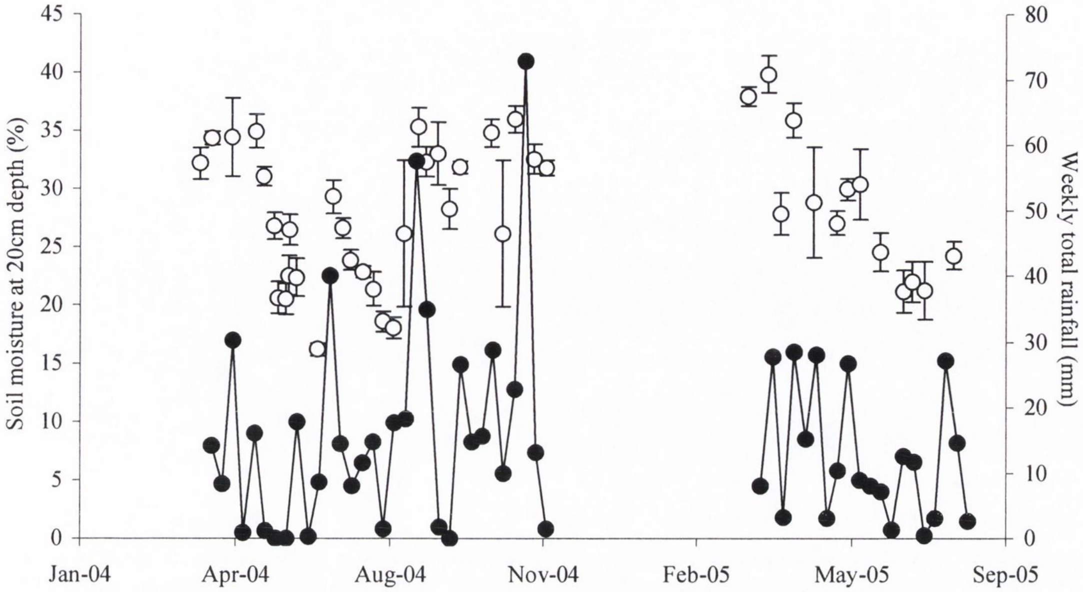

Figure 2.6: Correlation between weekly rainfall for 2004/2005 at the Teagasc Oak Park Research Centre, Carlow and soil moisture content at the grassland field. Symbols indicate weekly rainfall (•) and daily soil moisture content (○).

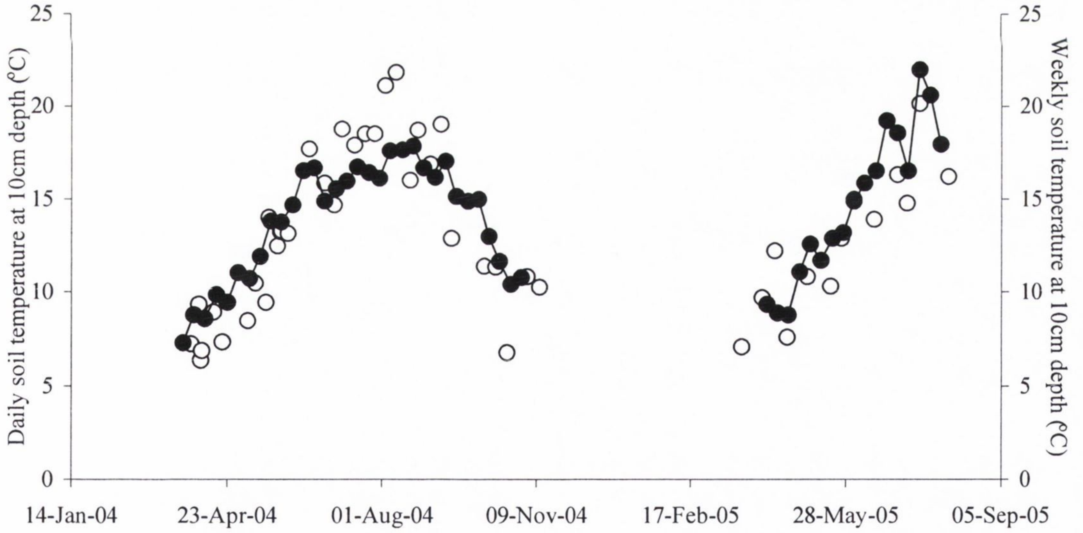

Figure 2.7: Correlation between the weekly average soil temperature for 2004/2005 at the Teagasc Oak Park Research Centre, Carlow and the daily average soil temperature measured at the grassland field. Both measurements were made at 10cm depth. Symbols indicate average weekly temperature (•) and average daily temperature (○).

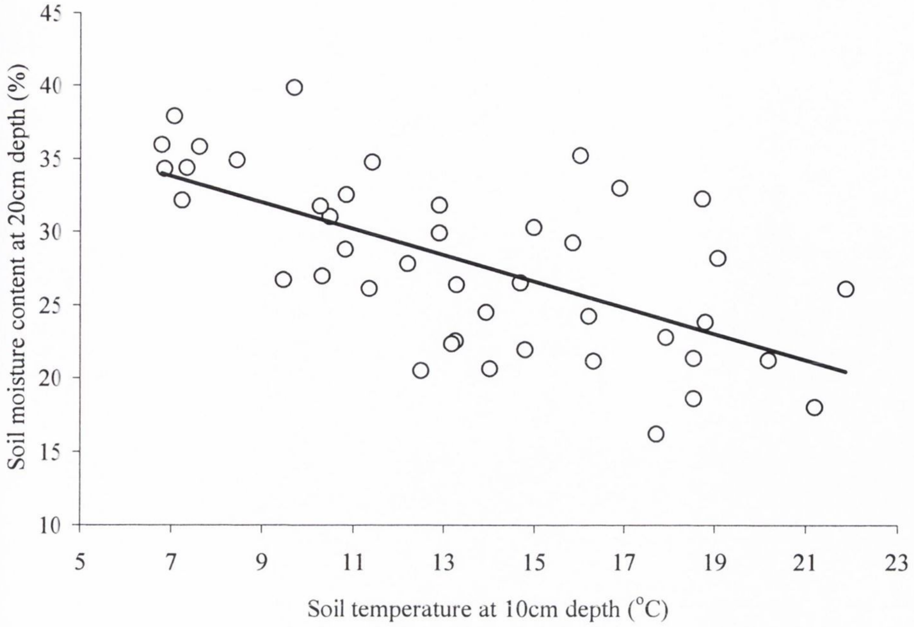

Figure 2.8: Correlation between daily average temperature at 10 cm depth and daily average soil moisture content at 20 cm depth at the grassland field. y = -0.8984x + 40.115, (R^2 = 0.41).

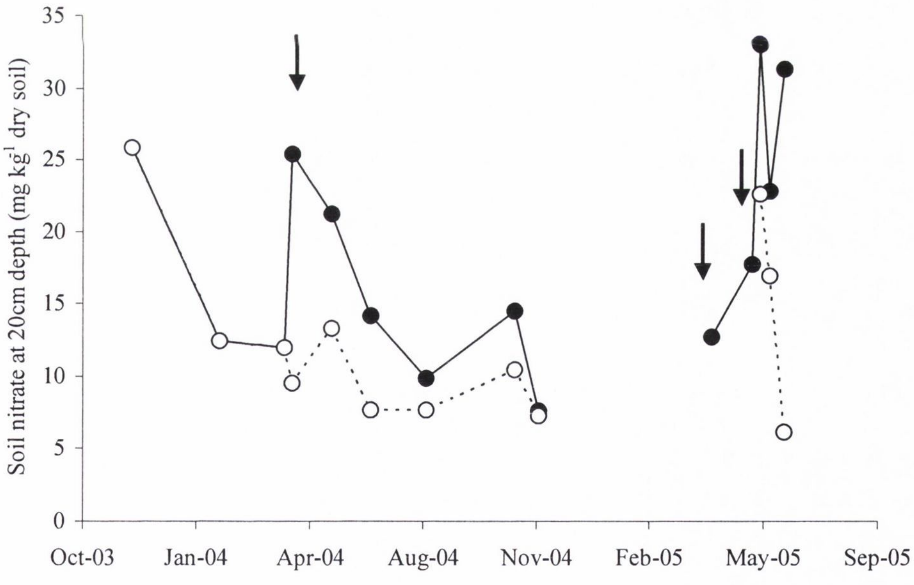

Figure 2.9: Changes in soil nitrate in the fertilised and control plots for 2004/2005 through out the experimental periods. Symbols indicate fertilized plots (●) and control plots (○). Arrows indicate first measurement following fertilizer application. Each point represents the mean ± se of four measurements.

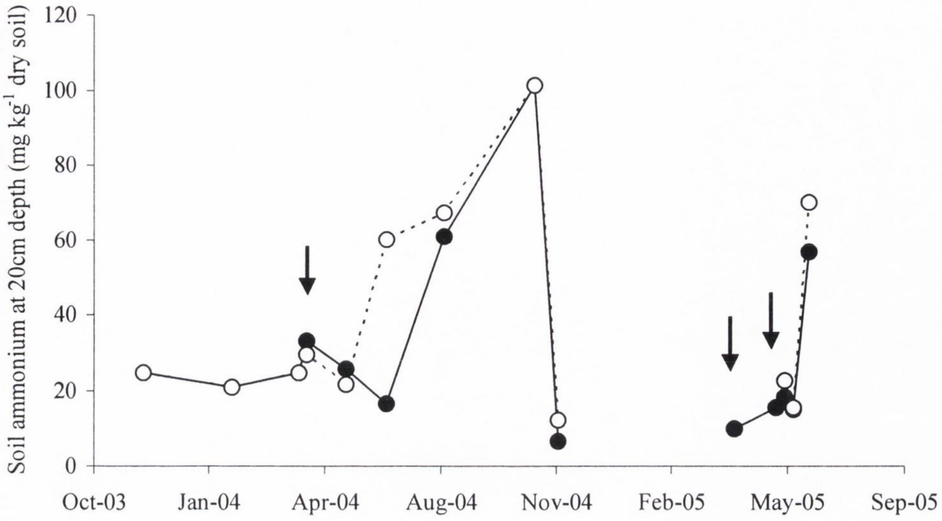

Figure 2.10: Changes in soil ammonium in the fertilised and control plots for 2004/2005 through out the experimental periods. Symbols indicate fertilized plots (●) and control plots (○). Arrows indicate first measurement following fertilizer application. Each point represents a mean ± se of four measurements.

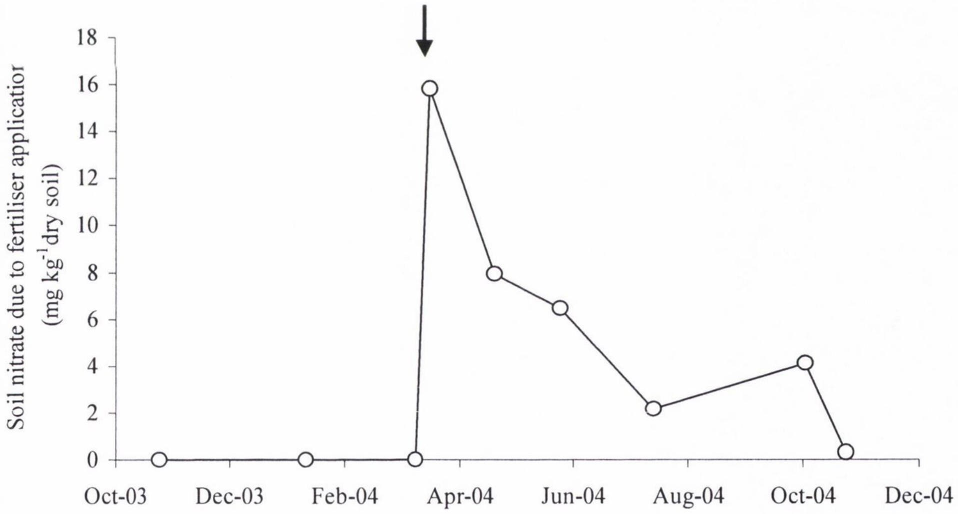

Figure 2.11: Changes in soil nitrate concentration in the grassland field due to fertilizer application rate for 2004. Arrow indicates first measurement following fertilizer application. Each point represents a mean ± se of four measurements.

Tables 2.1 and 2.2 illustrate the results of 2-way analyses of variance of the 2004 and 2005 nitrate data sets respectively where, the addition of N fertilizer (treatment) is a significant determinant of soil nitrate concentrations. According to a Bonferroni post-test, nitrate concentration from fertilized plots were significantly higher than from the control plots on the 7th of April 2004 ($P<0.05$) and on the 15th of June 2005 ($P<0.01$) corresponding to the 1st and 3rd week following fertilizer application.

Table 2.1: Summary of 2-way ANOVA for soil nitrate concentration in 2004

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	1	151	151.0	6.428	0.0207
Time	8	1006	125.7	5.350	0.0015
Interaction	8	227.2	28.40	1.209	0.3481
Residual (Error)	18	243	23.50		
Total	35	1627.2			

Table 2.2: Summary of 2-way ANOVA for soil nitrate concentration in 2005

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	1	571.3	571.3	32.65	0.0012
Time	2	197.4	98.68	5.64	0.0419
Interaction	2	205.5	102.8	5.873	0.0386
Residual (Error)	6	105	17.50		
Total	11	1079.2			

Tables 2.3 and 2.4 illustrate the results of 2-way analyses of variance for the soil ammonium of 2004 and 2005 data sets respectively. A Bonferroni posttest revealed that soil ammonium concentration from the fertilized plots were significantly higher than from the control plots on the 7th of April ($P<0.05$) and the11th of May ($P<0.01$) 2004. However soil ammonium concentration from control plots were significantly higher than from fertilized plots on the 15th of June ($P<0.001$), the 3rd of August ($P<0.001$) and on the 11th of November 2004 ($P<0.001$) and on the 15th of June 2005 ($P<0.01$).

Table 2.3: Summary of 2-way ANOVA for soil ammonium concentration in 2004

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	1	256.1	256.1	230.1	<0.0001
Time	8	25710	32.14	2888	<0.0001
Interaction	8	1734	216.7	194.8	<0.0001
Residual (Error)	18	20.03	1.113		
Total	35	27720.13			

Table 2.4: Summary of 2-way ANOVA for soil ammonium concentration in 2005

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	1	105.6	105.6	3.10	0.0111
Time	2	5579	2789	345.9	<0.0001
Interaction	2	86.43	43.21	5.359	0.0462
Residual (Error)	6	48.38	8.063		
Total	11	5819.41			

2.3.5 Nitrous oxide emissions

The experiments on the grassland field differed between the two years. The aim of the first year was to calculate an annual flux of N_2O from a grazed/fertilised field and to calculate a general emission factor for N_2O for this site. Secondly, by recording data on soil temperature, soil moisture, rainfall and soil nitrate, ammonium and total N at the time of N_2O measurement, both empirical and process models for N_2O flux can be developed. Due to time and financial limitations this approach was not possible for the second year where experiments focussed on the arable site and laboratory experiments. Hence for 2005 a limited program of measurement was adopted, the principal aim being the determination of the N_2O emission factor over the spring and summer months, this emission factor being related to an un-grazed pasture as for 2005 the cattle were excluded from the field during the experimental period.

2.3.5.1 2004 data set

Figure 2.12 shows the daily average nitrous oxide emission rates for 2004 incorporating two fertilizer applications; 128 kg ha^{-1} CAN-nitrogen applied on the 2nd of April and 72 kg ha^{-1} CAN-nitrogen applied on the 27th of May. Nitrous oxide emissions showed a typical pattern throughout the experimental period. The daily average emissions from control plots were consistently low with exception of some peaks which were not statistically significant. The emissions from these plots range from -6.8 to 14.8 g N_2O-N $ha^{-1}d^{-1}$. Nitrous oxide fluxes from fertilised plots showed maximum peaks soon after fertilizer application and reached a maximum daily mean of 67 g N_2O-N $ha^{-1}d^{-1}$, then declined steadily over a period of 7 weeks to reach background levels. Emissions of N_2O peaked again following the second fertilizer application and reached a maximum daily mean of 38.7 g N_2O-N $ha^{-1}d^{-1}$. These were also short-lived peaks which dropped to background levels 7 weeks later.

Some high fluxes were observed from the control plots immediately after fertilizer application and negative flux values were observed occasionally from both the control and treatment plots.

Table 2.5 illustrates a 2-way analysis of variance of the N_2O flux for 2004 data set. A Boneferroni post-test revealed that N_2O emissions from fertilized plots were significantly higher than from control plots ($P<0.001$), on the following dates; 5th April, 6th April, 7th April and 20th of April (corresponding to the third, fourth, fifth day following fertilizer application), 20th of April and 28th of May (corresponding to the second day following the second fertilizer application).

Table 2.5: Summary of 2-way ANOVA for N_2O flux in 2004

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	1	4830	4830	50.6	< 0.0001
Time	31	17600	568	6.0	< 0.0001
Interaction	31	9950	321	3.4	< 0.0001
Residual (Error)	160	15300	96		
Total	223	47860			

The mean cumulative N_2O flux for the whole of 2004 was calculated as 0.93 ± 0.16 kg N_2O-N ha^{-1} y^{-1}(mean ± standard error) for the control plots as compared with a flux of 2.4 ± 0.3 kg N_2O-N ha^{-1} y^{-1} from the fertilized plots. Using this data to calculate the emission factor, as described in section 2.2.2 a value of 0.83 ± 0.15 % was obtained which was less than 70% of the IPCC default value for applied N fertilizer.

2.3.5.2 2005 data set

Figure 2.13 shows the daily average nitrous oxide emission rates for 2005 incorporating three fertilizer applications; 70 kg ha^{-1} CAN-nitrogen applied on the 16th and 29th of March and 100 kg ha^{-1} CAN-nitrogen on the 20th of May. Nitrous oxide emissions in 2005 had the same pattern as in 2004. Emissions from the control plots were low and ranged from 1.1 to 32.8 g N_2O-N $ha^{-1}d^{-1}$. Maximum peaks of 283 and 175 gN_2O-N ha^{-1} d^{-1} were observed in the fertilized plots after the first and third fertilizer application, which were considerably higher than in 2004. After the second application of fertilizer there was no peak although the flux was high. From June to August 2005, N_2O emissions from the fertilized plots had decreased to background levels.

Table 2.6 illustrates a 2-way analysis of variance of the N_2O flux for 2005 data set. Note that in 2005 the unfertilized plots were installed after the second fertilizer application and therefore only the last period of the experiment was analyzed. Treatment, time and the interaction between the two are all significant. A Boneferroni post-test showed that N_2O flux from the control and fertilized plots were significantly different from one another on two days, the 23rd and 25th of May which correspond to the 3rd and 4th day after the final fertilizer application.

Table 2.6: Summary of 2-way ANOVA for N_2O flux in 2005

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	1	13380	13380	27.19	< 0.0001
Time	7	69130	9876	20.07	< 0.0001
Interaction	7	33830	4833	9.82	< 0.0001
Residual (Error)	40	19690	492		
Total	55	136030			

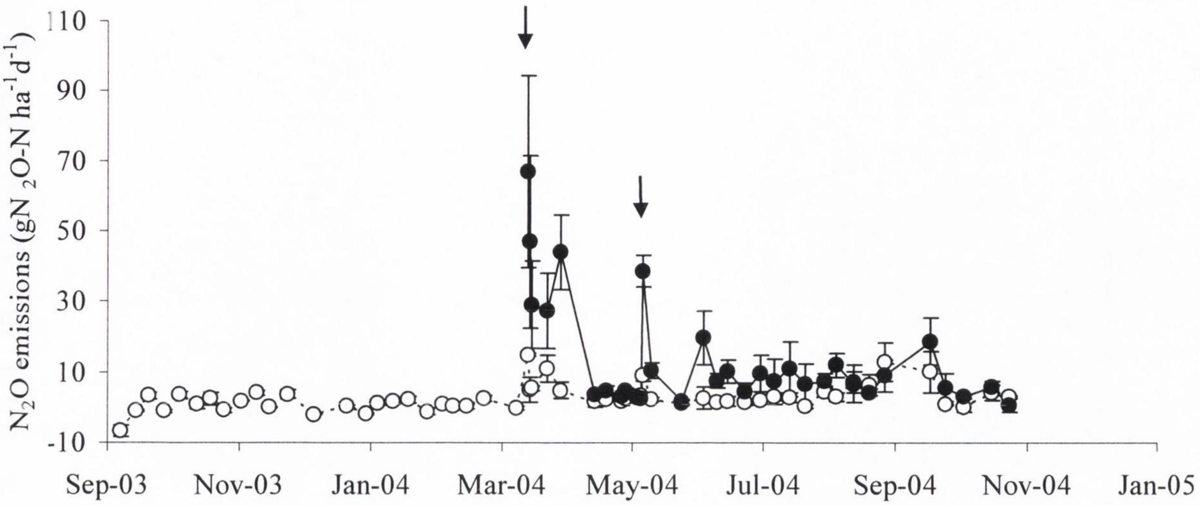

Figure 2.12: Daily N_2O emissions measured on a weekly basis from the cut and grazed pasture during 2004. Arrows indicate fertilizer application time (128kg N ha^{-1}, 72kg N ha^{-1}). Symbols indicate treatment at which N_2O flux was measured: fertilized plots (●) and control plots (○). Each point represents the mean ± se three to four replicates.

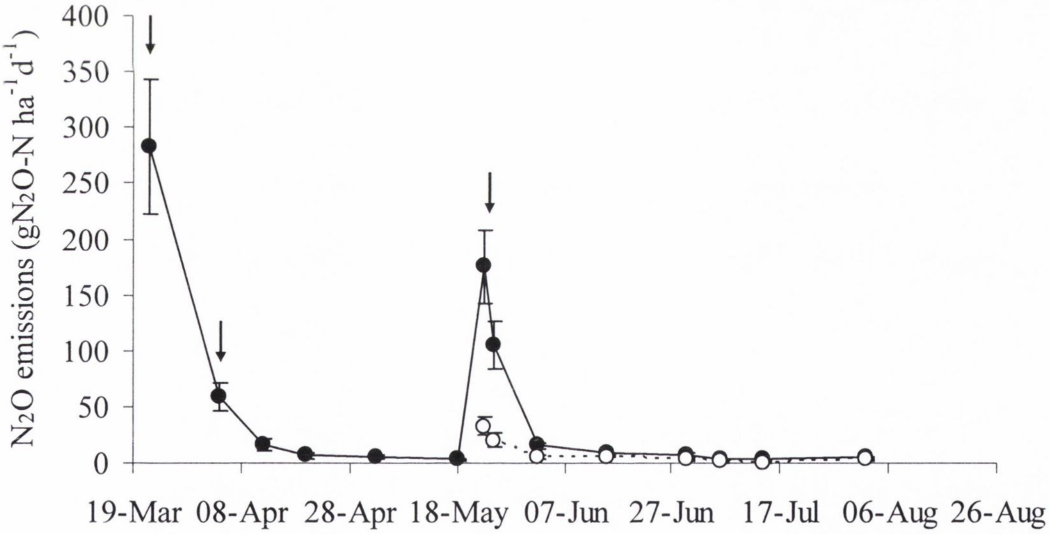

Figure 2.13: Daily N_2O emissions measured on a weekly basis from the cut and grazed pasture during 2005 experimental period. Arrows indicate fertilizer application time (70 kg N CAN ha^{-1}, 70 kg N CAN ha^{-1} and 100 kg N CAN ha^{-1}). Symbols indicate treatment at which N_2O flux was measured: fertilized plots (●) and control plots (○). Each point represents the mean ± se of three to four replicates.

The mean cumulative N_2O flux in 2005 from the control plots was 0.30 ± 0.06 kg N_2O-N ha^{-1} over the period from May to August, compared to 0.86 ± 0.03 kg N_2O-N ha^{-1} for the fertilized plots. Using this time period and the fertilizer treatment of 100 kg ha^{-1} CAN-nitrogen, an emission factor value of 0.61 ± 0.03 was calculated.

2.3.7 Multiple regression analysis

Table 2.7 illustrates the ordination of the measured flux values for N_2O with the single factors of soil nitrate, soil ammonium, soil temperature and soil moisture content. A multiple regression of this data set with log N_2O flux as the Y variable was carried out, results of which are given in Table 2.8. Accepting a threshold probability of 95%, only the concentration of nitrate in the soil at the time of flux measurement shows any correlation with emissions of N_2O with r^2 of 32%. However a best fit linear regression, that accounted for 46% of the variations, was calculated by including the interaction of soil moisture with both soil nitrate and soil temperature in the analysis and excluding the less correlated factors, the results of which is illustrated in Table 2.9. This regression revealed that the interaction between soil moisture and nitrate is significantly correlated with the flux ($P < 0.05$).

2.3.8 Correlation of N_2O flux with soil nitrate

Figure 2.14 illustrates the correlations of soil nitrate with log N_2O emission from the soil. The linear equation of nitrate accounted for 47% however, a plot of N_2O flux derived from N fertilizer (treatment – control) against the concentration of soil nitrate derived from N fertilizer (treatment – control) revealed a marked linearity, the equation for which accounting for over 66% of the variation in the data (Figure 2.15). This is further underlining the dominant effect of N-fertilizer application on the emission of N_2O from the soil.

Table 2.7: Ordination of the measured flux values for N_2O with soil nitrate, ammonium, temperature and moisture content

Sampling date	N_2O flux (gN_2O-N $ha^{-1}d^{-1}$)	Soil nitrate ($mg\ kg^{-1}$)	Soil ammonium ($mg\ kg^{-1}$)	Soil temperature (^oC)	Soil moisture (%)
18/11/03	-0.81	25.9	24.6	10.3	30.9
03/02/04	1.79	12.5	20.9	8.5	32.5
31/03/04	-0.29	11.9	24.6	7.2	32.2
07/04/04	5.42	9.5	29.7	6.9	34.4
11/05/04	2.30	13.3	21.5	10.5	31.1
15/06/04	1.22	7.7	60.1	17.7	16.2
03/08/04	2.80	7.7	67.2	21.2	18.1
21/10/04	0.00	10.4	101.5	6.8	35.9
11/11/04	3.08	7.3	12.3	10.3	31.8
25/05/05	20.4	22.7	22.7	12.9	29.9
02/06/05	5.30	17.0	15.4	15.0	30.4
15/06/05	6.20	6.2	70.0	13.9	24.5
07/04/04	29.06	25.4	33.0	6.9	34.4
11/05/04	4.68	21.2	25.7	10.5	31.1
15/06/04	1.60	14.2	16.6	17.7	16.2
03/08/04	10.92	9.8	60.8	21.2	18.1
21/01/04	3.08	14.5	101.5	6.8	35.9
11/11/04	0.63	7.6	6.5	10.3	31.8
12/05/05	16.0	12.7	10.0	12.2	27.8
18/05/05	3.00	17.7	15.5	10.3	27.0
25/05/05	105	33.1	18.5	12.9	29.9
02/06/05	15.1	22.8	15.0	15.0	30.3
15/06/05	3.20	31.4	56.8	13.9	24.5

Table 2.8: Results of the multiple regression analysis of log N_2O flux values with soil nitrate, log ammonium, temperature and moisture content

Source	Sum of Square	D.F	Mean Square	F-ratio
Regression	2.45234	4	0.613086	3.24
Residual	2.84253	15	0.189502	
Variable	*Coefficient*	*S.E of Coefficient*	*t-ratio*	*Probability*
Constant	-2.70723	1.753	-1.54	0.1433
Soil nitrate	0.0354735	0.01294	2.74	0.0152
Soil ammonium	0.152872	0.3278	0.466	0.6477
Soil temperature	0.0793618	0.05105	1.55	0.1409
Soil moisture	0.0588292	0.03716	1.58	0.1342

Table 2.9: Results of the best fit multiple regression analysis of log N_2O flux with moisture content, soil nitrate and interaction between soil moisture and soil nitrate

Source	Sum of Square	D.F	Mean Square	F-ratio
Regression	2.88116	3	0.960385	6.37
Residual	2.41371	16	0.150857	
Variable	*Coefficient*	*S.E of Coefficient*	*t-ratio*	*Probability*
Constant	2.13441	0.9889	2.16	0.0464
Soil nitrate*soil moisture	0.00668461	0.002728	2.45	0.0261
Soil nitrate	-0.149965	0.07777	-1.93	0.0718
Soil moisture	-0.0742825	0.03602	-2.06	0.0558

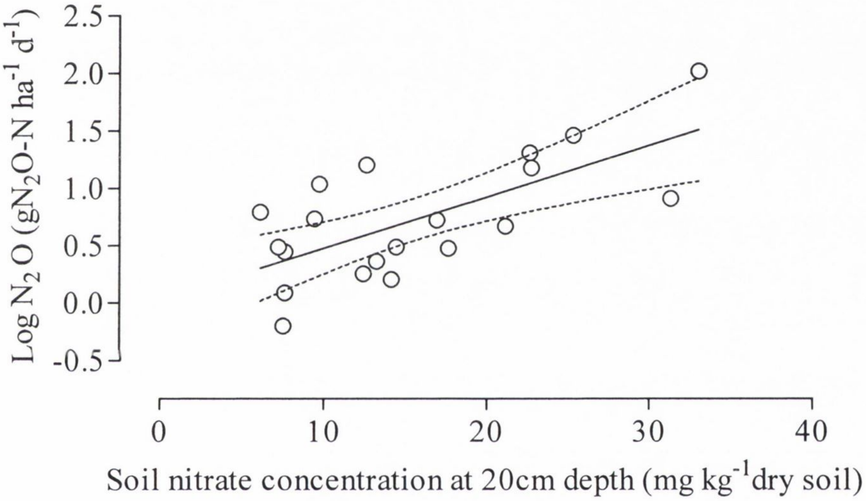

Figure 2.14: Correlation between soil nitrate concentration in the grassland field at the time of N_2O measurements and log N_2O emission. $y = 0.045x + 0.027$, (r^2 =0. 47). The dotted lines representing the 95% confidence interval.

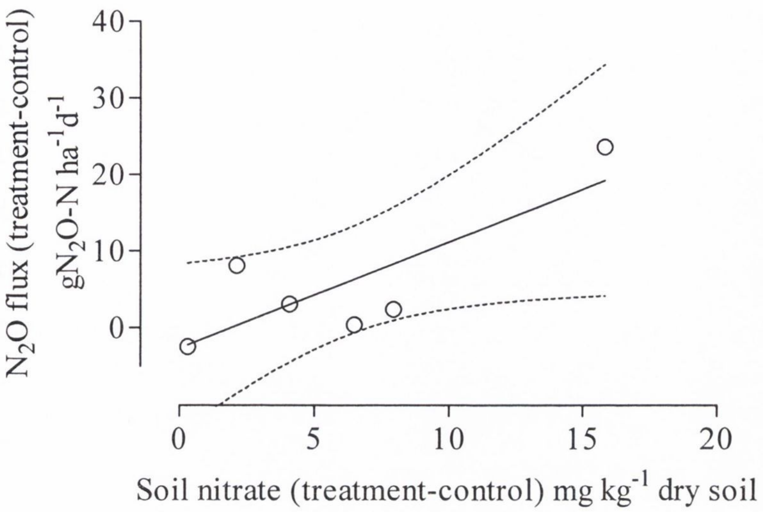

Figure 2.15: Correlation between soil nitrate concentration due to fertilizer application and N_2O emission due to fertilizer application. $y = 1.3812 - 2.629$, $(r^2 = 0.66)$. The dotted lines representing the 95% confidence interval.

2.4 Discussion

Results from this study support the concept that cumulative emissions of N_2O from agricultural soils are directly related to the amount of N-fertilizer applied both in terms of application rate and the post-application concentration of nitrate in the soil (Crill *et al.*, 2000; Bouwman *et al.*, 2002; Tilsner *et al.*, 2003). This result was found to be true for both long-term (12 month) and short term (5 month) measurements (Figures 2.12 and 2.13). Indeed, a multiple regression of log N_2O flux for 2004 and 2005 data, against the single factors of soil nitrate, soil ammonium, soil temperature and soil moisture revealed only soil nitrate to be a significant factor (Table 2.8). However, the best-fit regression analysis including interactions between soil moisture and both soil nitrate and soil temperature revealed that the interaction between soil moisture and soil nitrate is also positively correlated with the flux. As such a plot of N_2O flux derived from N fertilizer (treatment – control) against the concentration of soil nitrate derived from N fertilizer (treatment – control) revealed a marked linearity, the equation for which accounting for over 66% of the variation in the data (Figure 2.15). This suggests that the bulk of N_2O flux is derived from denitrification rather than nitrification. If nitrification were important then a correlation would exist between log N_2O flux and soil ammonium as the CAN fertilizer provides N for both nitrification and denitrification (Baggs and Blum, 2004; Freney, 1997). This strong correlation between soil nitrate and N_2O flux, with weak or no correlation with soil ammonium, reflecting soil denitrification, has also been observed in agricultural soils by Bouwman, (1996) and Smith *et al.* (1997). Thus peaks in N_2O flux were only associated with times of application of N-fertilizer, the mean background daily emission being 2.7 ± 0.4 g N_2O-N ha^{-1} d^{-1}, approximately equivalent to 1 kg N_2O-N ha^{-1} y^{-1}. This background emission is the same as that calculated by Bouwman, (1996) and used in the IPCC equation for annual flux calculations.

Surprisingly, neither soil temperature nor soil moisture were found to be significant determinants of N_2O flux alone and is most likely a reflection of the overall limitation on N_2O flux by soil nitrate. However, although the effect of soil moisture may have been masked by soil nitrate, regression analysis between the flux of N_2O and the interaction between soil moisture and soil nitrate was significantly positive. This suggests that soil moisture may affect the flux of N_2O through its interaction with soil nitrate, affecting the availability of this ion for denitrification. Here, both soil moisture and soil N availability were co-required for high N_2O emissions. Similar results of such interaction have also been demonstrated in maize (McSwiney and Robertson, 2005) and in forest and grassland systems (Abassi and Adams, 2000; Maddok *et al.,* 2001; Ball *et al.,* 2002; Maljanen *et al.,* 2002).

Soil moisture affects N_2O flux by affecting denitrification. Hence moisture stimulates denitrification by temporarily reducing the oxygen diffusion into the soil (Dobbie and Smith, 2001), as well as by increasing the solubility of organic carbon and nitrate (Bowden and Bormann, 1986). This effect of soil moisture on denitrification will be discussed further in Chapter 5 where the effect of soil moisture, in isolation, on denitrification has been investigated in a series of laboratory incubations.

The strong correlation between N_2O flux and the interaction between soil moisture and soil nitrate suggests that a high rainfall in winter and early spring, together with soil properties such as drainage characteristics, are important in the assessment of N_2O flux. In addition, application of fertilizer during these periods should be avoided as suggested by Choudhary *et al.* (2002).

A continuous data set of weekly measurements of N_2O flux over a 12 month period was only available in our study for 2004. Here cumulative values of 0.9 ± 0.2, and 2.4 ± 0.3 kg N_2O-N ha^{-1} y^{-1} were recorded for the control and fertilized plots respectively. Hence 63% of the total N_2O emitted was associated with the short period of fertilizer application.

An annual emission of 2.4 kg N_2O-N ha^{-1} y^{-1} is far less than that measured by eddy covariance for a fertilized and grazed grassland in Co. Cork for 2003 (Hsieh *et al.*, 2005). Here a value of approximately 12 kg N_2O-N ha^{-1} y^{-1} was measured. Annual flux values of 6.5 and 18.5 kg N_2O-N ha^{-1} y^{-1} have also been recorded using static chambers for a fertilized and grazed grassland site in Wexford for the years 2002 and 2003 (Hyde *et al.*, 2005). These four values represent the only annual data sets as yet available for Ireland and illustrate considerable spatial and annual variations. These differences maybe due to the nature of the soil, the amount of fertilizer added and the rainfall experienced at the time of fertilizer application. With regard to soil type, the Cork and Wexford sites have been classified as clay loams, whereas the Carlow site is classified as a sandy clay loam. Peaty soils and those of a low C/N ratio show the highest annual emissions of N_2O reported in the literature and may extend to 25 kg N_2O-N ha^{-1} y^{-1} (Maljanen *et al* ., 2004; Regina *et al.*, 2004). This may account in part for the low N_2O emission recorded in our study. In addition both the Cork and Wexford sites received more fertilizer. In the Cork study 207 kg ha^{-1} y^{-1} of synthetic N was applied in addition to 130 kg ha^{-1} y^{-1} organic N (Hsieh *et al.*, 2005), whilst in the Wexford study a total of 225 kg ha^{-1} y^{-1} of inorganic N (urea and CAN) was used. However the marked difference between the 2002 and 2003 annual emissions for the Wexford site has been explained in terms of variations in rainfall (Hyde *et al.*, 2005). This can also be seen for the 2004/2005 data set for Carlow. The total rainfall for 2004 over the fertilizer period of March to May was 155 mm, as opposed to 212 mm for the same period in 2005 and a 30 year mean of 169 mm. The lower rainfall in 2004 is associated with a peak flux of 67 g N_2O-N ha^{-1} d^{-1}, whilst the higher rainfall in 2005 is associated with peak fluxes of 175 to 283 g N_2O-N ha^{-1} d^{-1} (Figures 2.12 and 2.13). Assuming an annual flux of at least 3.5 kg N_2O-N ha^{-1} y^{-1} for 2005, climate can be seen as a dominating influence, the change from warm and dry weather in 2004 to cooler and wetter weather in 2005 influencing the higher emission values. Similar influences of rainfall on N_2O flux have also been reported by Clayton *et al.* (1997), Dobbie *et al.* (1999) and Hellebrand *et al.* (2003). Clearly a larger study encompassing a greater range of soil types in Ireland is required to obtain a better picture of the spatial variance in N_2O flux. Accepting the annual N_2O flux value for 2004 of 2.4 kg N_2O–N ha^{-1} y^{-1} is considerably lower than the Cork and Wexford estimates, it is comparable to fertilized grassland flux values cited in Flechard *et al.* (2006) where an overall mean of 2 kg N_2O-N ha^{-1} y^{-1} was calculated from 10 grassland sites in 8 European countries spanning a wide range of climatic, environmental and soil conditions.

The application of CAN fertilizer throughout our experiment increased soil nitrate and soil ammonium (Figures 2.9, 2.10 and 2.11), and consequently through its effect on nitrification/denitrification, increased N_2O efflux from the soil (Eichner, 1990; Davidson *et al.*, 1996; Smith *et al.*, 1998; Dobbie and Smith, 2003; McSwiney and Robertson, 2005). One means of relating N_2O emissions to N-fertilizer application is to calculate an emission factor whereby the percentage of applied N lost to the atmosphere as N_2O is determined. Such emission factors can be determined using short-term data associated with an isolated peak in N_2O flux, or annual data. In both cases an unfertilized control treatment is required. For the 2004 data set, an emission factor of 0.83 ± 0.15% was obtained. However, using short-term data associated with the final peak for 2005 where control values were available, the emission factor was calculated as 0.61 ± 0.03%. Higher emission factors for longer term measurements have also been observed by Bouwman, (1996) and Bouwman *et al.* (2002).

As with the annual flux data, an emission factor of 0.83% is significantly lower than that calculated by Hsieh *et al.* (2005) for the Cork grassland (3.4%), and for that calculated by Hyde *et al.* (2005) for the Wexford grassland (0.7 to 4.9%). For Scottish grasslands Dobbie and Smith, (2003) reported emission factors ranging from 1 to 3%. Again soil type and climate may account for such differences, but the more extensive study by Flechard *et al.* (2006) incorporating the 10 grassland sites in 8 European countries gave an overall emission factor of 0.75%. Our value is also in agreement with other studies such as Mosier *et al.* (1998a) for a short grass steppe (0.5%), Khan, (1999) for a grass/clover pasture (0.7%) and Kaiser *et al.* (1998) for a ryegrass pasture (0.7%).

That our emission factor of 0.83% is significantly less than the IPCC default value of 1.25% is of interest. Other authors have criticised the IPCC value for either underestimating (Laegreid or Aastveit, 2002) or overestimating (Schmid *et al.*, 2001), the N_2O flux from applied N. What is clear is that a more spatial approach to N_2O reporting is required, questioning the applicability of a single, national emission factor for Ireland.

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Chapter 3: Nitrous oxide emissions from an arable field under conventional and reduced tillage – Large plots

3.1 Introduction

Although crop production represents only 9% (< 0.4 million ha) of the agricultural area in Ireland (Meade and Mullins, 2005), it is still an important source for N_2O emissions from soils due to the application of inorganic N fertilizer (IPCC, 1996). Tillage practices may also make significant impacts on N_2O production through their effect on soil structural quality and water content (Ball *et al.*, 1999).

Conventional seedbed preparation and sowing is a type of tillage which through inversion disturbs the soil to depths of 20 - 25 cm involving mouldboard ploughing (Cunningham *et al.*, 2004). It is relatively slow, energy demanding and expensive, especially where large areas are being worked (Fortune, *et al.*, 2003). The intensive use of these cultivation practices has a huge impact on soil properties which may influence N_2O emissions (Choudhary *et al.*, 2002), and can result in the loss of soil organic matter and deterioration of soil structure (Shepherd *et al.*, 2001).

An alternative to conventional tillage is non-inversion tillage (NIT). Non-inversion tillage is also known as reduced tillage, no-till, ECO-tillage, minimum tillage or conservation tillage and disturbs the surface soil only to a depth of 10 – 15 cm (Cunningham *et al.*, 2004). It is used to prepare the seed bed for sowing and establishing the crop from the previous year's stubble. NIT can include various types of cultivation equipment that disturb the surface of the soil without inverting it, and incorporate, to varying degrees, the stubble of the previous crop. The percentage of crop residue left on the soil surface has been used as a way of defining NIT, i.e. over 30 % cover of previous crop residue (Gebhardt *et al.*, 1985). Moreover, NIT farming has been promoted as a very useful agricultural practice, which reduces soil erosion, has low labour intensities and lower costs (Forristal and Fortune, 2002) and enhancing agricultural sustainability concomitant with mitigating greenhouse gas emissions (Cole *et al.*, 1997; Paustian *et al.*, 1997; Schlesinger, 1999).

Worldwide non-inversion tillage is practiced on 45 million ha, predominantely in North and South America (Holland, 2004). Only about 10,054,000 ha have been under NIT cultivation in Europe (ECAF, 2004). In Ireland reduced cultivation and direct drilling never achieved the same degree of popularity as conventional ploughing, but some cereals were sown using these techniques (Fortune *et al.*, 2003), which represent an area of less than 10 % of the arable land i.e. < 40, 000 ha (ECAF, 2004) . The reasons for the fall off include increasing grass weed populations, topsoil compaction, restriction on straw burning and inability to sow in unclean conditions (Fortune *et al.*, 2003).

Due to the absence of country specific information on N_2O emission factors for applied N fertilizer, the IPCC default emission factor of 1.25 % is used for calculating the N_2O emission inventory in Ireland. However research has indicated that the use of default values may result in unreliable estimates of national emission inventories (Hyde *et al.*, 2005). Land use, fertilizer type, fertilizer application, irrigation, soil type and crop residues have been found to have profound effects on the N_2O emission factor from agricultural soils (Boeckx and Van Cleemput, 2001).

Spring barley is the most important crop in Ireland (Teagasc, 2003). World wide, different national emission factors for fertilized barley were calculated. In UK, they ranged from 0.2 to 0.7% (Dobbie *et al.*, 1999), in Germany from 1 to 8% (Kaiser *et al.*, 1998), in Denmark from 0.7 to 3.4% (Maag *et al.*, 1996) and in Canada from 0.8 to 0.9% of the applied N fertilizer (Wanger-Riddle and Thurtell, 1998).

The aim of the experiment reported in this Chapter was to calculate the N_2O emission factor for the spring barley field under conventional and reduced tillage systems. This was part of an existing study on greenhouse gas emissions from the arable field involving continuous measurements of CO_2 flux by eddy covariance. Here the two treatments were replicated twice only, this limitation being set by the replication of the eddy covariance systems. However, in Chapter 4 a fully replicated small plot trial is described involving an investigation of both soil tillage and fertilizer application.

3.2 Materials and Methods

3.2.1 Experimental site

Measurements of N_2O emissions were carried out from November 2003 – August 2004, and from April 2005 – July 2005 on a spring barley field at the Oak Park Research Centre, Carlow, Ireland. The experimental site had an elevation of 56 m, a mean annual rainfall of 824 mm and a mean air temperature of 9.4°C. The soil is classified as a free draining sandy loam derived from fluvial glacial gravels, with a low soil moisture holding capacity, a pH of 7 and a mean organic carbon and nitrogen content at 15 cm of 22.4 and 2.3 g kg^{-1} dry soil respectively. In both seasons the experiment was seeded with spring barley, variety cv Tavern, at a density of 140 kg ha^{-1} and managed under two different tillage regimes; conventional tillage where inversion ploughing to a depth of 22 cm was carried out in March five weeks prior to planting, and reduced tillage to a depth of 15 cm which was carried out in September of the year before. The field was sprayed with weed killer Roundup Sting at 4.0L ha^{-1}, three times per season, once pre and twice post planting.

Tillage treatments were replicated twice. Hence the field was divided into four large plots each measuring 2.5 hectares. In each plot three N_2O chambers were established along the diagonal as illustrated in Figure 3.1, one chamber in each plot being designated as a control (unfertilized).

3.2.2 Fertilizer treatment

In 2003-2004 nitrogen fertilizer (Calcium Ammonium Nitrate, CAN) was applied once on the 27th on April at a rate of 140 kg N ha^{-1}. In 2005 a higher concentration of fertilizer was applied. Here a total of 159 kg N ha^{-1} was applied over two dates, 106 kg N ha^{-1} on the 12th of April and 53 kg N ha^{-1} on the 10th of May.

3.2.3 Measurement of N_2O flux

Nitrous oxide fluxes were measured from 12 chambers as described in Chapter 2. Measurements were taken every week except for times of soil ploughing, when no measurements were taken, and fertilizer application when sampling was increased to 2 times per week.

3.2.4 Soil temperature, moisture, WFPS, nitrate and ammonium

Measurements of soil temperature and moisture and WFPS were made, as described in Chapter 2, on days of N_2O measurement. Soil N (nitrate and ammonium) was determined either every month (2003-2004) or every week following fertilizer application (2005), again as described in Chapter 2.

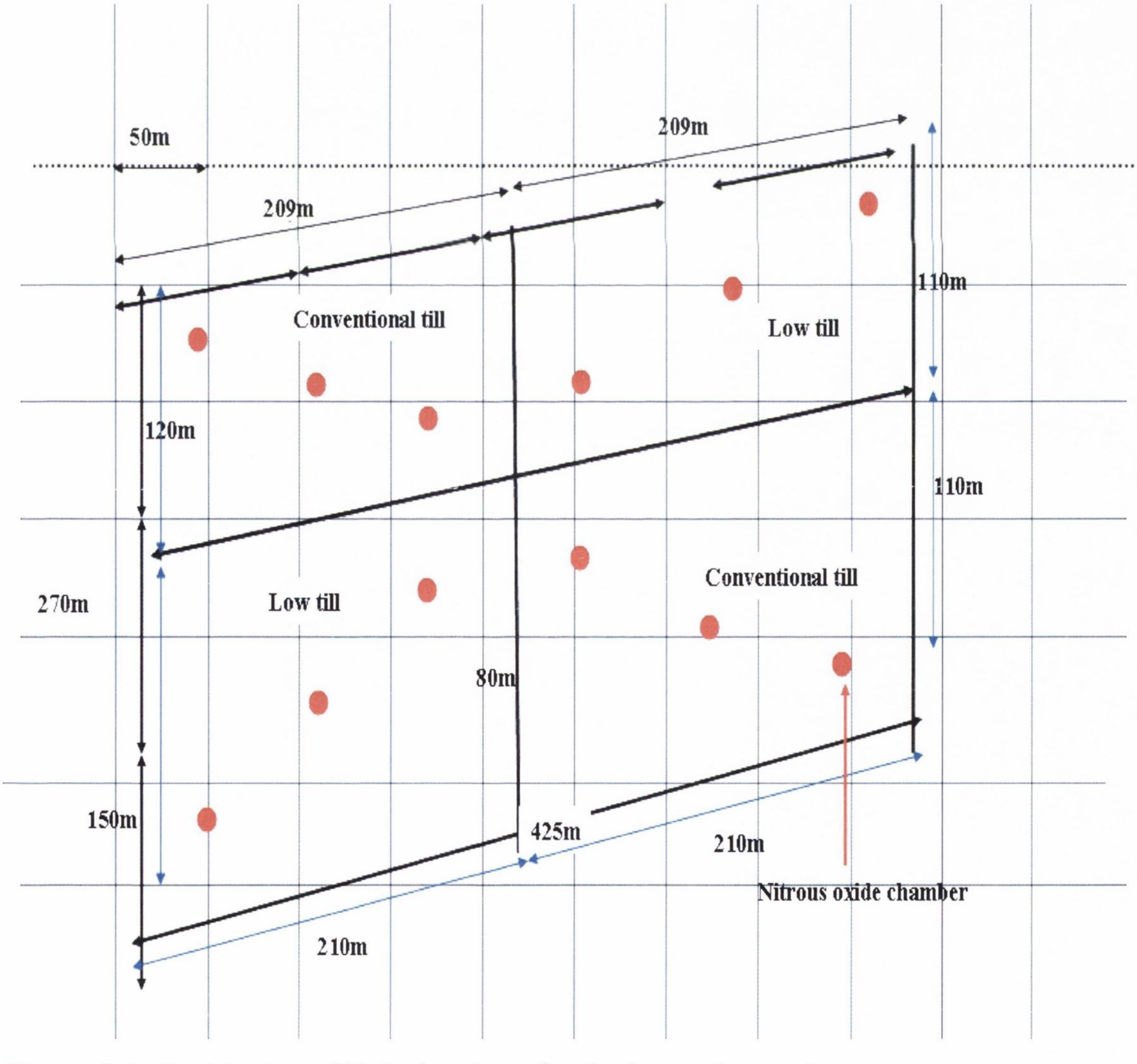


Figure 3.1: Positioning of N_2O chambers for the large plot trial

3.2.5 Statistics

All statistical analyses were carried out using PRISM (GraphPad, San Diego, USA) and Data Desk (Data Description Inc. New York, USA) software packages. Flux data was checked for normal distribution and log transformed where appropriate. Both 1-way and 2-way analysis of variance were applied to the N_2O flux, soil moisture, soil temperature and soil N data, and a multiple regression carried out for log N_2O flux against soil nitrate, ammonium, moisture and soil temperature.

3.3 Results

3.3.1. Soil moisture and temperature

Figure 3.2 relates the weekly rainfall data collected at the Teagasc Oak Park Research Centre weather station with direct daily measurements of soil water content taken from the large plots at the time of N_2O measurements. As in the case of the grassland field, limiting rainfall has resulted in low soil moisture contents. Hence, soil moisture values ranged from a minimum of 7.6%, applicable to WFPS of 14%, in the summer of 2004 to a maximum of 28.5, applicable to WFPS of 44%, in the spring of 2005. To put these values into perspective, the field capacity of the soil was measured as 37 ± 0.003 %, hence over the measuring period of 2004 to 2005, soil moisture content was less than the field capacity on most of N_2O measurement occasions (Appendix 5).

Tables 3.1 and 3.2 illustrate the results of 2-way analyses of variance of the soil moisture content 2003 - 2004 and 2005 data sets respectively. A Bonferroni post-test revealed that soil moisture content of the reduced tillage is significantly higher than the conventional tillage plots on the following dates; the 30th of June, 8th and 20th of July 2004 ($P< 0.05$, <0.001, <0.05). Soil moisture content from the conventional tillage was significantly higher ($P<0.05$) than the reduced tillage plots on the 20th of April 2005 only. Although these differences are statistically significant, they represent at most a difference in soil moisture of 4%.

Figure 3.3 compares the daily average soil temperature at a depth of 10 cm, measured at the Teagasc Oak Park Research Centre weather station, with direct daily average measurements of soil temperature at the same depth taken from both the conventional and reduced tillage plots at the time of N_2O measurements. The minimum and maximum daily average soil temperatures in 2004 were 8.5 and 19.8°C for conventional tillage and 8.4 and 19.2°C for reduced tillage, observed on the 29th of April and the 1st of June 2004 respectively. For 2005 the minimum and maximum daily average temperatures were 7.1 and 14.5°C for conventional tillage and 7.1 and 14.7°C for reduced tillage, observed on the 20th of April and 1st of June 2005 respectively.

Table 3.1: Summary of 2-way ANOVA statistics for the large plot soil moisture 2003-2004 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	1	26.44	26.44	15.81	0.0003
Time	16	1234	17.33	46.14	< 0.0001
Interaction	16	129	8.063	4.82	< 0.0001
Residual (Error)	34	56.84	1.672		
Total	67	1446			

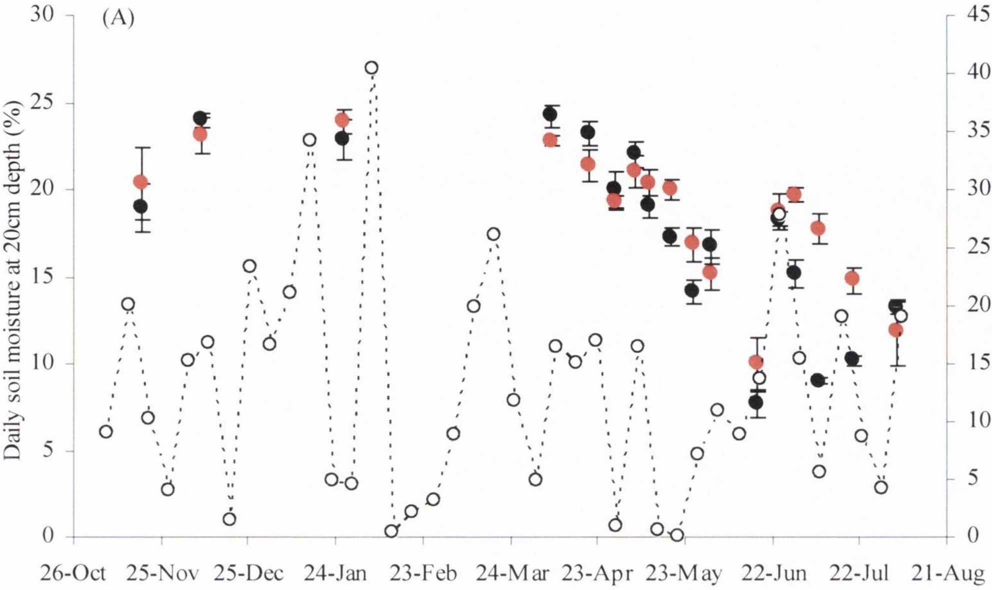
Table 3.2: Summary of 2-way ANOVA statistics for the large plot soil moisture 2005 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	1	19.76	19.76	6.18	0.0203
Time	11	1232	112	35	< 0.0001
Interaction	11	43.14	3.922	1.23	< 0.3234
Residual (Error)	24	76.78	3.199		
Total	47	1371			

Table 3.3 illustrates a 2-way analysis of variance of the soil temperature 2004 and 2005 data sets combined. A Bonferroni post test revealed a significant difference between the conventional and reduced tillage treatments ($P<0.001$) on one day only, the 18th of May 2004, where the soil temperature of the conventional tillage plots was 1°C higher than that of the reduced tillage plots. No significant differences were observed between conventional and reduced tillage plots in 2005.

Table 3.3: Summary of 2-way ANOVA statistics for the large plot soil temperature 2004 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	1	0.4420	0.4420	5.82	0.0194
Time	11	1263	50.52	664.78	< 0.0001
Interaction	25	4.04	0.1616	2.13	0.0110
Residual (Error)	52	3.95	0.076		
Total	103	1271			



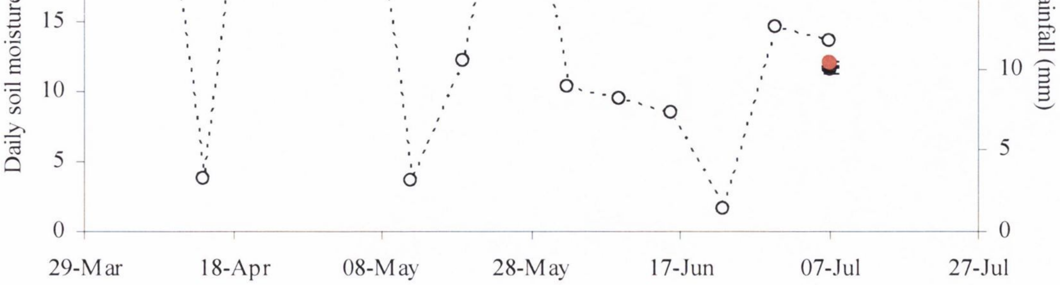


Figure 3.2: Weekly rainfall data collected at the Teagasc Oak Park Research Centre weather station and direct daily field measurements of soil water contents in 2003-2004 (A) and 2005 (B). Symbols indicate conventional tillage (●), reduced tillage (●) and weekly total rainfall (○). Each point represents the mean ± se of four measurements.

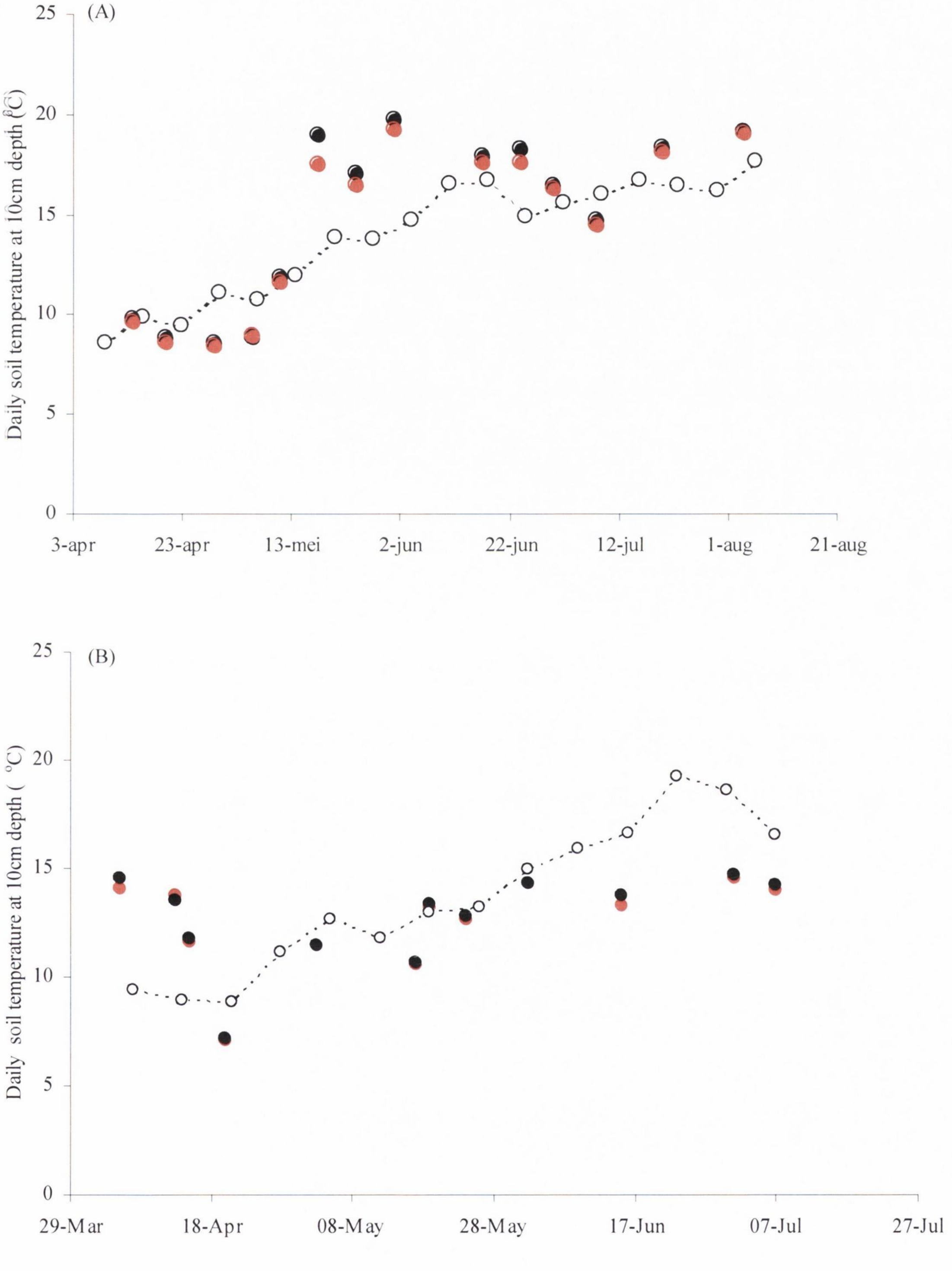


Figure 3.3: Daily soil temperatures from the Teagasc Oak Park Research Centre weather station and direct field measurements of soil temperature in 2004 (A) and 2005 (B). Symbols indicate conventional tillage (●), reduced tillage (●) and average soil temperature from Teagasc (○). Each point represents the mean ± se of six measurements.

A positive linear correlation between the Oak Park weather station temperature data and the direct measurement temperature data, illustrated in Figure 3.4, accounted for 76% of the observed variation in the data. Hence missing soil temperature data from the large plots required for the multiple regressions of the N_2O emission data may be estimated using the continuous data set from the Oak Park weather station.

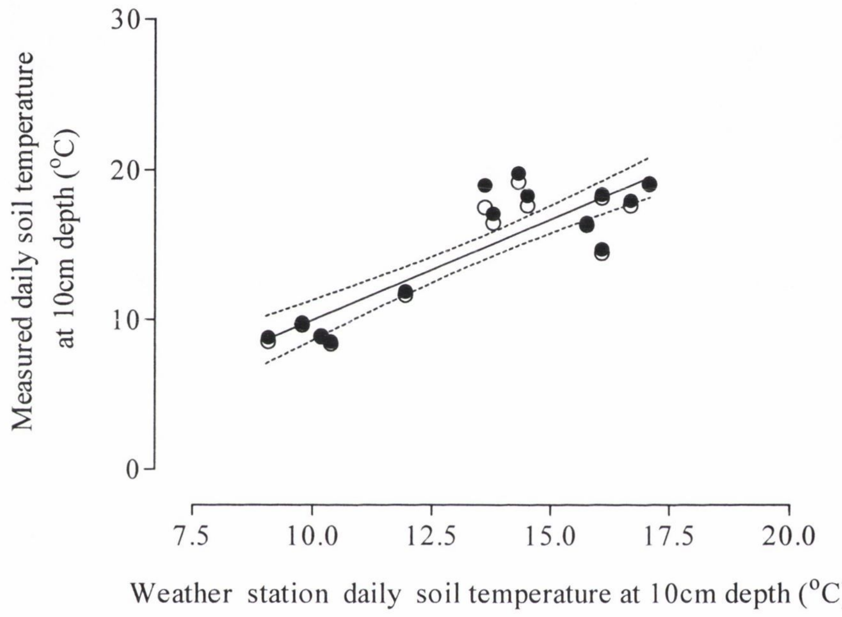
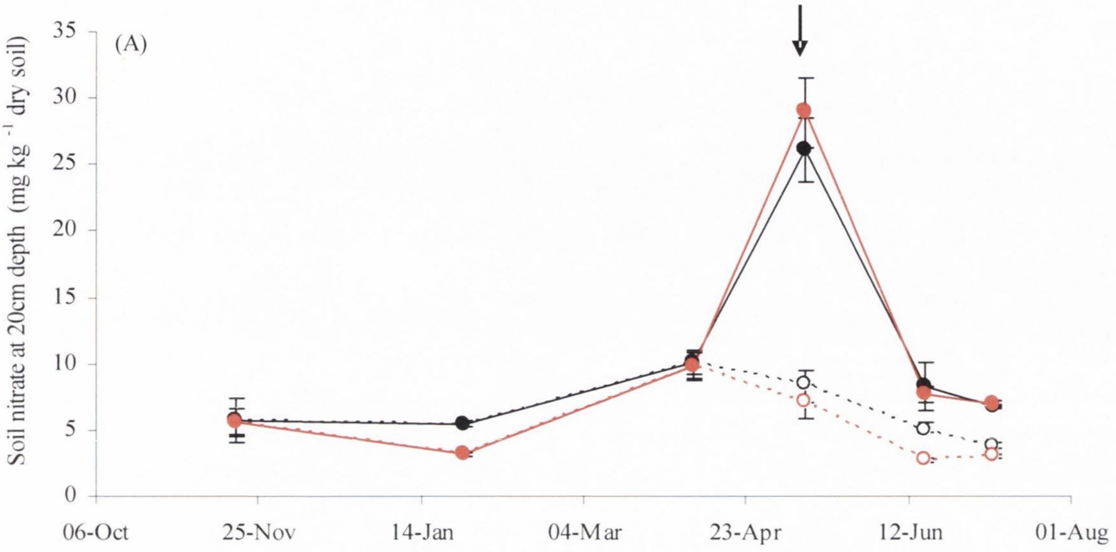


Figure 3.4: Correlation between the daily average temperature data collected at the Teagasc Oak Park Research Centre weather station and direct field measurements of soil temperature. Symbols indicate conventional tillage (●) and reduced tillage (○). Each point represents the mean ± se of six measurements. $y = 1.34x - 3.5$, $(r^2 = 0.76)$. *The dotted lines representing the 95% confidence interval.*

3.3.2 Soil nitrate and ammonium

Figure 3.5 illustrates the change in soil nitrate for 2003 - 2004 and 2005 in the control and fertilised conventional tillage plots with fertiliser application dates shown by arrows. Peaks in soil nitrate corresponded to times of fertilizer application.



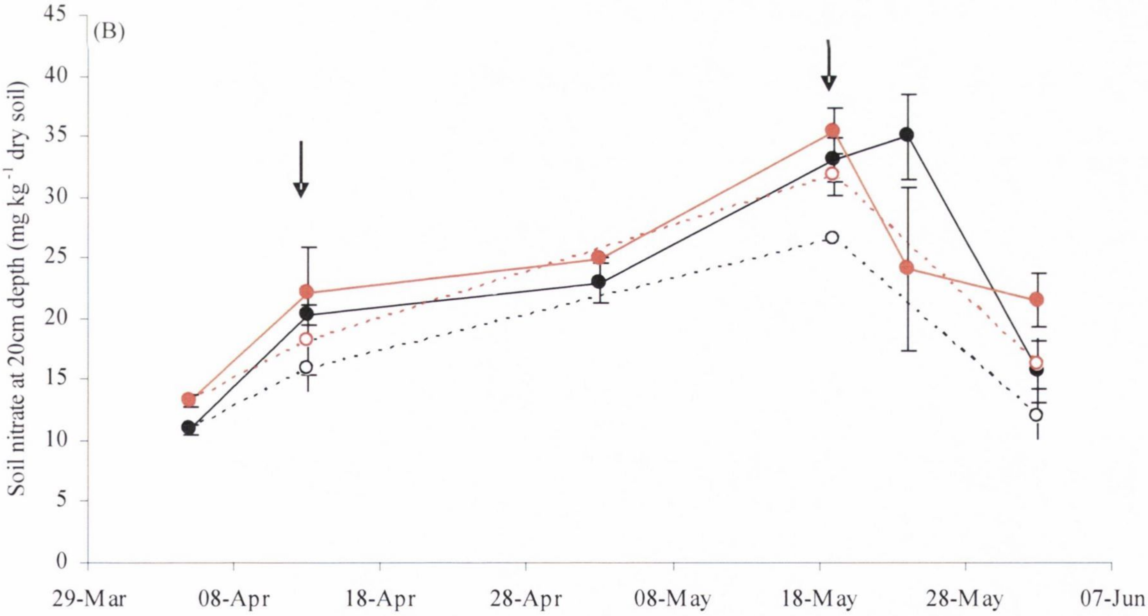


Figure 3.5: Soil nitrate concentration in 2003-2004 (A) and 2005 (B) for control and fertilized conventional and reduced tillage plots. Symbols indicate fertilized conventional (●), control conventional (○), fertilized reduced (●) and control reduced (○). Arrows indicate first measurement following fertilizer applications. Each point represents the mean ± se of four measurements.

A 2-way analysis of variance of the soil nitrate data set for the large plots, illustrated in Tables 3.4 and 3.5, revealed no significant difference between the soil nitrate of the conventional and reduced tillage treatments for 2003-2004 and 2005 respectively. However, soil nitrate from the fertilized conventional plots was significantly higher ($P<0.001$) than that from control conventional plots on the 11th of May 2004 corresponding to the 2nd week following fertilizer application and on the 13th of April ($P<0.001$), 19th of May ($P<0.001$) and the 2nd of June ($P<0.001$) 2005, corresponding to the 1st day following first fertilizer application; 2nd and 3rd week following second fertilizer application. Soil nitrate from fertilized reduced plots was significantly higher than from control reduced plots on 11th of May ($P<0.001$) and the 17th of June ($P<0.05$) 2004 corresponding to the 2nd and 3rd week following fertilizer application and on the 13th of April ($P<0.001$), 19th of May ($P<0.001$) and the 2nd of June ($P<0.001$) 2005.

Table 3.4: Summary of 2-way ANOVA statistics for the large plot soil nitrate 2003-2004 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	3	263.5	87.84	31.08	<0.0001
Time	5	1047	209.4	74.08	<0.0001
Interaction	15	617.6	41.17	14.57	<0.0001
Residual (Error)	26	73.49	2.826		
Total	49				

Table 3.5: Summary of 2-way ANOVA statistics for the large plot soil nitrate 2005 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	3	2059	686.3	166.3	<0.0001
Time	2	291.9	146	35.37	<0.0001
Interaction	6	233.1	38.86	9.42	0.0006
Residual (Error)	12	49.52	4.127		
Total	23	2633			

On the other hand, Figure 3.6 illustrates the change in soil ammonium, for 2003-2004 and 2005, in the control and fertilised conventional and reduced tillage plots with fertiliser application dates shown by arrows. Overall, peak concentrations of soil ammonium were significantly lower than soil nitrate but unlike grassland field soil ammonium, were related to times of fertilizer application.

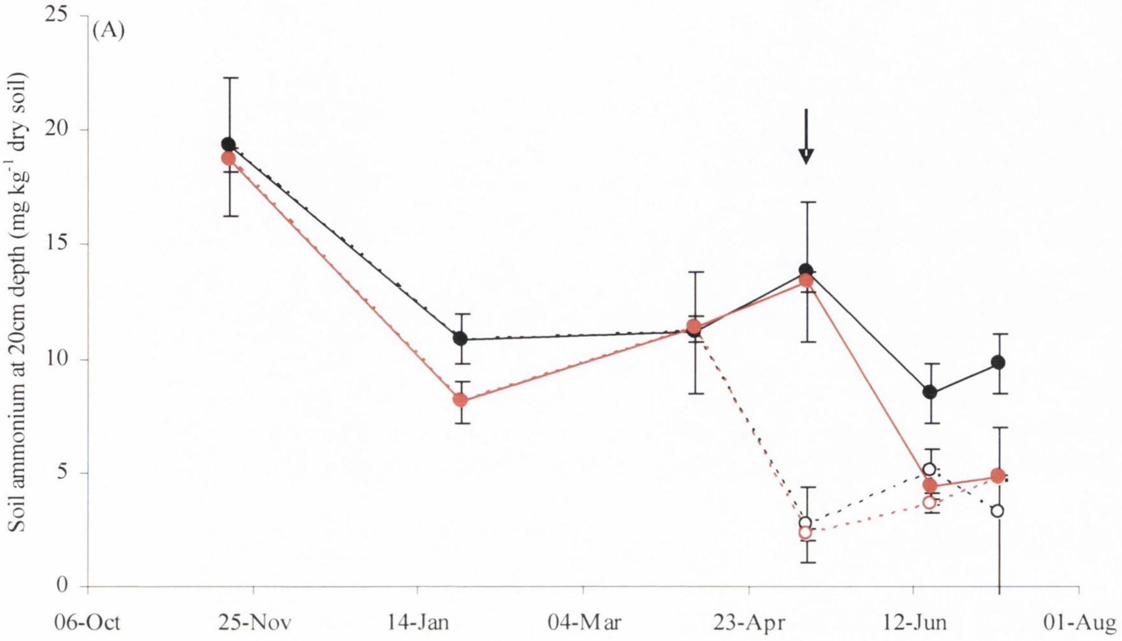
A 2-way analysis of variance of the soil ammonium data for the large plots, illustrated in Tables 3.6 and 3.7, revealed no significant difference between soil ammonium concentration of the conventional and reduced tillage plots for 2003-2004 and 2005 respectively. However, soil ammonium from the fertilized conventional plots was significantly higher than from control conventional plots on the 11th of May 2004 ($P<0.001$) and the 13th of April 2005 ($P<0.01$) corresponding to the 2nd week following first fertilizer application and 1st week following second fertilizer application. Soil ammonium from fertilized reduced plots was significantly higher than from control reduced plots on 11th of May ($P<0.001$) 2004.

Table 3.6: Summary of 2-way ANOVA statistics for the large plot soil ammonium 2003-2004 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	3	120.9	40.30	6.92	0.0016
Time	5	1014	202.7	34.8	<0.0001
Interaction	15	220.2	14.68	2.52	0.0211
Residual (Error)	24	139.8	5.825		
Total	47	1494			

Table 3.7: Summary of 2-way ANOVA statistics for the large plot soil ammonium 2005 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	3	96.27	32.09	4.306	0.0280
Time	2	833.5	416.7	55.92	<0.0001
Interaction	6	61.52	10.25	1.376	0.2998
Residual (Error)	12	89.43	7.452		
Total	23	1081			



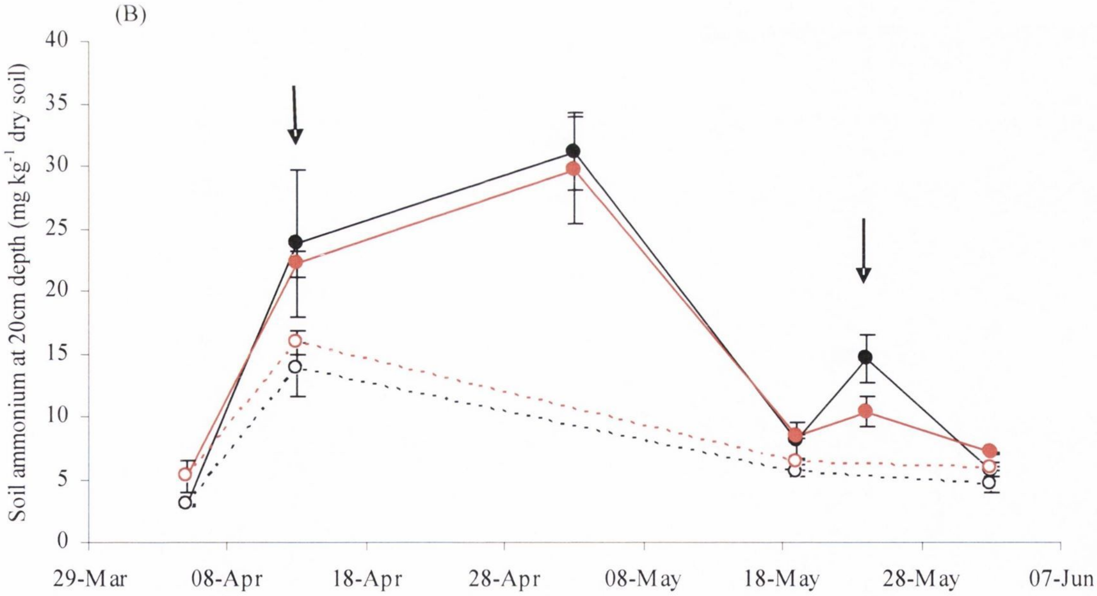


Figure 3.6: Soil ammonium concentrations in 2003-2004 (A) and 2005 (B) for control and fertilized conventional and reduced tillage plots. Symbols indicate: fertilized conventional (●), control conventional (○), fertilized reduced (●) and control reduced (○) tillage. Each point represents the mean ± se of four measurements. Arrows indicate first measurement following fertilizer application.

3.3.3 Nitrous oxide emissions

Nitrous oxide emissions were measured from November 2003 to August 2004 inclusive and from April 2005 to July 2005.

3.3.3.1 2003-2004 data set

Figure 3.7 illustrates the daily average N_2O emissions measured on a weekly basis from November 2003 to August 2004. Nitrogen fertilizer during this experimental period was incorporated once, on the 27th of April 2004. As with the grassland field, N_2O emissions showed a typical pattern throughout the experimental period. Emissions from the unfertilized plots were consistently low, with values ranging from -2.7 to 5.2 g N_2O-N $ha^{-1}d^{-1}$ and from -3.1 to 9.7 g N_2O-N $ha^{-1}d^{-1}$ for the conventional and reduced tillage plots respectively. The emissions from both tillage systems peaked after nitrogen fertilizer application to reach a maximum of 9 g N_2O-N $ha^{-1}d^{-1}$ for the conventional tillage plots, and 23.5 g N_2O-N ha^{-1} d^{-1} for the reduced tillage plots. Peaks were short lived with fluxes returned back to background level four weeks after fertilizer application.

Table 3.8 illustrates a 2-way analysis of variance of N_2O flux for the 2003-2004 data sets. No significant difference was observed between N_2O emission from control plots of conventional and reduced tillage systems, however N_2O emissions from fertilized reduced plots were significantly higher ($P<0.05$, <0.01) than those from fertilized conventional plots on the 6th and 11th of May corresponding to the 2nd and 3rd week after fertilizer application, and on the 24th of June ($P<0.001$) corresponding to the 8th week following fertilizer application. For the reduced tillage treatment, N_2O emissions from the fertilized plots were significantly higher than the control plots ($P<0.01$, <0.001) on the 6th and 11th of May and on the 1st and 24th of June ($P<0.05$, <0.001). No significant difference was observed between the fertilized and control plots for the conventional tillage treatment.

Table 3.8: Summary of 2-way ANOVA statistics for the large plot N_2O flux for 2003-2004 data sets.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	3	573.6	191.2	15.69	< 0.0001
Time	26	1286	49.47	4.06	<0.0001
Interaction	78	1626	20.84	1.71	0.005
Residual (Error)	108	1316	12.19		
Total	215	4802			

Table 3.9 illustrates the total N fertilizer application rate, mean cumulative emissions of N_2O and EFs for the period from April to August 2004. For both tillage plots, cumulative N_2O was increased by N fertilizer application. The EF of the conventional tillage was very low compared with that of the reduced tillage.

Table 3.9: Total amount of N-fertilizer applied, cumulative N_2O-N emitted and emission factors of conventional and reduced tillage during the period April –August 2004.

Treatment	Total N input (kg N ha^{-1})	Cumulative N_2O-N (kg N_2O-N ha^{-1})	Emission factors (%)
2004			
Conventional	140	0.261 ± 0.08	0.1 ± 0.13
	0	0.168 ± 0.08	-
Reduced	140	0.756 ± 0.20	0.58 ± 0.1
	0	0.083 ± 0.01	-

Table 3.10 illustrates a one-way analysis of variance of the cumulative N_2O flux for 2004 data set. A Tuke post test revealed that the mean cumulative N_2O flux from the fertilized reduced tillage plots were significantly higher than the control reduced plots ($P<0.05$). No significant difference was found between the cumulative fluxes from fertilized and control conventional tillage or between conventional and reduced tillage plots.

Table 3.10: Summary of one-way ANOVA statistics for the large plot mean cumulative of N_2O flux for 2004 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	P value
Treatment (between column)	3	0.5456	0.1819	0.04
Residual (within column)	4	0.1058	0.0265	
Total	7	0.6514		

3.3.3.2 2005 data set

Figure 3.8 illustrates the daily average N_2O emissions measured on a weekly basis during the growing season of the crop from April 2005- July 2005. The same patterns of nitrous oxide emissions as in 2004 were observed. The emissions from control plots were low and ranged from -1.3 to 8 g N_2O-N $ha^{-1}d^{-1}$ and from -1.3 to 9.2 g N_2O-N $ha^{-1}d^{-1}$ for the conventional and reduced tillage plots respectively. Emissions from both tillage treatments peaked following nitrogen fertilizer application, reaching maximum value of approximately 24 g N_2O-N $ha^{-1}d^{-1}$ for both tillage systems following the second fertilizer application.

Table 3.11 illustrates a 2-way analysis of variance of N_2O flux for the 2005 data set. Although the effect of tillage was not significant, for the conventional tillage treatments N_2O emissions from the fertilized plots were significantly higher ($P<0.01$, <0.05, <0.001, <0.05) than that from the control plots on the 17th, 19th and 24th of May and the 15th of June which corresponded to the 1st, 2nd, 3rd and 5th week following second fertilizer application. For the reduced tillage treatments, N_2O emissions from the fertilized plots were significantly higher than that from the control plots on the 17th, 19th and 24th of May ($P<0.01$, <0.001, <0.001). Though no significantly higher peaks in N_2O were observed following the first application of fertilizer.

Table 3.12 illustrates the total N fertilizer application rate, mean cumulative emissions of N_2O and EFs for the period April to July 2005. For both tillage plots, cumulative N_2O was increased by N fertilizer application. The cumulative emissions and EFs of the conventional and reduced tillage were approximately similar.

Table 3.11: Summary of 2-way ANOVA statistics for the large plot N_2O flux for 2005 data set.

Source of variation	DF	Sum of squares	Mean square	F	P value
Treatment	3	2001	667.1	40.54	< 0.0001
Time	11	2166	196.9	11.97	<0.0001
Interaction	33	1106	33.51	2.04	0.012
Residual (Error)	48	789.9	16.46		
Total	95	6063			

Table 3.12: Total amount of N applied, cumulative N_2O-N emitted and emission factors of conventional and reduced tillage during April- July 2005.

Treatment	Total N input (kg Nha^{-1})	Cumulative N_2O-N (kg N_2O-Nha^{-1})	Emission Factors (%)
Conventional	159	0.985 ± 0.16	0.6 ± 0.25
	0	0.15 ± 0.05	-
Reduced	159	0.944 ± 0.27	0.5 ± 0.19
	0	0.17 ± 0.02	-

Table 3.13 illustrates a one-way analysis of variance of the cumulative flux for the 2005 data set. A Tuke post test revealed that the cumulative fluxes of N_2O from fertilized conventional and reduced tillage plots were significantly higher ($P<0.05$) than that from control plots.

Table 3.13: Summary of one-way ANOVA statistics for the large plot mean cumulative of N_2O flux for 2005 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	P value
Treatment (between column)	3	1.297	0.4322	0.03
Residual (within column)	4	0.2028	0.0507	
Total	7	1.499		

A comparison between the emission factors of the conventional and reduced tillage systems revealed no statistically significant difference between conventional and reduced tillage systems throughout the experiment.

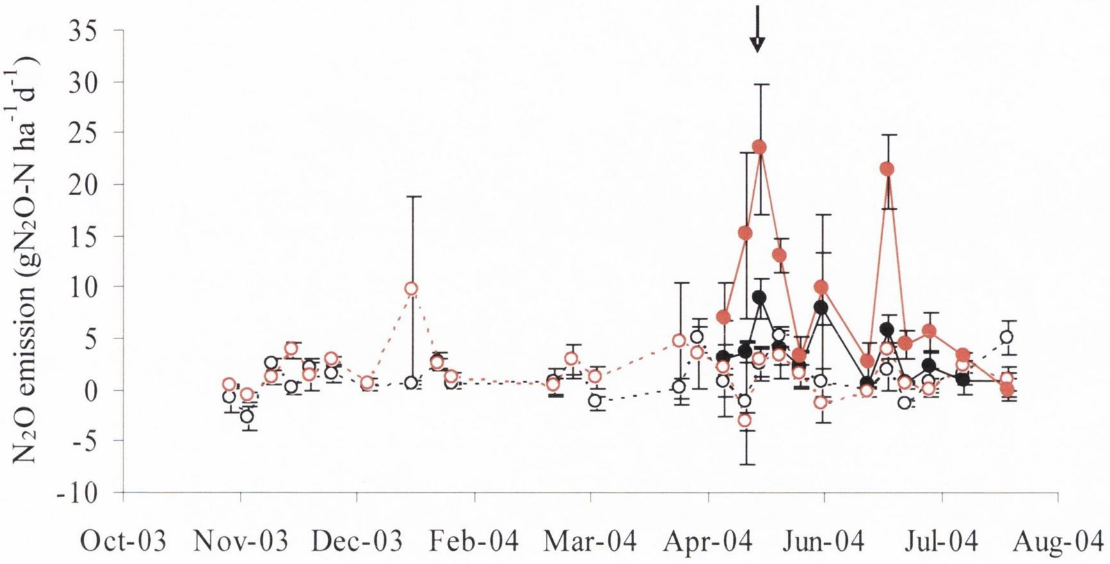


Figure 3.7: Daily N_2O emissions measured on a weekly basis from conventional and reduced tillage plots in 2003-2004. Symbols indicate tillage/fertilizer combination at which N_2O flux was measured: fertilized conventional (●), control conventional (○), fertilized reduced (●) and control reduced (○). Arrows indicate first measurement following fertilizer application. Each point represents the mean ± se of two-six measurements.

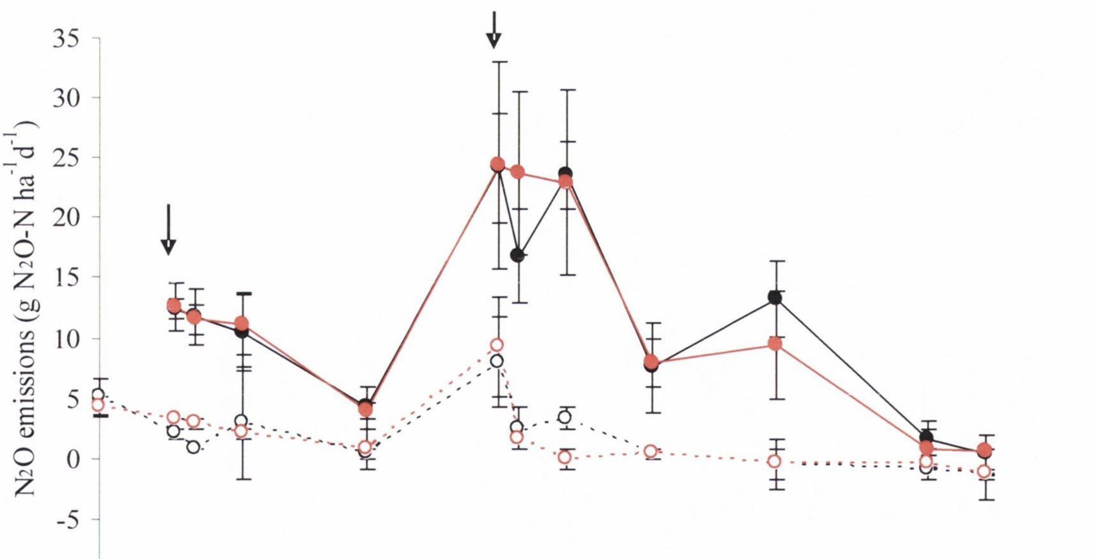


Figure 3.8: Daily N_2O emissions measured on a weekly basis from conventional and reduced tillage in 2005 season. Symbols indicate tillage/fertilizer combination at which N_2O flux was measured: fertilized conventional (●), control conventional (○), fertilized reduced (●) and control reduced (○). Each point represents the mean ± se of two-six measurements. Arrows indicate first measurement following fertilizer application.

3.3.4 Multiple regression analysis

A multiple regression of the single factors of soil nitrate, soil ammonium, soil temperature and soil moisture content vs log N_2O flux as the Y variable was carried out (Appendix 1), results of which are given in Table 3.14. Accepting a threshold probability of 95%, only the concentration of nitrate in the soil at the time of flux measurement shows any correlation with emissions of N_2O with an r^2 of 37%. However a best fit linear regression, that accounted for 42% of the variations, was calculated by including the interaction of soil moisture with both soil nitrate and soil temperature in the analysis and excluding the less correlated factors, the results of which is illustrated in Table 3.15. This regression revealed that the interaction between soil moisture and nitrate is significantly correlated with the flux ($P = 0.005$).

Table 3.14: Results of the multiple regression analysis of log measured flux with soil nitrate, ammonium, temperature and moisture content.

Source	Sum of Square	DF	Mean Square	F-ratio
Regression	4.00287	4	1.00072	4.73
Residual	4.44655	21	0.21174	
Variable	*Coefficient*	*S.E of Coefficient*	*t-ratio*	*Probability*
Constant	-0.402977	0.9573	-0.421	0.8781
Nitrate	0.0364972	0.013	2.81	0.0106
Log ammonium	0.14743	0.3647	0.404	0.6901
Temperature	0.00886918	0.03776	0.235	0.8166
Soil moisture	0.00219711	0.03177	-0.0692	0.9455

Table 3.15: Results of the best fit multiple regression analysis of log N_2O flux with moisture content, soil temperature and interaction between soil moisture and both soil nitrate and soil temperature.

Source	Sum of Square	DF	Mean Square	F-ratio
Regression	4.32855	4	1.08214	5.51
Residual	4.12087	21	0.196232	
Variable	*Coefficient*	*S.E of Coefficient*	*t-ratio*	*Probability*
Constant	5.11443	3.189	1.6	0.1237
Moisture*temperature	0.0126512	0.007663	1.65	0.1136
Moisture*nitrate	0.00171068	0.0005377	3.18	0.0045
Soil temperature	-0.289416	0.1812	-1.6	0.1251
Soil moisture	-0.230448	0.1367	-1.69	0.1066

3.3.5 Correlation of N_2O flux with soil nitrate

Figure 3.10 illustrates the relationships between soil nitrate with log N_2O flux. Linear correlations best describe the relationships, the equations for which accounting for 47%.

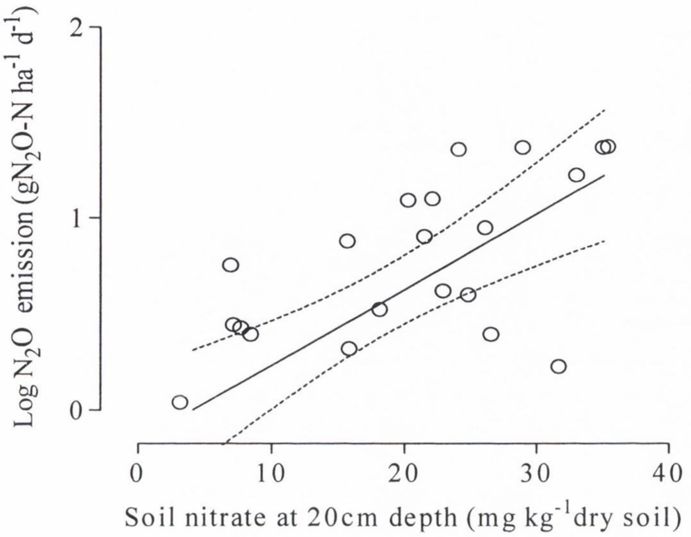


Figure 3.9: Correlation between soil nitrate and log N_2O emissions for 2004 and 2005 data combined. $y = 0.039x - 0.158$, ($r^2 = 0.47$). The dotted lines representing the 95% confidence interval.

3.4 Discussion

Results described in this Chapter concern the determination of N_2O emission factor for a spring barley crop managed under conventional and reduced tillage. In addition a multiple regression has been carried out to determine the major influencing factor(s) on N_2O flux.

With regard to cumulative emissions of N_2O over the growing season for 2004 and 2005, no statistical difference was observed between the two tillage treatments although, as expected, fertilizer application increased N_2O flux. This pattern was also seen in the calculation of the EF for both years where again no effect of tillage was observed. Interestingly, although a low EF value of 0.1 ± 0.13% was calculated for the conventional tillage plots in 2004, this was not significantly different from the following year's value of 0.6 ± 0.25%. As reduced tillage has been proposed as a means of reducing greenhouse gas emissions from agriculture, some comment is required. In effect what one is seeing is a slight increase in cumulative N_2O flux, in the first year, in the fertilized reduced tillage plots, although this increase was not statistically significant (Table 3.9). In the following year there is no difference at all (Table 3.12). Such an initial increase in N_2O flux from reduced or no-tillage plots has been a consistent observation in the literature (Aulakh *et al.*, 1984; Bouwman, 1996; Baggs *et al.*, 2000; Linn and Doran, 1984; Baggs *et al.*, 2003). A long-term study by Six *et al.*, (2004) has also shown an increase in N_2O flux from reduced tillage plots over the first 10 years, following which emissions decline. Therefore our experiment needs to be continued for at least another 8 years to possibly see any difference, although Six *et al.* (2004) has suggested a period of 20 years to see mitigation effects of reduced tillage on greenhouse gas emissions in general.

That the experiment requires to be continued for a significant amount of time may also explain why reduced tillage has had no consistent effect on the retention of soil moisture, or differences in soil nitrate and ammonium between treatments (Figures 3.2, 3.5 and 3.6). This is in contrast to Belvins *et al.* (1971), Cox *et al.* (1990) and Ball *et al.* (1999), who reported a greater soil moisture content following the adoption of no-till in cereal crops. It may also be the case that in our study, limiting rainfall over the growing season when compared with the 30 y mean, limited the extent to which differences in soil moisture between treatments could occur.

With regard to weekly flux values, our results are similar to those obtained from the cut and grazed pasture and are in agreement with those summarized by Bouwman, (1996), where N_2O emissions from fertilized soils are decisively influenced by N supply. As mentioned in Chapter 2, the significant differences in cumulative N_2O emissions observed between the control and fertilized plots are due to peaks in N_2O flux following fertilizer application.

Although an annual flux was not measured directly from the arable crop, the longest span of measurements is available from November 2003 to August 2004 (Figure 3.7). For the control plots only, an overall daily mean value calculated over this time period was 1.2 ± 0.37 and 1.8 ± 0.45 g N_2O-N ha^{-1} d^{-1} (conventional and reduced tillage), equivalent to 0.43 ± 0.14 and 0.64 ± 0.17 kg N_2O-N ha^{-1} y^{-1}. These are lower than the annual background emissions determined for the cut and grazed pasture and for that used by the IPCC (1 kg N_2O-N ha^{-1} y^{-1}). It is most likely that grazing of the control plots in the pasture has accounted for the higher value. Using the EFs determined for 2004, coupled with the fertilizer application rate of 140 kg N ha^{-1} gives an annual flux for the fertilized plots of 0.6 ± 0.1 and 1.4 ± 0.1 kg N_2O-N ha^{-1} for conventional and reduced tillage respectively; approximately 25 to 56% of the annual N_2O emissions calculated for the cut and grazed pasture over the same time period.

Comparable studies in the literature for cereal crops vary according to each study. A far better comparison therefore would be the EF, either determined in the short or long-term as discussed by Bouwman *et al.* (2002). In our study there was no significant difference between EFs calculated for both tillage treatments in 2004 and 2005, although the value for conventional tillage in 2004 was less than 20% of the value for the reduced tillage plots. It is uncertain as to why this is the case. I have argued in Chapter 2 that limiting rainfall occurred at the time of fertilizer application in 2004 (155 mm for March to May, as opposed to 212 mm for the same period in 2005, and a 30 year mean of 169 mm). This may have affected the tillage treatments unequally. Evidence for this is apparent in the difference between the two fertilizer-induced N_2O peaks that occurred on the 11th of May. For the conventional plots the average peak flux was 8.9 g N_2O-N ha^{-1} d^{-1} as opposed to 23.5 g N_2O-N ha^{-1} d^{-1} for the reduced tillage plots, although a similar difference in soil moisture was not recorded at this date (Figure 3.2), and neither did the concentration of soil nitrate differ between the two treatments (Figure 3.5). Accepting that this EF may be an outlier, an overall EF of approximately 0.56% can be calculated. This is lower than the EF for the cut and grazed grassland discussed in the previous chapter (0.83 %). However, literature EF values for cereal crops are extremely variable, ranging from 0.2 to 8% (Eichner, 1990; Kaiser *et al.,* 1998; Smith *et al*., 1998, Dobbie *et al*., 1999) and are dependent upon temperature, moisture and soil type (Flechard *et al*., 2006). Using the predictive model DNDC for the small plot trial in the cereal field, as described in Chapter 6, which accounts for interactions between soil temperature, moisture, N-content, soil type and management on N_2O emissions, gave an overall EF value of 0.45%. This is discussed further in Chapter 6.

As with the cut and grazed grassland, a multiple regression of the flux data against soil moisture, temperature, soil ammonium and nitrate was carried out, where soil nitrate and interaction between soil nitrate and soil moisture were found to be the significant determinants of N_2O flux (Tables 3.14 and 3.15). This make soil moisture together with soil nitrate as a co-required factors for higher N_2O flux as discussed earlier in Chapter 2. This will be discussed further in Chapter 5.

A comparison of the two regression slopes for log N_2O flux against soil nitrate (grassland and cereal field: large plots) is shown in Figure 3.10. An analysis of the slopes revealed them to be statistically not significantly different ($P = 0.7$). Hence an overall regression equation can be calculated. Here:

Log N_2O flux = 0.039 (soil nitrate) – 0.032.

This equation accounts for 42% of the variance of the data and would suggest that the two soils are similar with regard to their capacity for N_2O flux as a function of available nitrate. It also suggests that as with the cut and grazed pasture, the bulk of N_2O flux is derived from denitrification rather than nitrification.

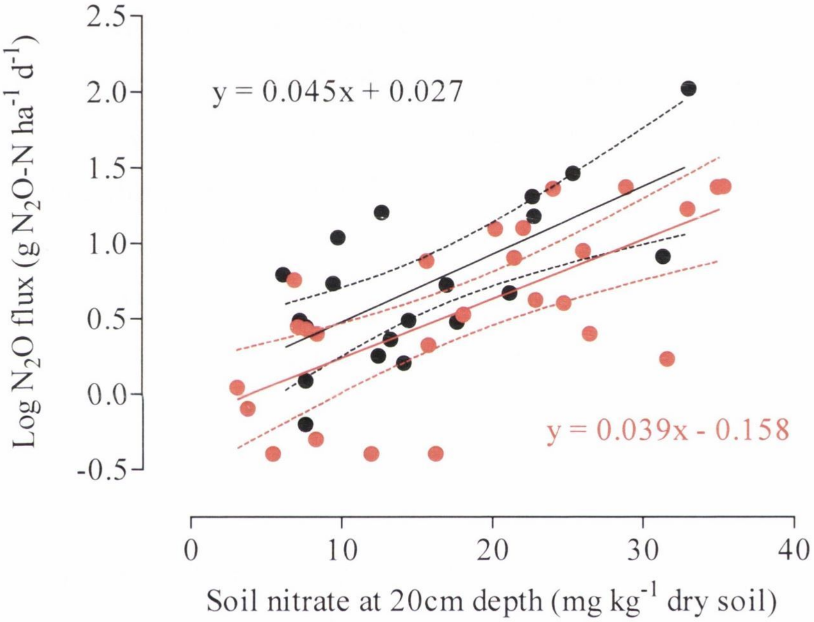


Figure 3.10: Correlation between log N_2O emissions and soil nitrate for both the grassland (●) and the large plots spring barley field (●). Dotted lines indicate 95% confidence interval. Each point represents the mean ± se.

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Chapter 4: Nitrous oxide emissions from an arable field under conventional and reduced tillage and different N fertilizer rates– small plots

4.1 Introduction

The use of nitrogen fertilizer in agriculture over the past 100 years has dramatically changed the global nitrogen budget (Vitousek *et al.*, 1997). For instance, in 1950 global synthetic N input into soils constituted 7% of the total N input of ≈ 56Tg. In 1996 however synthetic N input was ≈ 43% of a greater total input of ≈ 190 Tg N (Mosier, 2001). Therefore over this 46 years period, the global input of synthetic N into soil has increased from 4 Tg to 82 Tg.

At present, this anthropogenic input is considered equal in quantity to that from biological N fixation (Galloway, 1998). In Ireland approximately 443 tonnes of nutrient N were applied to agricultural soils in 1996 (IFA, 2000). This increased input of N has been considered important for optimum crop yields.

In terms of nitrification and denitrification, the relationship between N inputs and N_2O production is complex. In particular N_2O emissions from agricultural soils exhibit a threshold response to N inputs (McSwiney *et al.*, 2005). At low levels of soil N competition between plant uptake and soil microbes favours plant assimilation, such that proportionally less N_2O is produced than at higher fertilizer concentrations. In other words, if plants are better competitors for soil N than the N_2O producing microbes, N_2O fluxes will be relatively low (McSwiney *et al.*, 2005).

As discussed in Chapters 2 and 3, N_2O emissions also depend on a complex interaction between soil properties, climatic factors and agricultural practices, the main soil factors being NH_4^+ and NO_3^- concentration (Ball *et al.*, 1997; Castaldi and Smith, 1998; Senevirante and Van Holm, 1998) soil aeration status and soil water content (Carran *et al.*, 1995; MacKenzie *et al.*, 1998; Teira-Esmatges *et al.*, 1998), microbial activity (Ineson *et al.*, 1998; Kaiser *et al.*, 1998) and finally soil pH and soil temperature

(Mahmood *et al.,* 1998). Due to the complexity of interaction, one single factor may not always correlate with N_2O flux.

Worldwide, it has been stated that N_2O emission from agriculture can be most effectively reduced in high intensity agricultural systems by minimizing surplus N (IPCC, 2001a). This can be achieved through the application of a range of measures aiming to synchronize N application with crop demand, including the application of N fertilizer taking into account soil and plant N-content (Eichner, 1990; Van Kessel *et al.*, 1993). The results in this Chapter refer to two years of field experiments, where not only soil tillage, but also N-fertilizer levels were varied.

Due to the large number of treatments required, this experiment was a smallplot design established on the same field as the large plot experiment described in Chapter 3. In addition to the effect of varying N on N_2O flux, the relationship between crop yield and N-induced flux is also discussed.

4.2 Materials and Methods:

4.2.1 Experimental site

Measurements of N_2O flux were carried out for two consecutive seasons on a spring barley field at the Oak Park Research Centre, Carlow, Ireland; April - August 2004 and April - August 2005. The soil is classified as a sandy loam to loamy soil with a pH of 7 and a mean organic carbon and nitrogen content at 15 cm of 19.4 and 1.9 g kg^{-1} dry soil respectively. Experimental site and tillage management is as described in Chapter 3.

4.2.2 Fertilization treatments

In 2004, three rates of N-fertilization (N_1 = 140, N_2 = 70 and N_3 = 0 kg N ha^{-1}) were applied once on 27th of April 2004, whereas in 2005, two fertilizer applications took place on 12th of April 2005 (N_1 = 106, N_2 = 53 and N_3 = 0 kg N ha^{-1}) and on the10th of May 2005 (N_1 = 53, N_2 = 26 and N_3 = 0 kg N ha^{-1}). The total amount of N-fertilization rates applied in 2005 were therefore N_1 = 159, N_2= 79 and N_3 = 0 kg N ha^{-1}. Fertilizer was applied in the form of CAN.

4.2.3 Experimental design

The experimental area was divided in to two blocks containing six randomized main plots, three conventional (C) and three reduced (L) tillage. Each main plot was divided into two subplots containing different fertilizer treatments (N_1 = high N, N_2 = medium N and N_3 = 0 N). In total 24 x 6 x 25 m were used representing all treatments, each plot containing a 0.27 m^2 chamber. Treatments were randomly distributed and each treatment was replicated four times (Figures 4.1, 4.2, 4.3 and 4.4).

4.2.4 Measurement of N_2O flux

Nitrous oxide fluxes were measured from 24 chambers as described in Chapter 2. Measurements were taken every week except for times of fertilizer application where sampling was increased to 2 times per week.

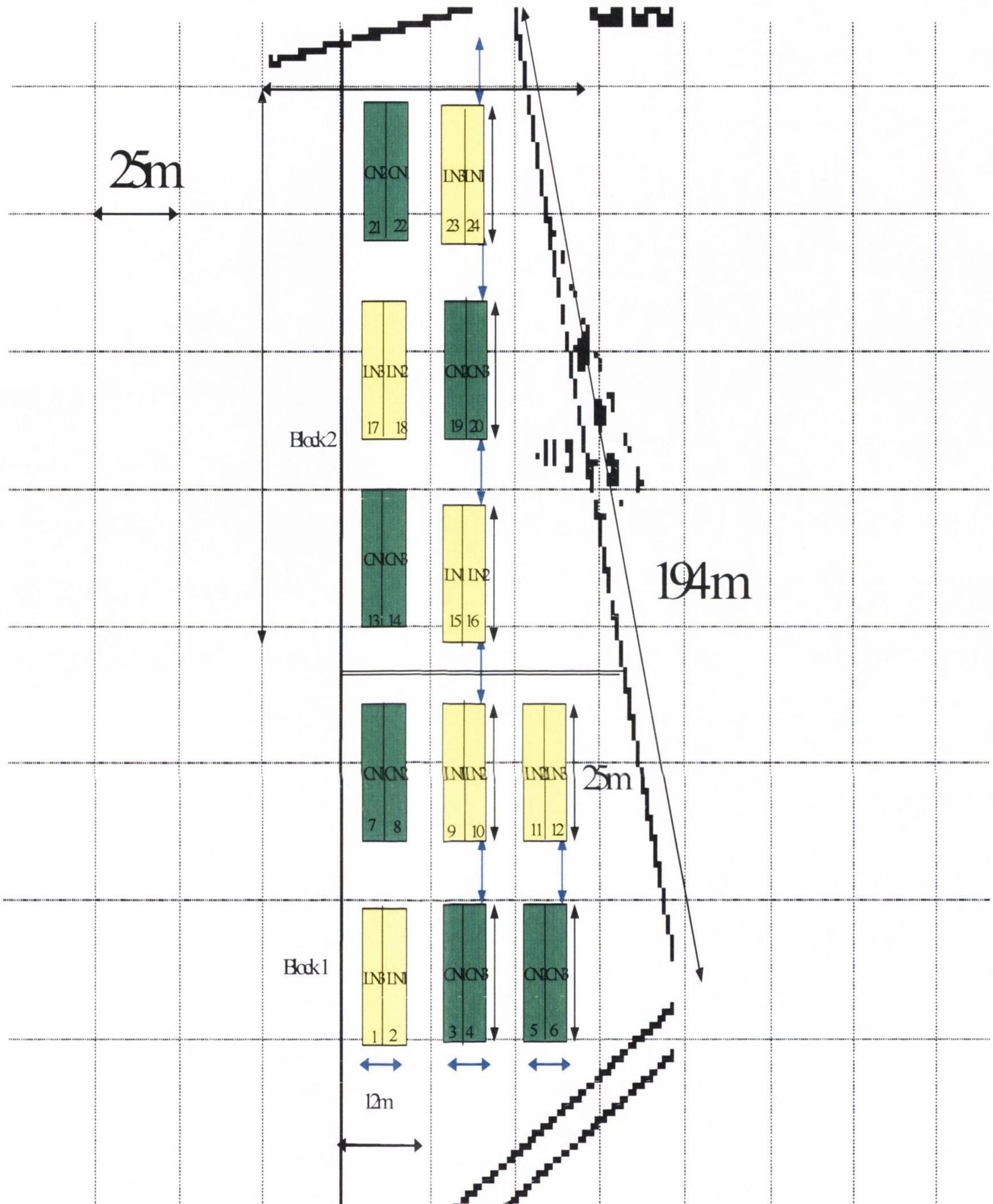


Figure 4.1: Small plot experimental design (See 4.2.2 and 4.2.3 for list of treatments)

Figure 4.2: Experimental field showing conventional and reduced tillage plots

Figure 4.3: Experimental field showing growing barley and installed chambers

Figure 4.4: Experimental field showing positioning of N_2O chambers

4.2.5 Soil temperature, moisture, WFPS, nitrate and ammonium

Measurements of soil temperature, moisture and WFPS were made, as described in Chapter 2, on days of N_2O measurements. Soil N (nitrate and ammonium) was determined either every month (2004) or every week following fertilizer application (2005), again as described in Chapter 2.

4.2.6 Grain yields

Crop grain yield samples representing all treatments and tillage systems were collected from the field by the Teagasc Research Centre team. Average grain yields at 15% moisture were determined for each N fertilizer/tillage combination.

4.2.7 Statistics

All statistical analyses were carried out using SPSS, PRISM (GraphPad, San Diego, USA) and Data Desk (Data Description Inc. New York, USA) software packages. Flux data was checked for normal distribution and log transformed where appropriate. Both 1-way and 2-way analysis of variance were applied to the flux, soil N data, soil moisture and temperature and a multiple regression carried out for N_2O flux vs soil nitrate, ammonium, moisture and soil temperature. Grain yield averages, standard error and ANOVA tables were carried out for the 15% moisture grain yield.

4.3 Results

4.3.1 Soil moisture and temperature

Figures 4.5 and 4.6 relate the total weekly rainfall data collected at the Teagasc Oak Park Research Centre weather station with direct average daily measurements of soil moisture content taken from conventional and reduced tillage plots at the time of N_2O measurements respectively. As mentioned in Chapter 3, the relationship between rainfall and soil moisture content was strong and limiting rainfall has resulted in low soil moisture contents for both tillage systems. Hence soil moisture ranged from a minimum of 8.9%, applicable to WFPS of 21%, in the summer of 2004 to a maximum of 23%, applicable to 55% in the spring of 2005 (Appendix 6).

Tables 4.1 and 4.2 illustrate the results from 2-way analyses of variance of soil moisture for 2004 and 2005 respectively. In both cases time and treatments were significant. However, a Bonferroni post-test revealed differences between treatments to be due to N-fertilizer application rate and not tillage, with no consistent pattern being observed over the two years. In 2004 growing season, for instance, significant differences in soil moisture between the measurements were limited to 2 days. Here the mean soil moisture of the LN_3 plots was significantly higher ($P<0.05$) than that of the LN_1 plots on the 20th of June and the mean soil moisture of the CN_1 plots was significantly higher ($P<0.05$) than that of the CN_2 and CN_3 plots on the 17th of May.

In the 2005 growing season, significant differences in soil moisture between treatments occurred on only three days. Here the mean soil moisture of the CN_3 plots was significantly higher ($P<0.05$) than of CN_2 plots on the 30th of June and 14th of July, and the mean soil moisture of LN_3 plots was significantly higher ($P<0.05$) than the of LN_1 plots on the 2nd of May.

Figures 4.7 and 4.8 compare the average daily soil temperature at a depth of 10cm, for each tillage/fertilizer treatment. Soil temperatures were measured at the time of N_2O

measurements and ranged from a minimum of 7°C in the spring to a maximum of 20°C in the summer.

Table 4.1: Summary of 2-way ANOVA statistic for the soil moisture data set in 2004.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	5	300.6	60.11	7.72	<0.0001
Time	14	3882	277.3	35.6	<0.0001
Interaction	70	554.6	7.923	1.02	0.4494
Residual (Error)	270	2103	7.789		
Total	359	6840			

Table 4.2: Summary of 2-way ANOVA statistic for the soil moisture data set in 2005.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	5	364.3	72.86	10.55	<0.0001
Time	15	6842	456.1	66.02	<0.0001
Interaction	75	895.9	11.94	1.73	0.0008
Residual (Error)	288	1990	6.909		
Total	383	10090			

Tables 4.3 and 4.4 illustrate the results from 2-way analyses of variance of soil temperature for 2004 and 2005, where treatment, time and interaction were all significant. Unlike the large plot data, tillage has had an effect on soil temperature although on two days only, the 20th of July and 10th of August 2004, where soil temperature from the reduced tillage plots LN_2 and LN_3 were significantly higher ($P<0.001$, <0.05) than that from the conventional tillage plots CN_2 and CN_3. These differences being at the most 1°C.

Soil temperatures were also significantly different between different fertilizer application rates within the same tillage treatment, although again at most such differences were 1°C. For conventional tillage soil temperature of CN_3 plots was significantly higher than that of the CN_1 on the 6th of July 2004 and on the 31st of May, 16th of June and 14th of July 2005 ($P<0.001$), and was significantly higher than that of the CN_2 plots on the 20th of

July 2004 ($P<0.01$). Soil temperature of the CN_1 plots was significantly higher than that of the CN_2 plots on one day only, the 20th of July 2004 ($P<0.001$).

For the reduced tillage treatment, soil temperature of the LN_3 plots were significantly higher ($P<0.001$) than that of the LN_1 plots on the 6th of July and 10th of August 2004 and on the 16th of June and 17th of July 2005. Soil temperature of the LN_3 plots was also significantly higher ($P<0.001$) than that of the LN_2 plots on the 6th of July 2004 and on the 14th of July 2005.

Table 4.3: Summary of 2-way ANOVA statistic for soil temperature data set in 2004.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	5	12.04	2.409	10.89	<0.0001
Time	16	7089	443.1	2003.34	<0.0001
Interaction	80	45.92	0.5740	2.60	<0.0001
Residual (Error)	306	67.68	0.2212		
Total	407	7215			

Table 4.4: Summary of 2-way ANOVA statistic for soil temperature data set in 2005.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	5	8.307	1.661	7.91	<0.0001
Time	15	4136	275.8	1313.12	<0.0001
Interaction	75	28.97	0.3862	1.84	0.0002
Residual (Error)	288	60.48	0.2100		
Total	383	4234			

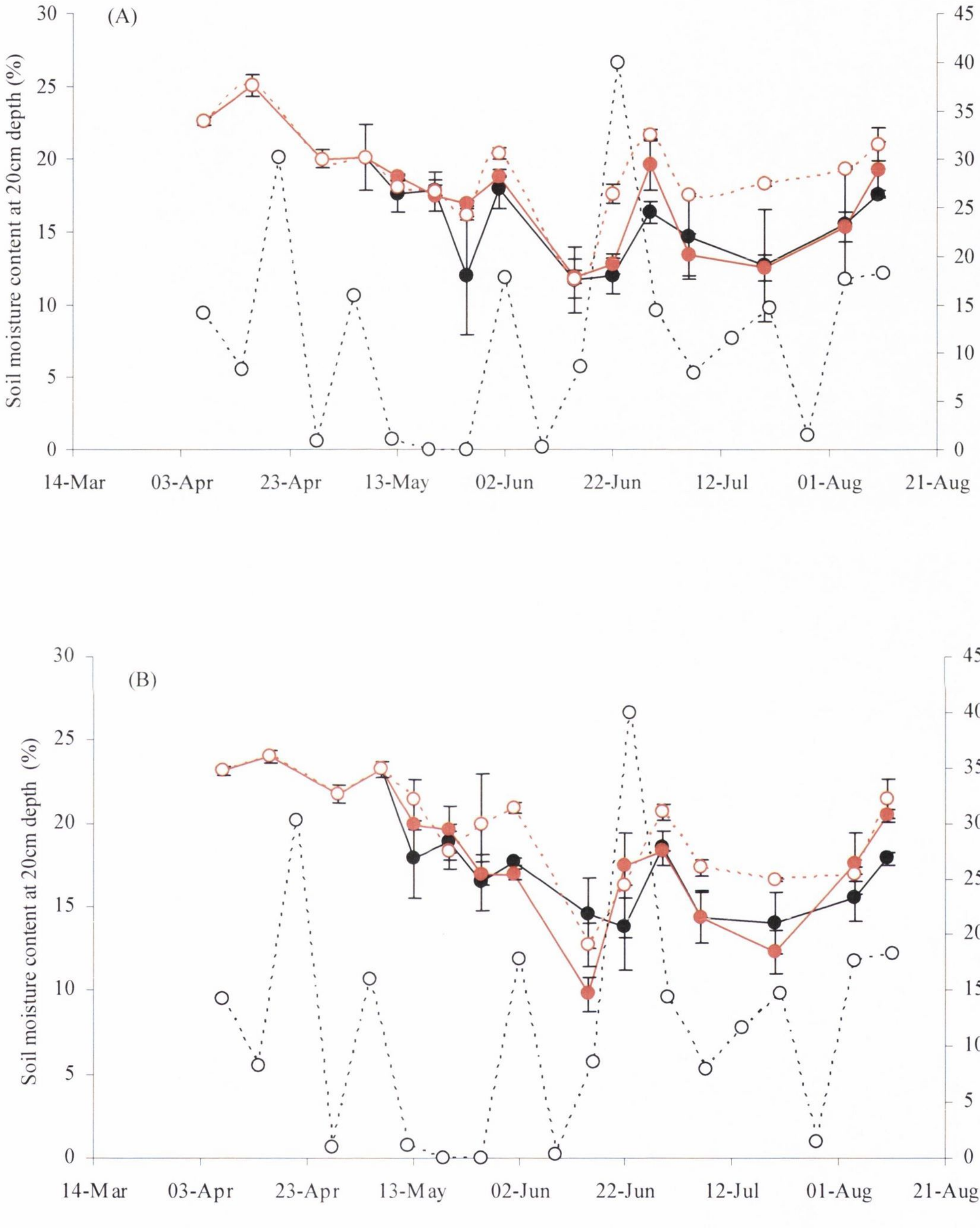
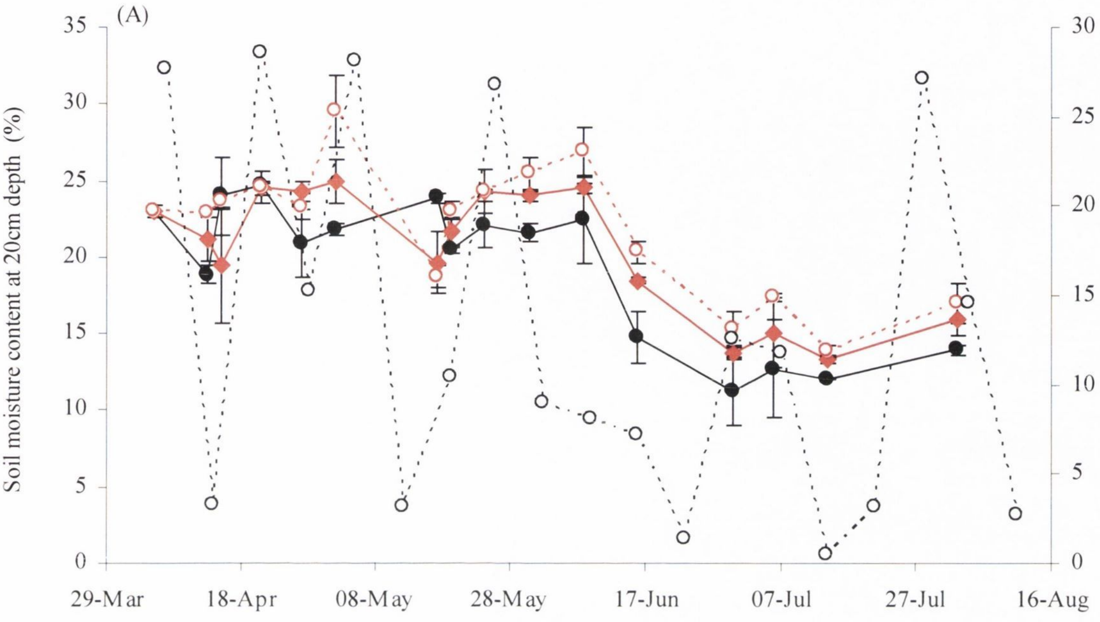


Figure 4.5: Weekly total rainfall data collected at the Teagasc Oak Park Research Centre weather station and average daily soil moisture contents from the conventional (A) and reduced (B) tillage plots for 2004. Symbols indicate soil moisture at the fertilizer rate level: N_1 (●), N_2 (●), N_3 (○) and weekly total rainfall (○).



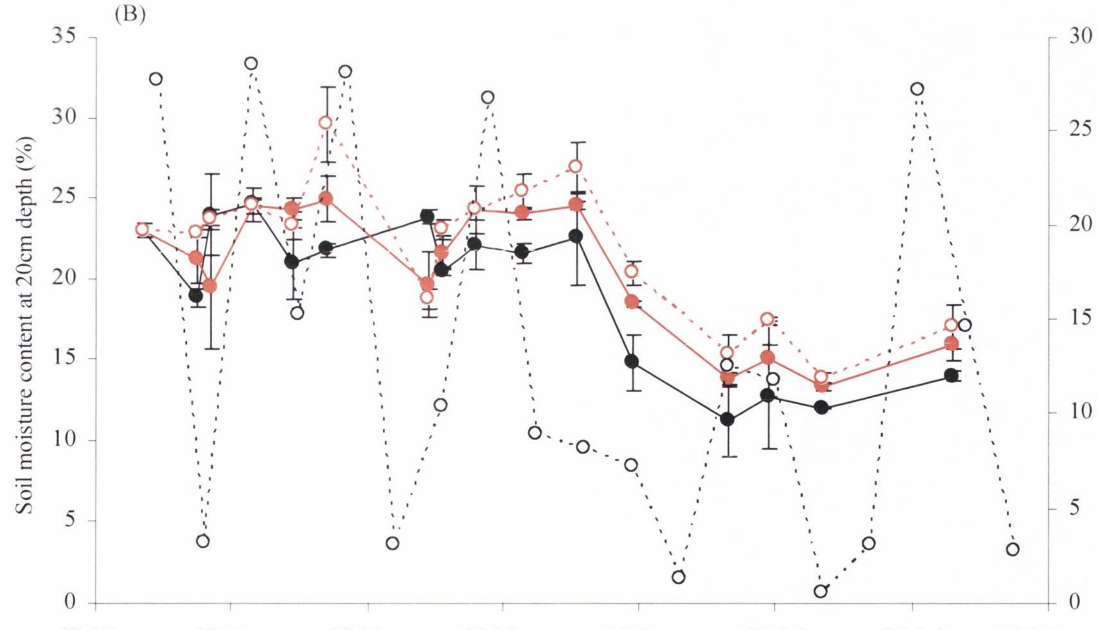
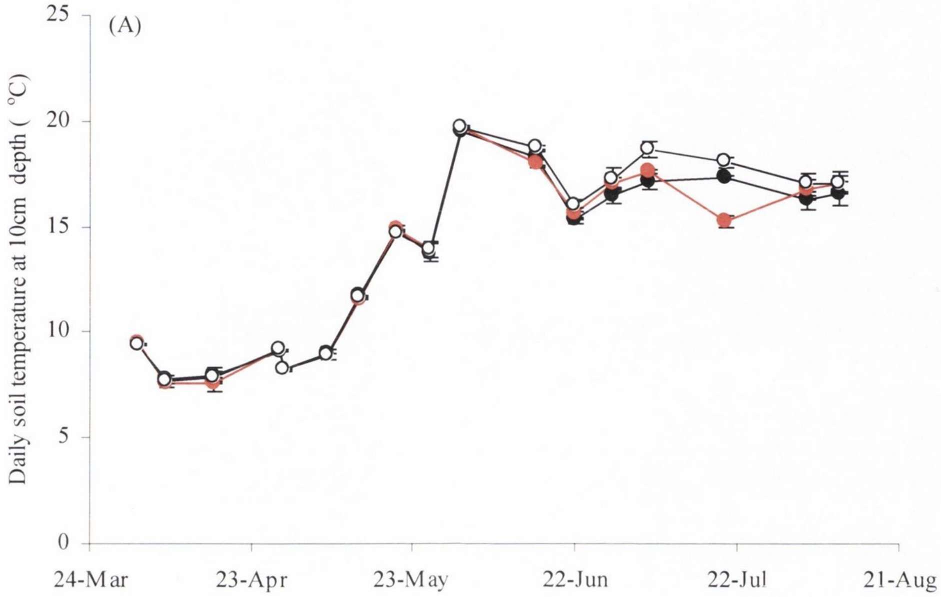


Figure 4.6: Weekly total rainfall data collected at the Teagasc Oak Park Research Centre weather station and average daily soil moisture contents from the conventional (A) and reduced (B) tillage plots for 2005. Symbols indicate soil moisture at the fertilizer rate level: N_1 (●), N_2 (●), N_3 (○) and weekly total rainfall (○).



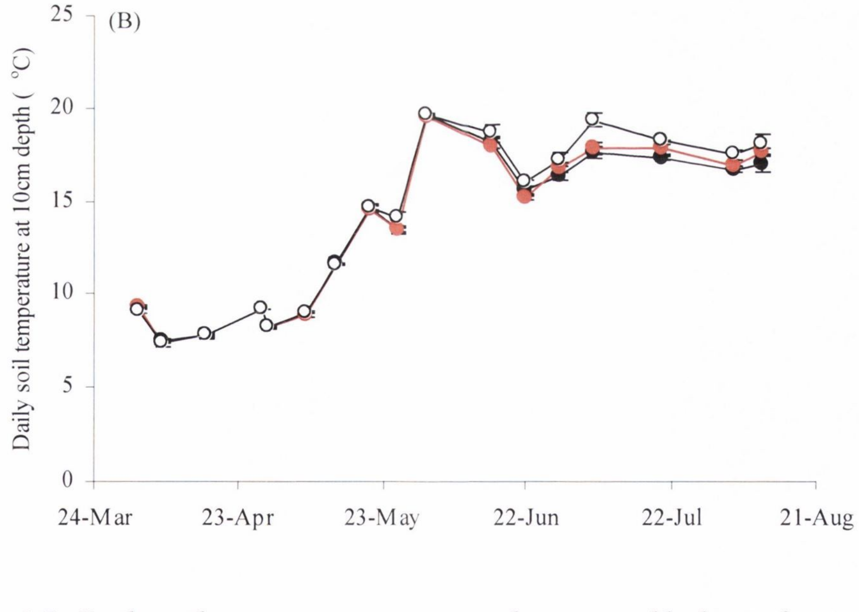
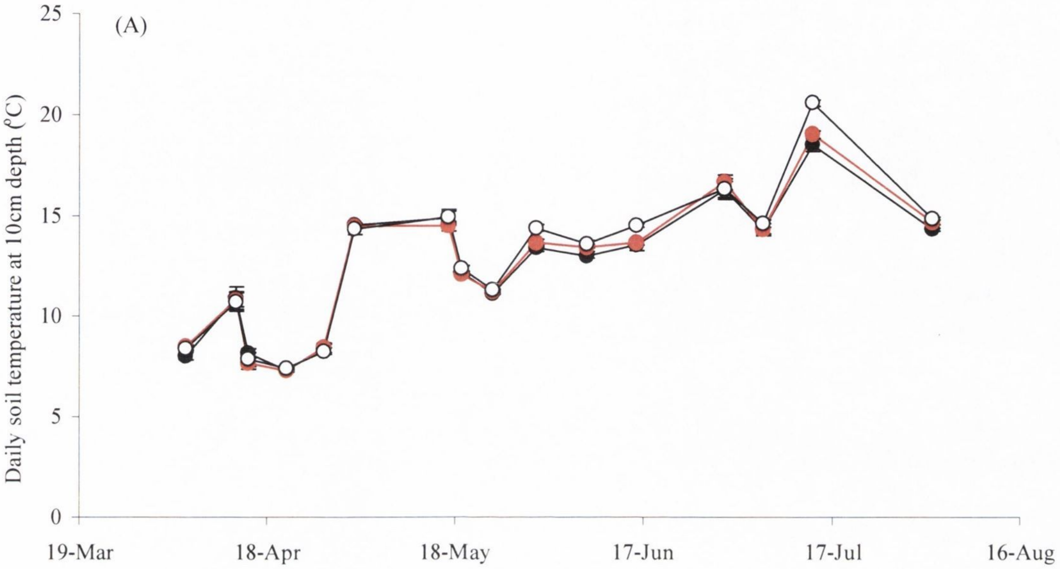


Figure 4.7: Daily soil temperatures measured on a weekly basis from conventional (A) and reduced (B) tillage plots for 2004. Symbols indicate soil temperature at the fertilizer rate level: N_1 *(●),* N_2 *(●) and* N_3 *(○). Each point represents the mean ± se of four measurements.*



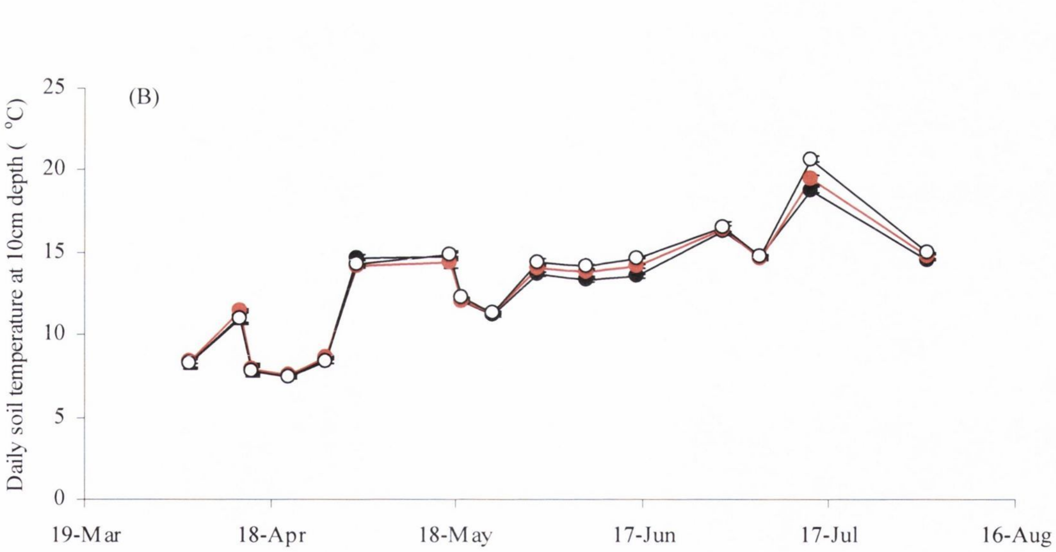


Figure 4.8: Daily soil temperatures measured on a weekly basis from conventional (A) and reduced (B) tillage plots for 2005. Symbols indicate soil temperature at the fertilizer rate level: N_1 (●), N_2 (●) and N_3 (○). Each point represents the mean ± se of four measurements.

4.3.2 Soil nitrate and ammonium

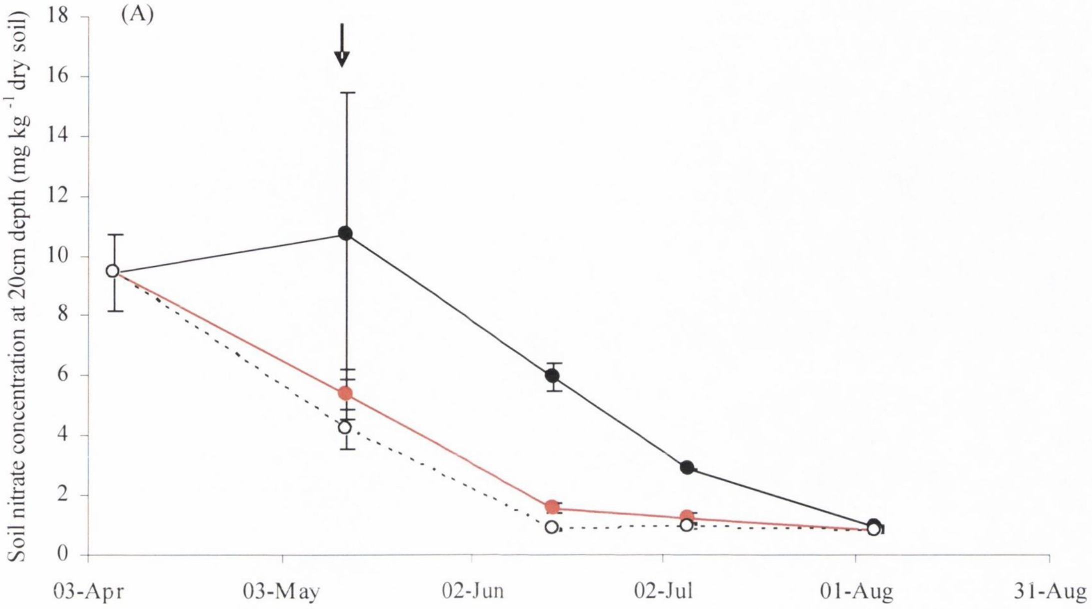
Figures 4.9 and 4.10 illustrate the change in soil nitrate concentration for the conventional and reduced tillage plots from April to August, 2004 and 2005 respectively. The concentration of soil nitrate corresponded with the time of fertiliser application. The concentration of soil nitrate in 2005 overall was significantly higher than in 2004.

Tables 4.5 and 4.6 illustrate the results from 2-way analyses of variance of soil nitrate for 2004 and 2005 respectively, in which treatment, time and interaction were all significant. However, with regard to significant difference between tillage treatments, this occurred on only one day in 2005, the 2nd of May, corresponding to the 3rd week following 2nd fertilizer application, where the concentration of soil nitrate for the CN_1 plots was significantly higher ($P<0.001$) than that for LN_1 plots. This difference was 18 mg kg^{-1} dry soil.

The greatest numbers of significant differences were associated between the three fertilizer treatments within a single tillage scheme. The maximum differences being approximately 8 and 40 mg kg^{-1} dry soil, between the control and highest fertilizer application rate for 2004 and 2005 respectively.

Table 4.5: Summary of 2-way ANOVA statistics for the soil nitrate 2004 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	5	80.09	16.02	6.521	0.0003
Time	4	674.3	168.6	68.63	<0.0001
Interaction	20	108.2	5.41	2.202	0.0245
Residual (Error)	30	73.69	2.456		
Total	59	936.3			



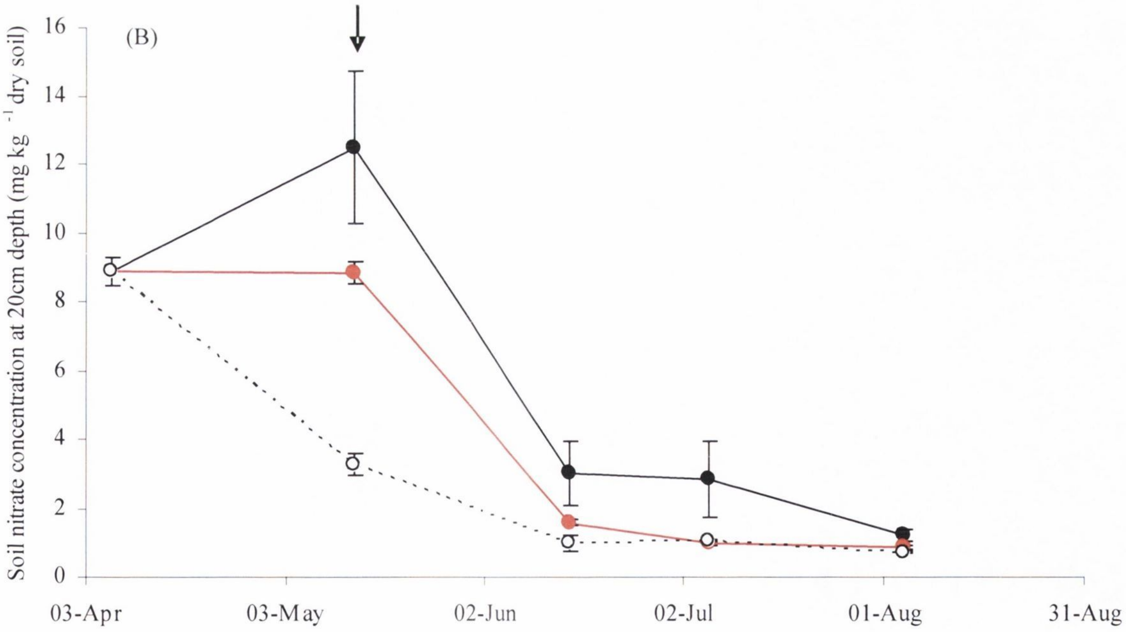
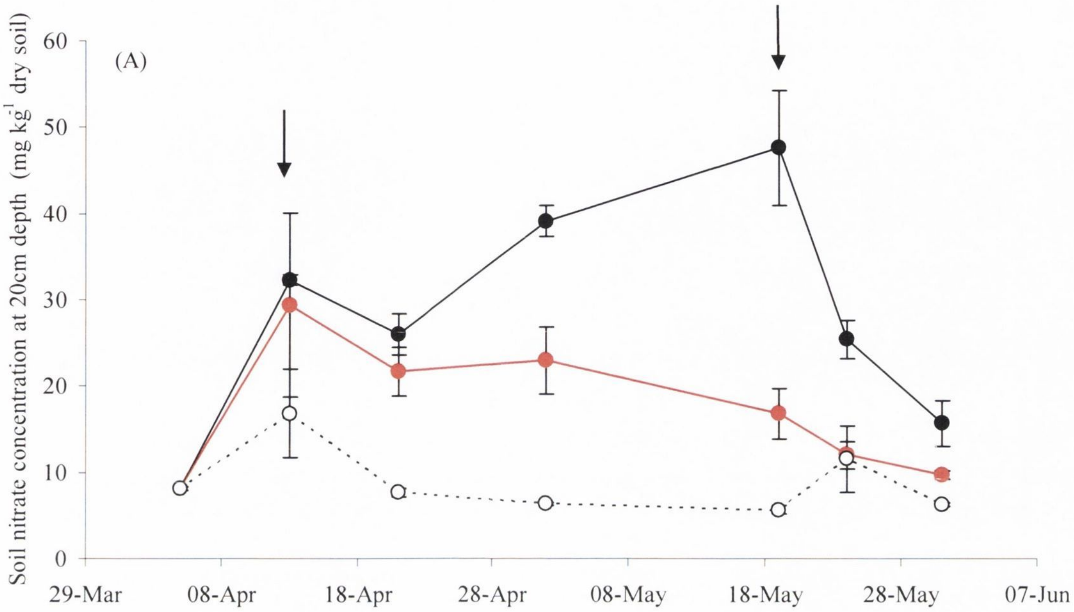


Figure 4.9: Soil nitrate concentration of the conventional (A) and reduced (B) tillage plots for 2004. Symbols indicate soil nitrate at the fertilizer rate level: N_1 *(●),* N_2 *(●) and* N_3 *(○). Arrows indicate first measurements following fertilizer application. Each point represents the mean ± se of four measurements.*



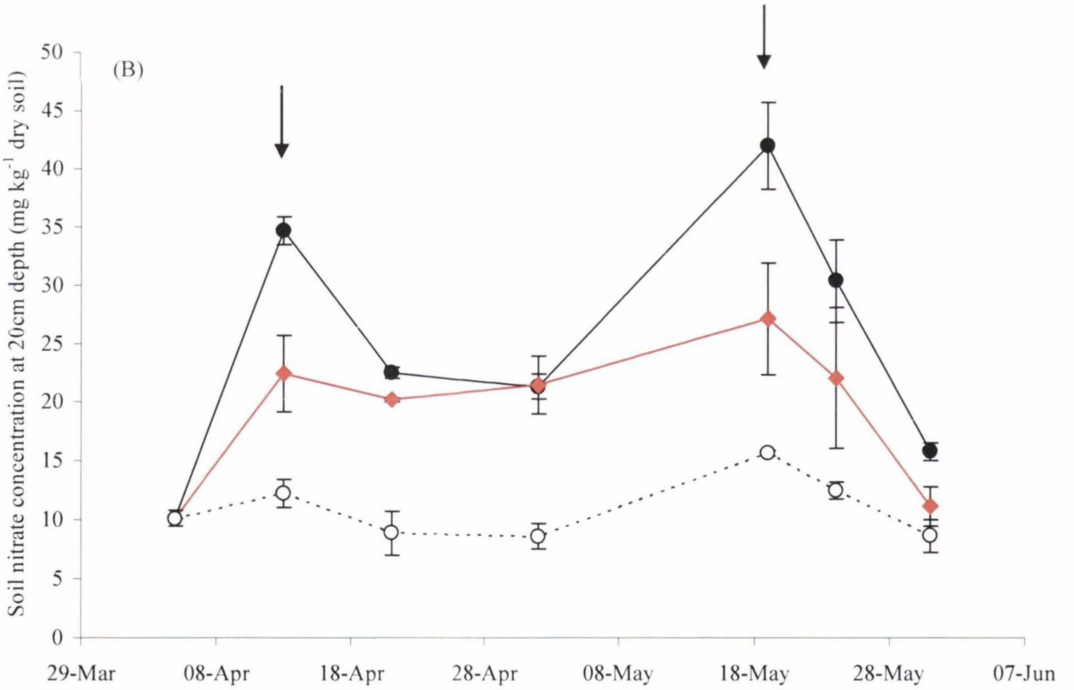


Figure 4.10: Soil nitrate concentration of the conventional (A) and reduced (B) tillage plots for 2005. Symbols indicate soil nitrate at the fertilizer rate level: N_1 (●), N_2 (●) and N_3 (○). Arrows indicate first measurements following fertilizer application. Each point represents the mean ± se of four measurements.

Table 4.6: Summary of 2-way ANOVA statistics for the soil nitrate 2005 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	5	3941	788.2	44.19	<0.0001
Time	6	2821	470.2	26.36	<0.0001
Interaction	30	2304	76.80	4.306	<0.0001
Residual (Error)	42	749.1	17.84		
Total	83	9816			

Figures 4.11 and 4.12 illustrate the change in soil ammonium concentration for the conventional and reduced tillage plots, from April to August 2004 and 2005 respectively. Overall soil ammonium concentration in 2005 was significantly higher than in 2004.

Tables 4.7 and 4.8 illustrate the results from 2-way analyses of variance of the soil ammonium 2004 and 2005, in which treatment, time and interaction were all significant. However, with regard to significant difference between tillage treatments, this occurred on only one day, the 13th of May 2004, corresponding to the 3rd week following fertilizer application, where the concentration of soil ammonium from CN_1 was significantly higher ($P<0.001$) than from LN_1. This difference was 11mg kg^{-1} dry soil.

The greatest numbers of significant differences were associated between the three fertilizer treatments within a single tillage scheme. The maximum differences being approximately 12 and 48 mg kg^{-1} dry soil, between the control and highest fertilizer application rate for 2004 and 2005 respectively.

Table 4.7: Summary of 2-way ANOVA statistics for the soil ammonium 2004 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	5	55.62	11.12	2.655	0.0421
Time	4	615.7	153.9	36.74	<0.0001
Interaction	20	235.4	11.77	2.810	0.0052
Residual (Error)	30	125.7	4.190		
Total	59	1032			

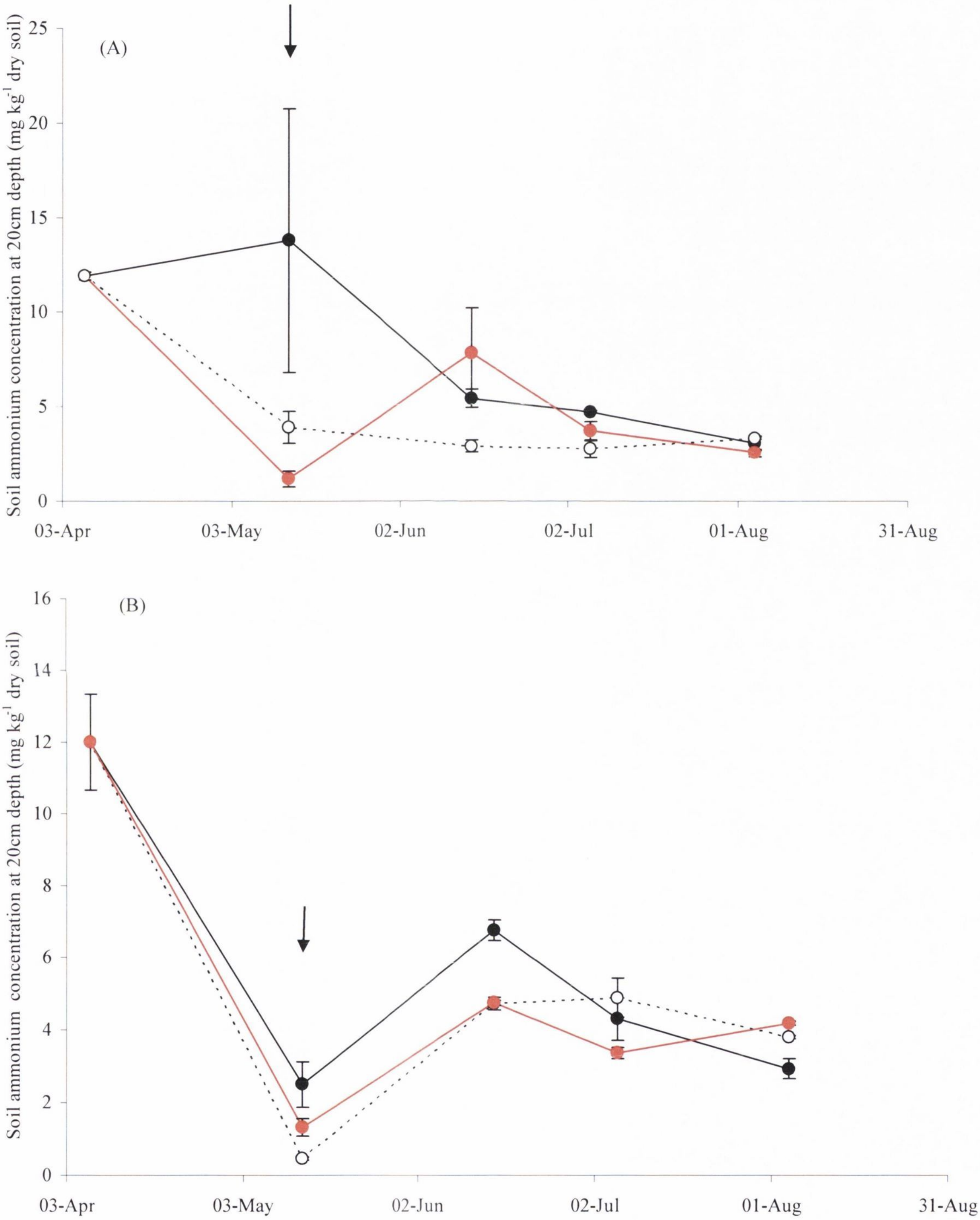


Figure 4.11: Soil ammonium concentration of the conventional (A) and reduced (B) tillage plots for 2004. Symbols indicate soil ammonium at fertilizer rate level: N_1 *(●),* N_2 *(●) and* N_3 *(○). Arrows indicate first measurements following fertilizer application. Each point represents the mean ± se of four measurements.*

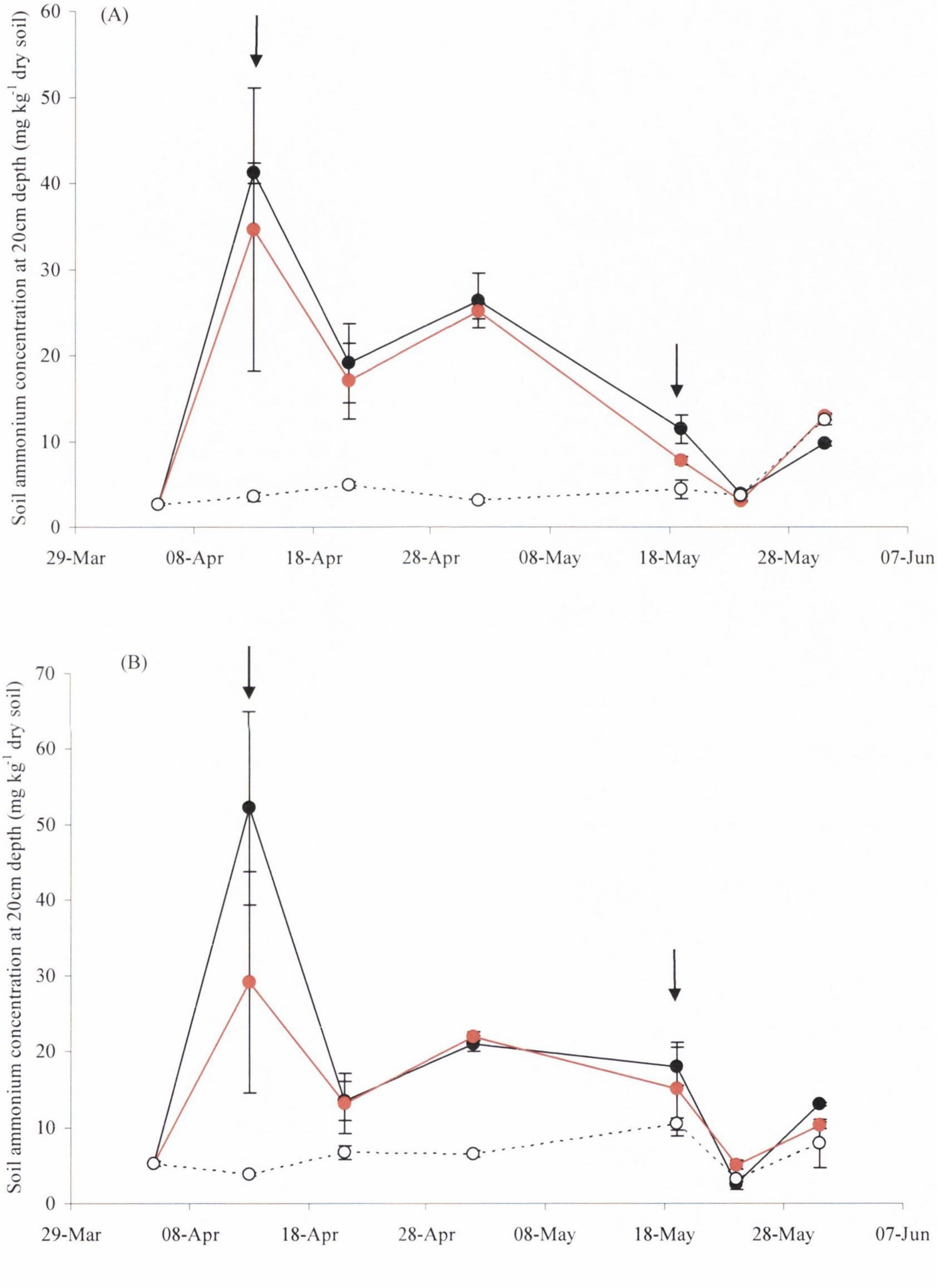


Figure 4.12: Soil ammonium concentration of the conventional (A) and reduced (B) tillage plots for 2005. Symbols indicate soil ammonium at fertilizer rate level: N_1 (●), N_2 (●) and N_3 (○). Arrows indicate first measurements following fertilizer application. Each point represents the mean ± se of four measurements.

Table 4.8: Summary of 2-way ANOVA statistics for soil ammonium 2005 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Treatment	5	2072	414.5	11.06	<0.0001
Time	6	4835	805.8	21.51	<0.0001
Interaction	30	3512	117.1	3.125	0.0004
Residual (Error)	42	1574	37.47		
Total	82	11990			

4.3.3 Emissions of N_2O

The 2-way analyses of variance for the N_2O flux data in this Chapter differs from the analyses in other Chapters in that N_2O flux data was available from each of the 24 plots, as opposed to nitrate, ammonium and total nitrogen where pooled data was available, or crop yield where only the mean and standard error was provided by Teagasc.

4.3.3.1 2004 data set

Figure 4.13 illustrates the daily average emissions of N_2O measured on a weekly basis, from April to August 2004, for the conventional and reduced tillage plots. Nitrogen fertilizer during the barley-growing season was incorporated once, on the 27th of April 2004. As with the grassland field, N_2O emissions showed a typical pattern throughout the experimental period. Emissions from the unfertilized plots were consistently low, with values ranging from -9.5 to 4.9 g N_2O-N ha^{-1} d^{-1} and from -2.5 to 4.6 g N_2O-N ha^{-1} d^{-1} for the conventional and reduced tillage plots respectively. For both tillage systems emissions of N_2O from fertilized plots (N_1 and N_2) peaked after fertilizer application, but peaks were short lived with fluxes returned back to background level approximately four weeks after fertilizer application. The highest peaks observed were 56 and 19.3 g N_2O-N ha^{-1} d^{-1} for CN_1 and CN_2 and 56.1 and 33.1 g N_2O-N ha^{-1} d^{-1} for LN_1 and LN_2 respectively. These peaks were observed one day following the fertilizer application.

A 2-way analysis of variance of the log transformed flux data is illustrated in Table 4.9, where time, fertilizer, plots and interaction between time and fertilizer were all significant. No significant difference was found between N_2O flux from the conventional and reduced tillage plots. However, fluxes were significantly different between fertilizer treatments, these differences being formed on the first day after fertilizer application only. Here the daily flux for CN_1 (56g N_2O-N ha^{-1}) was significantly higher ($P<0.001$) than that for CN_2 (19g N_2O-N ha^{-1}) and CN_3 (0.1g N_2O-N ha^{-1}). With respect to reduced tillage plots, the daily flux for LN_1 (56g N_2O-N ha^{-1}), was significantly higher ($P<0.001$) than that for LN_2 (33g N_2O-N ha^{-1}) and LN_3 (1.3g N_2O-N ha^{-1}), as was the daily flux of LN_2 greater than LN_3.

Table 4.9: Summary of 2-way ANOVA statistics for the 2004 N_2O flux data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Fertilizer	2	0.106	0.053	13.56	0.0003
Time	16	0.510	0.032	22.94	<0.0001
Tillage	1	0.003	0.003	0.89	0.358
Plot	18	0.070	0.004	2.81	0.0002
Constant	1	982.74	982.74	2.50E +05	<0.0001
Time * fertilizer	32	0.661	0.021	14.87	<0.0001
Tillage * fertilizer	2	0.003	0.002	0.4	0.677
Time *tillage	16	0.033	0.002	1.47	0.11
Time * tillage * fertilizer	32	0.039	0.001	0.87	0.674
Error	281	0.390	0.001		
Total	400	1.977			

Table 4.10 illustrates the fertilizer application rate, cumulative emissions of N_2O and EFs for the growing season, April to August 2004, where the effect of fertilizer on cumulative flux is apparent. A one-way analysis of variance of the mean cumulative N_2O flux within tillage and fertilizer treatments is illustrated in table 4.11. Here, treatment was significant, a Tuke post-test revealing that CN_1 was significantly higher than CN_3 ($P<0.05$) and that LN_1 was significantly higher than LN_3 ($P<0.05$). A similar analysis of variance for emission factors, illustrated in Table 4.12 revealed no significant effect of treatment, either tillage or fertilizer application rate.

Table 4.10: Total amount of N applied, cumulative N_2O-N emitted and emission factors for the conventional and reduced tillage plots in 2004.

Treatment	N_2O cumulative emissions (kg N_2O-N ha^{-1})	Emission factor (%)
Conventional tillage		
140 kg N ha^{-1}	0.79 ± 0.08	0.63 ± 0.06
70 kg N ha^{-1}	0.26 ± 0.26	0.42 ± 0.41
0 kg N ha^{-1}	0.01 ± 0.13	-
Reduced tillage		
140 kg N ha^{-1}	0.98 ± 0.21	0.63 ± 0.2
70 kg N ha^{-1}	0.49 ± 0.28	0.65 ± 0.45
0 kg N ha^{-1}	0.09 ± 0.03	-

Table 4.11: Summary of one-way ANOVA statistics of the mean cumulative N_2O fluxes for 2004 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	P value
Treatment (between column)	5	3.642	0.7284	0.004
Residual (within column)	18	2.572	0.1429	
Total	23	6.214		

Table 4.12: Summary of one-way ANOVA statistics of the EFs for 2004 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	P value
Treatment (between column)	5	0.1419	0.0473	0.95
Residual (within column)	18	4.970	0.4142	
Total	23	5.112		

4.3.3.2 2005 data set

Figure 4.14 illustrates the average daily emissions of N_2O measured on a weekly basis, from April to August 2005, for the conventional and reduced tillage respectively. Nitrogen fertilizer during the barley growing season was incorporated twice, on the 12th of April and 10th of May. As in 2004, N_2O emissions showed a typical pattern throughout the experimental period. Emissions from the unfertilized plots were also consistently low, with values ranging from -0.2 to 4.6 gN_2O-N ha^{-1} d^{-1} and from -2.5 to 8.8 gN_2O-N ha^{-1} d^{-1} for conventional and reduced tillage respectively.

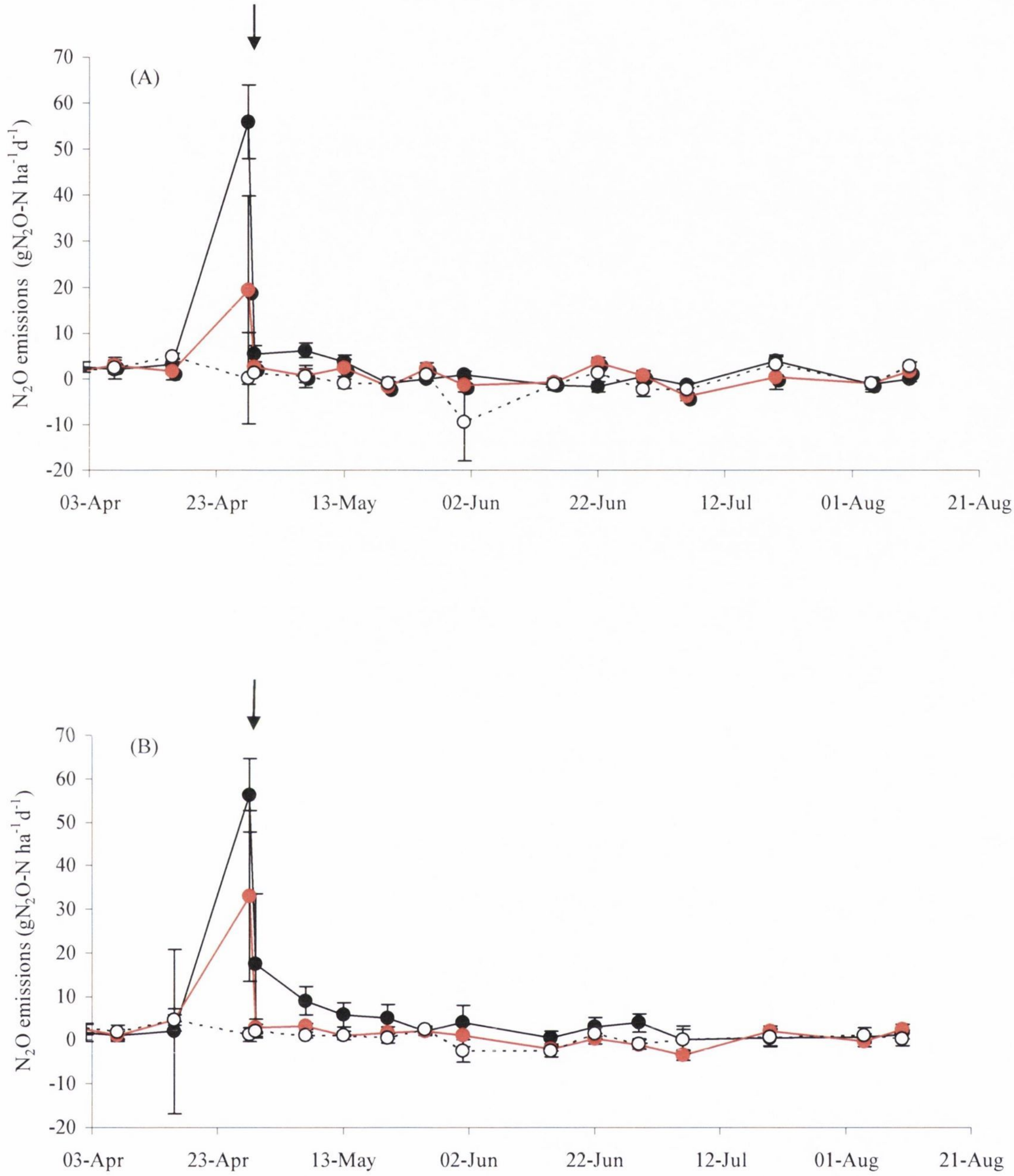


Figure 4.13: Daily emissions of N_2O from the conventional (A) and reduced (B) tillage plots measured on a weekly basis in 2004. Symbols indicate fertilizer rate level at which N_2O flux was measured: N_1 (●), N_2 (●) and N_3 (○). Arrows indicate first measurements following fertilizer application. Each point represents the mean ± se of four measurements.

For both tillage systems emissions of N_2O from fertilized plots (N_1 and N_2) peaked after each fertilizer application, but peaks were short lived with fluxes returned back to background level 3 - 6 weeks following fertilizer application. The highest N_2O peaks observed were 28.8 and 19.3 g N_2O-N ha^{-1} d^{-1} for CN_1 and CN_2 and 32.1 and 20.6 g N_2O-N ha^{-1} d^{-1} for LN_1 and LN_2 respectively. These peaks were observed 9 days following the second fertilizer application.

A 2-way analysis of variance for the log transformed N_2O data is illustrated in Table 4.13, where time, fertilizer, plots and interaction between time and fertilizer were all statistically significant. No significant difference was found between log N_2O fluxes from the conventional and reduced tillage plots. However, log fluxes were significantly higher between fertilizer treatments within each tillage, hence higher and medium fertilized plots were significantly higher ($P<0.001$) than from the control plots on the 15th of April, 27th of April and the 2nd of May corresponding to the 3rd day and the 3rd and 4th week following the first fertilizer application. Moreover, log fluxes from higher and medium fertilized plots were also significantly higher ($P<0.001$) than from control plots following the second fertilizer application on the 19th of May, 24th of May, 31st of May, 16th of June, 30th of June and the 6th of July

Table 4.13: Summary of 2-way ANOVA statistics of N_2O emissions for 2005 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Fertilizer	2	1.941	0.971	41.6	0.0003
Time	15	2.598	0.173	17.6	<0.0001
Tillage	1	0.00001	0.00001	0.0004	0.358
Plot	18	0.420	0.023	2.37	0.0002
Constant	1	632.312	632.312	2.71E+04	<0.0001
Time * fertilizer	30	0.811	0.027	2.75	<0.0001
Tillage * fertilizer	2	0.0002	0.00008	0.004	0.677
Time *tillage	15	0.128	0.009	0.868	0.11
Time * tillage * fertilizer	30	0.259	0.009	0.89	0.674
Error	269	2.648	0.01		
Total	382	8.809			

Table 4.14 illustrates the fertilizer application rate, cumulative emissions of N_2O and EFs for the growing season 2005, where as in 2004, the effect of the fertilizer on cumulative flux is apparent.

Table 4.14: Total amount of N applied, cumulative N_2O-N emitted and emission factors for the conventional and reduced tillage in 2005.

Treatment	N_2O Cumulative emissions (kgN_2O- N ha^{-1})	Emission factor (%)
Conventional tillage		
159 kg N ha^{-1}	0.870 ± 0.04	0.61 ± 0.03
79 kg N ha^{-1}	0.39 ± 0.097	0.54 ± 0.13
0 kg N ha^{-1}	0.16 ± 0.03	-
Reduced tillage		
159 kg N ha^{-1}	0.941 ± 0.2	0.65 ± 0.14
79 kg N ha^{-1}	0.424 ± 0.02	0.59 ± 0.03
0 kg N ha^{-1}	0.13 ± 0.09	

A one-way analysis of variance of the mean cumulative N_2O flux within tillage and fertilizer treatments is illustrated in table 4.15. Here, a Tuke post-test revealed that treatment was significant hence, CN_1 was significantly higher than CN_2 ($P<0.05$) and CN_3 ($P<0.01$) and that LN_1 was significantly higher than LN_2 ($P<0.05$) and LN_3 ($P<0.001$). A similar analysis of variance for emission factors, illustrated in Table 4.16 revealed no significant effect of treatment, either tillage or fertilizer application rate.

Table 4.15: Summary of one-way ANOVA statistics for the mean cumulative N_2O flux for 2005 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	P value
Treatment (between column)	5	2.402	0.4804	<0.0001
Residual (within column)	18	0.7249	0.04026	
Total	23	3.127		

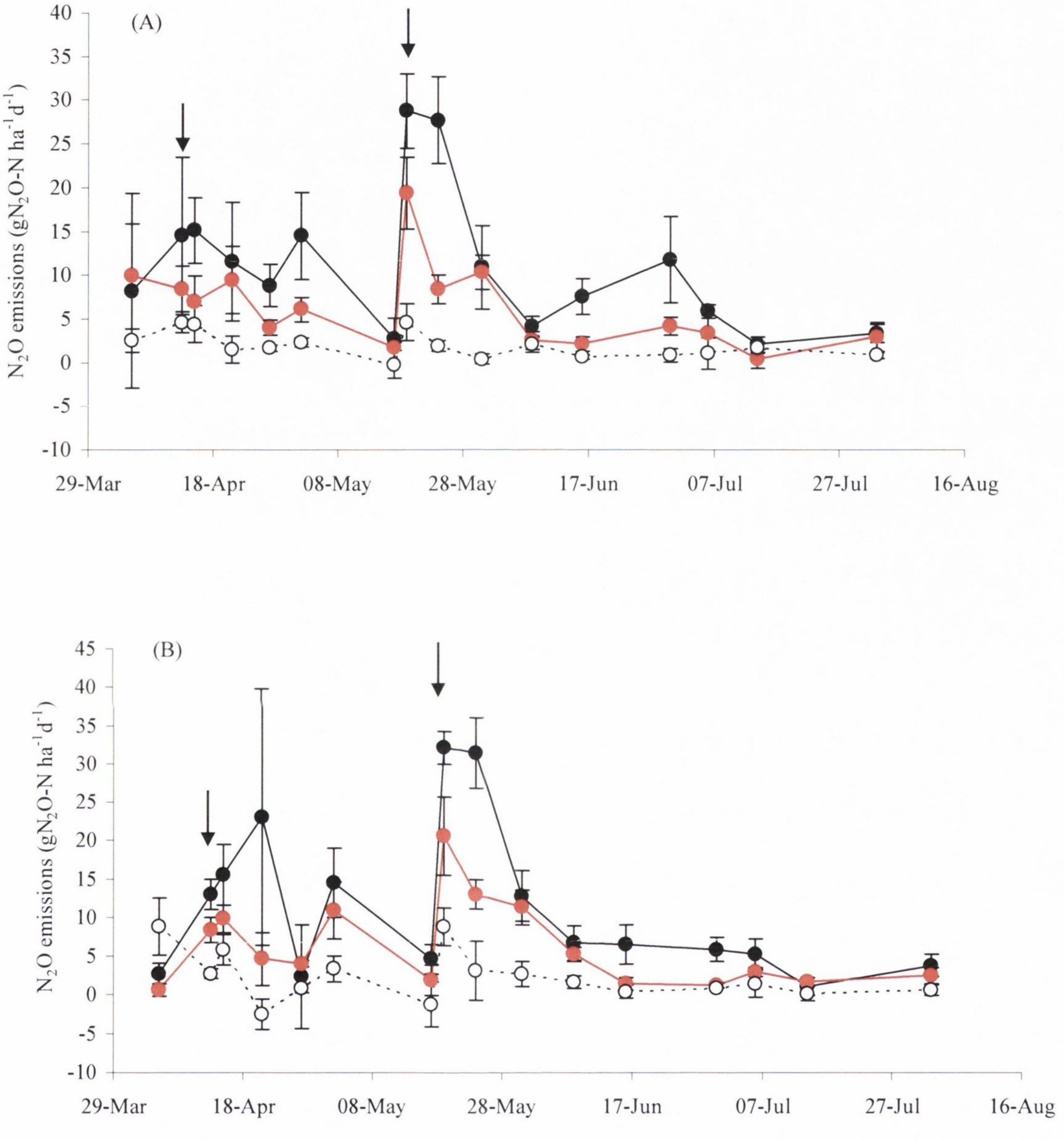


Figure 4.14: Daily emissions of N_2O from the conventional (A) and reduced (B) tillage plots measured on a weekly basis in 2005. Symbols indicate fertilizer rate level at which N_2O flux was measured: N_1 (●), N_2 (●) and N_3 (○). Arrows indicate first measurements following fertilizer application. Each point represents the mean ± se of four measurements.

Table 4.16: Summary of one-way ANOVA statistics for the EFs for 2005 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	P value
Treatment (between column)	3	0.02510	0.00836	0.925
Residual (within column)	12	0.6516	0.0543	
Total	15	0.6767		

4.3.4 Crop grain yield

Figure 4.15 illustrates the grain yield at 15% moisture for both tillage treatments in response to N fertilizer for both 2004 and 2005. The grain yield increased non-linearly with the increasing N fertilizer. In both years the proportional increase in grain yield was highest at the lower fertilizer application rate.

Table 4.17 illustrates a 2-way analysis of variance of the grain yield data set for 2004, where only fertilizer treatment was significant. A Bonferroni post-test revealed significant differences ($P<0.001$) between the N_1 and N_3 and the N_2 and N_3 treatments in each case.

A similar analysis for the 2005 grain yield data set is illustrated in Table 4.18. Here again only fertilizer and not tillage treatment was significant. As in 2004, a Bonferroni post-test revealed significant differences ($P<0.001$) between the N_1 and N_3 and the N_2 and N_3 treatments in each case. With regard to the maximum yield in 2004 compared with 2005, no significant difference was observed ($P = 0.17$).

Table 4.17: Summary of 2-way ANOVA statistics for the 15% moisture content grain yields for 2004 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Fertilizer	2	80.04	40.02	41.47	<0.0001
Tillage	1	0.05014	0.05014	0.05196	0.8223
Interaction	2	0.09934	0.04967	0.05147	0.9500
Residual (Error)	18	17.37	0.9650		
Total	23	97.56			

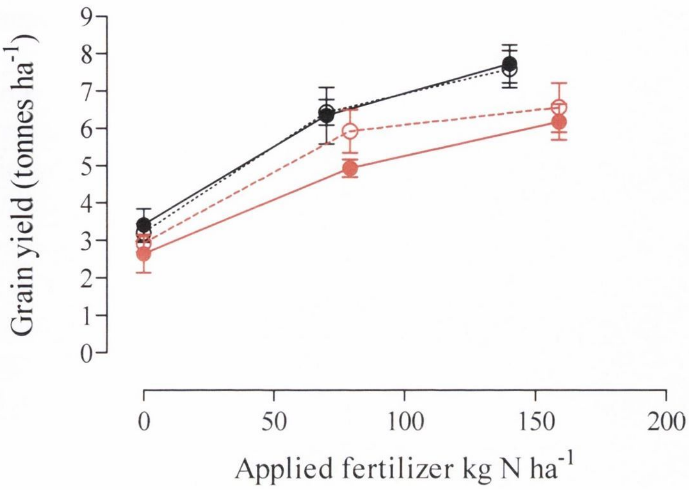


Figure 4.15: Grain yield from the conventional and reduced tillage for 2004 and 2005. Symbols indicate tillage/year combination: conventional 04 (●), reduced 04 (○), conventional 05 (●) and reduced 05 (○). Each point represents the mean ± se of four measurements.

Table 4.18: Summary of 2-way ANOVA statistics for the 15% moisture content grain yields for 2005 data set.

Source of variation	Degree of freedom	Sum of squares	Mean square	F	P value
Fertilizer	2	55.32	27.66	30.17	<0.0001
Tillage	1	1.813	1.813	1.977	0.1767
Interaction	2	0.5892	0.2946	0.3214	0.7292
Residual (Error)	18	16.50	0.9167		
Total	23	74.23			

4.3.5 Multiple regression analysis

Two multiple regression analysis were carried out, one for the log N_2O flux values with the single variable of soil nitrate, soil ammonium, temperature and moisture content of the conventional and reduced tillage data (Appendices 2 and 3). Here, log N_2O flux was considered as y variable, results of which are given in Tables (4.19). Accepting a threshold probability of 95%, only the concentration of soil nitrate in the soil at the time of flux measurement shows any correlation with emissions of N_2O ($r^2 = 64.5$). The other is when the interactions between these factors were considered, results of which are given in Table 4.20, both soil moisture and interaction between soil moisture and nitrate were well correlated with the flux, the regression accounting for 65.4% of the variance in the data.

Table 4.19: Results of multiple regression analysis of log N_2O flux with soil nitrate, soil ammonium, temperature and moisture content in 2004 and 2005

Source	Sum of Square	DF	Mean Square	F-ratio
Regression	12.5958	4	3.14894	26.4
Residual	6.19398	52	0.119115	
Variable	*Coefficient*	*S.E of Coefficient*	*t-ratio*	*Prob.*
Constant	-1.20807	0.4324	-2.79	0.007
Log nitrate	1.32357	0.1655	8	<0.0001
Log ammonium	-0.130105	0.1364	-0.954	0.3447
Temperature	0.0146068	0.01515	0.964	0.3393
Soil moisture	0.0200655	0.0169	1.19	0.2406

Table 4.20: Results of the best fit multiple regression analysis of log N_2O flux with moisture content and interaction between soil moisture and soil nitrate in 2004 and 2005.

Source	Sum of Square	DF	Mean Square	F-ratio
Regression	12.5184	2	6.25921	53.9
Residual	6.27133	54	0.116136	
Variable	*Coefficient*	*S.E of Coefficient*	*t-ratio*	*Prob.*
Constant	-1.59714	0.3334	-4.79	<0.0001
Soil moisture	-0.0349827	0.1476	-2.37	0.0214
Moisture *Nitrate	1.25431	0.1275	9.84	<0.0001

4.3.6 Correlation between grain yield and N_2O flux

The relationship between the final grain yield and the cumulative flux of N_2O measured from April to August 2004 and 2005 is illustrated in figure 4.16, for both conventional and reduced tillage plots combined. The line of best fit ($r^2 = 0.69$) is an exponential curve, such that proportionally low N_2O emitted from the soil at low fertilizer application rates. Hence a reduction in fertilizer application of 50% with regard to the normal field rate has resulted in a reduction in yield of approximately 16%, but has decreased the cumulative N_2O emissions by 57%.

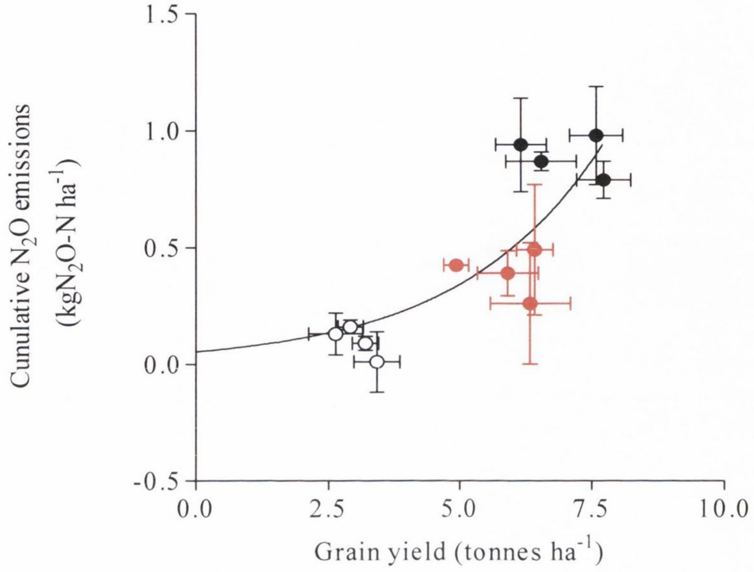


Figure 4.16: Relationship between the grain yield of spring barley (at 15% moisture) and the cumulative flux of nitrous oxide over the growing season for both 2004 and 2005 combined. Each point represents the mean ± se of 4 values. Symbols indicate fertilizer rate level: N_1 (●), N_2 (●) *and* N_3 (○). *Line indicates curve of best fit where* $y = 0.053*e^{0.373x}$, $(r^2 = 0.69)$.

4.4. Discussion

Results described in this Chapter concern the investigation of soil tillage and N fertilization rate on N_2O emissions from a spring barley crop field. In addition a multiple regression has been carried out to determine the major influencing factor(s) on N_2O flux.

With regard to tillage treatments there was no statistically significant effect on N_2O flux, grain yield, soil moisture or total nitrogen in the soil. In the case of soil temperature, soil nitrate and soil ammonium, tillage had a significant effect on the values observed only on two days at the most, the absolute differences between the tillage treatments being inconsequential. However, a trend would appear to be developing with regard to N_2O flux that, as mentioned in Chapter 3, may become more significant as more years of reduced tillage are allowed (Six *et al.,* 2004). Here higher (although not statistically significant) mean daily fluxes of N_2O were observed for the reduced tillage fertilized plots than for the conventional tillage fertilized plots. If this was to continue then it would agree with observations by Six *et al.* (2004) in which any benefit of reduced or no-till on increasing carbon storage may be offset by increases in N_2O emissions to the atmosphere, given the GWP of this greenhouse gas.

The main difference between the small plot experiment described in this chapter and the large plot experiment discussed in Chapter 3 is that here, the amount of CAN-N fertilizer applied was varied. Hence the effect of soil nitrate on N_2O flux, EF, and crop yield could be considered together. With regard to cumulative emissions of N_2O from April to August of 2004 and 2005, fertilizer treatment was highly significant, higher application rates yielding higher fluxes of N_2O (Sections 4.3.3.1, 4.3.3.2). If these data sets are plotted together, as illustrated in Figure 4.17 below, the relationship between cumulative flux and fertilizer application rate is linear, and when the individual slopes are compared, there is no significant difference between them ($P = 0.25$), such that an overall equation can be calculated which accounts for 93% of the variation of the data:

Cumulative flux = 0.0052*(fertilizer application rate) - 0.03

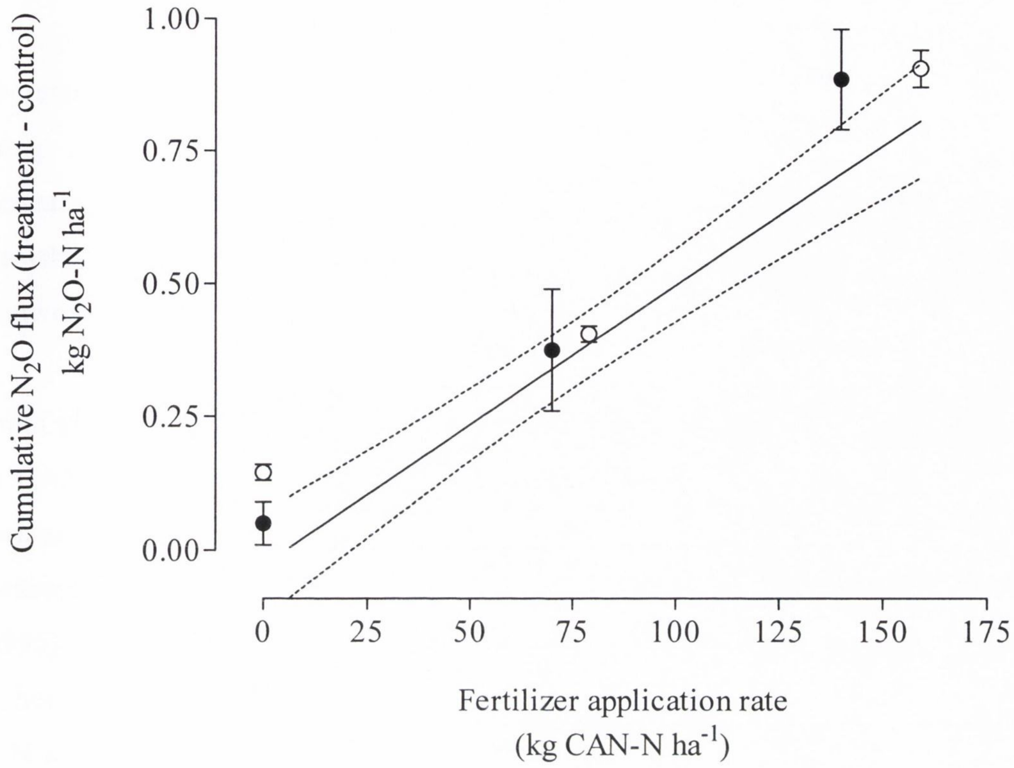


Figure 4.17: Correlation between fertilizer application rate and cumulative N_2O flux over the growing season for both 2004 and 2005. Each point represents the mean ± se of 4 values. Symbols indicate growing season: 2004(●) and 2005(○). $y = 0.0052x - 0.03$ and ($r^2 = 0.93$). The dotted lines representing the 95% confidence interval.

In effect the gradient of this relationship is the overall proportion of applied fertilizer that is given off as N_2O, or 0.5%. By changing the values for fertilizer application rate to represent the 10% of CAN that is lost due to ammonia volatilization, the slope becomes the overall emission factor for 2004 and 2005 growing seasons. This gives a slope of 0.0058 ± 0.0005, or an EF of 0.58 ± 0.05%. Separate EFs for each tillage, fertilizer treatment and year are given in Tables 4.10 and 4.14, and range from 0.42 to 0.65%. As tillage treatment was not significant on EF, and that there was no significant difference between the EFs for the two years, the EF determined as the slope of cumulative flux vs fertilizer application rate represents a more accurate determination. This compares very well, as expected, to the EFs for the large plot experiment (Chapter 3), but is less than the

EF for the grassland soil (Chapter 2). The possible reasons for this difference have been discussed already in Chapter 3.

The estimation of an annual cumulative flux from this experiment, as done in Chapter 3 using the EF and control plot data, is not possible. This is because N_2O flux measurements in both 2004 and 2005 took place from April to August only, where crop growth occurred which would lead to a conservative estimate (Bouwman, 1996; Bouwman *et al.*, 2002a; Helgason, *et al.*, 2005).

Grain yield as a function of fertilizer application rate suggests that reducing the field rate of CAN-N application by 50% had no significant effect on the grain yield (at 15% moisture), although the nutritional quality or protein content of the grain was not measured (Figure 4.15). This was also reported by others like McTaggart and Smith (1995), who suggested that grain yields don't increase linearly with increments of applied N, but leveled off at 90 - 120 kg N ha^{-1} , Chantigny *et al.* (1998), who found the increase in N amounts from 120 to 180 kg N ha^{-1} hardly affected maize yields and Sehy *et al.* (2003), who reported no significant increase in maize yields by the increase of N from 125 to 175 kg N ha^{-1}.

Using data from Conry, (1997) where the yield of the spring barley variety cv. Blenheim grown at the Oak Park research centre was calculated for 4 years, an interesting comparison can be made. This is illustrated in Figure 4.18, where the grain yields of cv. Tavern (variety used in this experiment) under reduced and conventional tillage is plotted alongside the data for cv. Blenheim. There is no marked difference between the performance of the two varieties, and in Conry, (1997) where grain quality data was also measured (reproduced here in Figure 4.19) the argument is made that reducing fertilizer may not necessarily affect grain quality for malting, where the acceptable standard for the N content of malting barley is < 17.5 g kg^{-1}. I would like to extend this argument and say that reducing fertilizer application rate by 50% is an acceptable strategy for low input agriculture in that there was no significant effect on grain yield, but seasonal emissions of N_2O were significantly reduced. This is illustrated clearly in the exponential relationship between cumulative flux and grain yield shown in Figure 4.17, where the proportional increase in N_2O was higher at the higher fertilizer application rate but that the proportional increase in crop yield was higher at the lower fertilizer application rate. This suggests that N_2O has a threshold response to N fertilization where the amount of N lost to the atmosphere depends on the amount of N taken up by the crop, exceeding this threshold value results in a higher release of N_2O to the atmosphere. This was also observed by McSwiney *et al.* (2005), who suggested that agricultural N_2O fluxes could be reduced with no or little yield penalty by reducing N fertilizer inputs to level that just satisfy crop needs.

With regard to the major determinant of N_2O flux, as defined by multiple regression, this was again found to be soil nitrate and soil moisture, but as a greater variation in soil nitrate was possible due to the design of the experiment, a far higher correlation coefficient was observed than for the similar multiple regressions described in Chapters 2 and 3. Here log N_2O flux could be described in terms of the interaction between soil nitrate and soil moisture, the r^2 value for the correlation being 65%. This is further discussed in Chapter 5 where soil moisture has been varied in isolation to other variables which have been fixed as non-limiting. That soil ammonium was not a significant factor on N_2O flux, and that in this experiment a broader range of soil ammonium values were possible again points to denitrification as the major source of N_2O flux in the arable field. As with soil moisture this will be discussed further in Chapter 5.

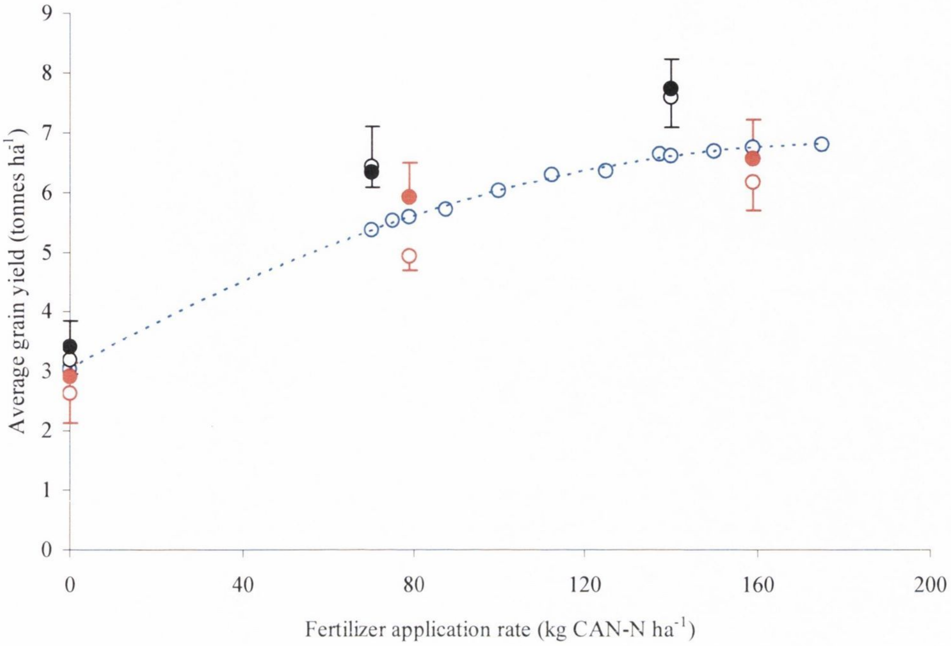


Figure 4.18: Comparison between the effect of applied N fertilizer on grain yield for spring barley variety Blenheim, data from Conry, (1997) and variety Tavern used in this experiment. Symbols indicate grain yield from tillage/year combination: conventional 04 (●), reduced 04 (○), conventional 05 (●), reduced 05 (○) and variety Blenheim data (○).

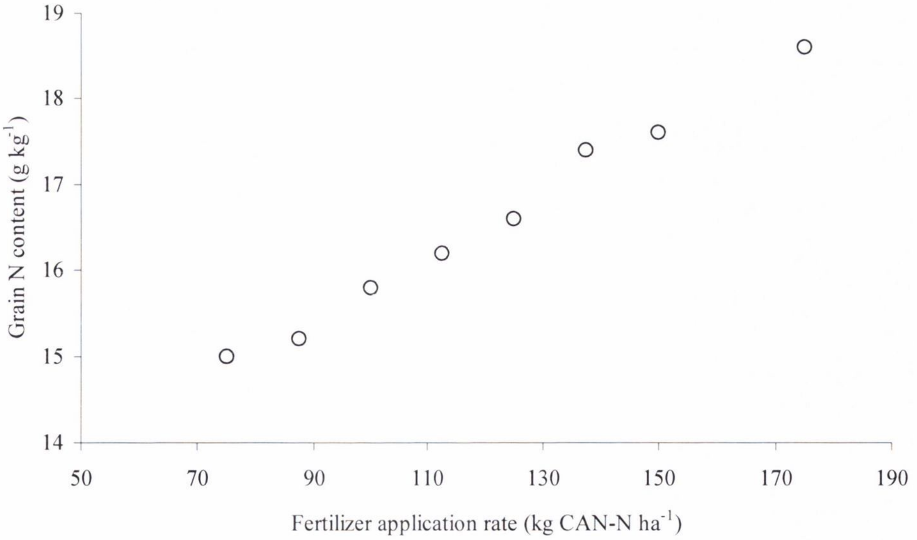


Figure 4.19: Effect of Applied Fertilizer on Grain Quality for Hordeum vulgare cv Blenheim, data from Conry, (1997).

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Chapter 5: Effects of organic carbon, soil moisture, temperature and N fertilizer on soil denitrification

5.1 Introduction

Soil denitrification is an important pathway for nitrogen losses from agriculture. It is a microbial process in which heterotrophic facultative bacteria reduce NO_3 to N_2O and N_2 gases under anaerobic conditions (Tiedje, 1982). The reactions are carried out by denitrifiers, which are widely distributed across the bacterial taxa, including *Pseudomonas*, *Bacillus*, *Thiobacillus*, *Propionibacterium* and others (Firestone, 1982). These predominantly heterotrophic microorganisms are facultative anaerobes that are able to use NO_3^- in place of O_2 as an electron acceptor in respiration to cope with low oxygen or anaerobic conditions. Enzymes catalyzing the reactions are nitrate reductase, nitrite reductase, nitric oxide reductase and nitrous oxide reductase (Hochstein and Tomlison, 1988).

Denitrification is mainly regulated by soil moisture, availability of an organic carbon substrate and soil nitrate concentration (Tiedje, 1982). Other factors, which have effects on this process, are soil pH, temperature and soil particle distribution. These factors in turn are influenced by soil topography, climate, vegetation type, geology and the pattern of organic carbon production and decomposition. Moreover, in agro-ecosystems, soil management affects one or more of the controlling factors of denitrification (Khalil, *et al.,* 2002), which can either enhance or retard denitrification rates. The availability of carbon substrate dictates the denitrification rate when other environmental and soil physical, chemical and biological factors are not limiting (Webster *et al.*, 1989).

The most commonly used approach for quantifying denitrification is the application of acetylene (C_2H_2) to the soil (Tiedje *et al.*, 1989). This technique relies on C_2H_2 selectively inhibiting N_2O reduction to N_2 allowing the total denitrification flux to be measured as N_2O (Robertson and Tiedje 1987; Klemedtsson *et al.*, 1988; Klemedtsson and Mosier, 1994). Acetylene blocks the activity of the enzyme nitrous oxide reductase.

A concentration of 5 - 10% v/v is needed to block N_2O reductase (Tiedje *et al.*, 1989), but a concentration of 0.01% v/v is sufficient to block nitrification (Berg *et al.*, 1982). The incubation period must be short because a long-term incubation will be affected by a decline in the pool of nitrate that is available for denitrification (Davidson *et al.*, 1986).

Due to the complexity of interactions between these factors in the field, one single factor may not always correlate with denitrification. The aim of this study was therefore to investigate the effects of organic carbon, soil moisture, incubation temperature and N fertilizer separately on denitrification by varying one parameter and fixing the others in each experiment. Hence a series of laboratory incubations were carried out.

5.2 Materials and Methods

5.2.1 Soil incubation

A series of laboratory incubations using grassland soil was conducted to study denitrification potential and the effects of organic carbon, soil moisture, temperature and N fertilizer on soil denitrification. Soil samples from the grassland field at Oak Park (0-10cm depth) were collected in January 2004 for experiment 1, and June 2005 for experiments 2 to 4. All soil samples were randomly collected across the field.

Soil samples were sieved using 2mm mesh to remove stones, and the chemical and physical characteristics of the soil were determined. 200 g samples of fresh soil were weighed and put in 500 ml volume bottles. 50 ml of helium gas was added to each bottle to reduce O_2 concentration in the headspace from 21% to about 18% (Scholefield *et al.*, 1997). A 10 % v/v concentration of acetylene was maintained in the headspace of each bottle following the removal of an equal amount of gas. Calcium ammonium nitrate (CAN) and D-glucose were used as a source of N and C respectively, 2.5 mg of glucose g^{-1} oven dry soil being added for each experiment. The fertilizer and the glucose were dissolved in de-ionized water and spread evenly on the surface of the soil using a syringe.

After each sampling of gas, the same amount of helium was added to the bottles to maintain anaerobic conditions. A suba seal, through which sampling took place, was fixed at the bottle-cap. Five incubation times were studied (0 h, 6 h, 12 h, 24 h and 2 days). Each treatment was replicated 6 times, with the bottles being placed randomly in each incubator. A total of 36 x 500 ml bottles for each experiment were used, 12 of which were for nitrate extraction.

5.2.2 Experiment 1: Effects of organic carbon on denitrification

In this experiment a fertilizer rate of 175 µg CAN g^{-1} oven dry soil was used following the procedure of Malone *et al.*, (1997). Organic carbon in the form of glucose was added at three different rates ($G_1 = 0$, $G_2 = 2.5$ and $G_3 = 5$ mg glucose g^{-1} oven dry soil). Soil moisture was maintained at 40 % using de-ionized water and the incubation temperature maintained at 20°C. Sixty mls of headspace gas were removed at each sampling and transferred to 3ml vials as described in Chapter 2. Gas samples were then sent to Denmark for N_2O analysis by GC.

5.2.3 Experiment 2: Effects of soil moisture content on denitrification

In this experiment 4 levels of soil moisture were maintained, 30%, 35%, 40%, and 45%. One N fertilizer rate of 175 μg CAN g^{-1} oven dry soil was applied to each bottle. Gas samples were removed at each sampling time and sent off for analysis as described in section 5.2.2.

5.2.4 Experiment 3: Effects of incubation temperature on denitrification

In this experiment 4 temperature treatments of 10 °C, 15 °C, 20°C and 25°C were applied. Soil moisture content was maintained at 40% and one N fertilizer rate of 175 μg CAN g^{-1} oven dry soil was used throughout. Gas samples were removed at each sampling time and sent off for analysis as described in section 5.2.2.

Q10 was calculated by dividing denitrification rate at (T + 10) °C by denitrification rate at T°C.

5.2.5 Experiment 4: Effects of N fertilizer rate on denitrification

In this experiment 4 N fertilizer treatments of 0, 175, 350 and 525 μg CAN g^{-1} oven dry soil were applied. Soil moisture content was maintained at 40%. Gas samples were removed at each sampling time and sent off for analysis as described in section 5.2.2.

5.2.6 Statistics

All statistical analyses were carried out using PRISM (GraphPad, San Diego, USA) and Data Desk (Data Description Inc. New York, USA) software packages. Flux data was checked for normal distribution and log transformed where appropriate. Both 1-way and 2-way analysis of variance were applied to the N_2O flux values.

5.3. Results

5.3.1 Experiment 1: Effects of organic carbon on soil denitrification

5.3.1.1 Soil denitrification rate as influenced by organic carbon

Figure 5.1 illustrates the change in denitrification rate over two days as a function of increasing glucose concentration. Denitrification rates from control bottles were low throughout the experiment and ranged from 0 to 0.5μg N_2O-N kg^{-1}dry soil h^{-1}. Similarly, in the absence of added glucose, the N-fertilizer treatment also showed low rates of denitrification (0.1 to 1μg N_2O-N kg^{-1}dry soil h^{-1}). Only after the addition of 2.5 or 5 mg of glucose g^{-1} dry soil were maximum rates of denitrification observed (17 to 18 μg N_2O-N kg^{-1}dry soil h^{-1}). Such maximum rates were not maintained and fell to background values after 12 hours.

Analysis of variance of the data illustrated in Table 5.1, revealed a significant effect of glucose on the observed rate of denitrification ($P<0.001$), although doubling the glucose concentration had no further significant effect.

Table 5.1: Summary of 2-way ANOVA statistics for the denitrification rate as influenced by organic carbon

Source of variation	DF	Sum of squares	Mean of square	F	Probability
Treatment	9	818.9	273	3.12	0.0005
Time	3	1354	451.2	6.56	<0.0001
Interaction	3	1166	129.5	10.85	0.0029
Residual	80	3329	41.58		
Total	95	6665			

5.3.1.2 Cumulative denitrification as influenced by organic carbon

Figure 5.2 illustrates the cumulative denitrification over 48 h of incubation. Cumulative denitrification values for the control bottles were also low with a mean value of 7 μg N_2O-N kg^{-1}dry soil. These values were increased after the addition of N fertilizer (175 μg CAN g^{-1}dry soil) to reach a mean value of 14.5 μg N_2O-N kg^{-1}dry soil. Addition of the same amount of N fertilizer rate and 2.5 mg D-glucose g^{-1}dry soil also increased denitrification to a mean value of 146 μg N kg^{-1}dry soil. However, addition of more organic carbon (5mg D-glucose g^{-1}dry soil) increased cumulative denitrification only slightly to reach a mean value of 158μg N_2O-N kg^{-1}dry soil.

Table 5.2 illustrates a one-way analysis of variance for the cumulative denitrification over 48 hours. A Tuke post-test revealed that cumulative denitrification values for T_2 (175 μg CAN +2.5mg C g^{-1}dry soil) and T_3 (175 μg CAN + 5mg C g^{-1}dry soil) were significantly higher than that from the control treatment ($P<0.05$). Moreover, denitrification from T_3 was significantly higher than that from T_1 ($P<0.05$).

Table 5.2: Summary of one-way ANOVA statistics for the mean cumulative denitrification as influenced by organic carbon

Source of variation	Degree of freedom	Sum of squares	Mean square	P value
Treatment (between columns)	3	120500	40180	<0.0001
Residual (within columns)	20	137000	6850	
Total	23	257500		

5.3.2 Experiment 2: Effects of soil moisture on soil denitrification

5.3.2.1 Soil denitrification rate as influenced by soil moisture

Figure 5.3 illustrates the change in denitrification rate over 48 hours as influenced by soil moisture content. Denitrification rates at low soil moisture contents (30% and 35%) were constant throughout the incubation time. However, denitrification rates from high soil moisture contents (40% and 45%) were maximum following the first 6 h of the incubation, then decreased steadily with time to reach minimum values following 48 h of incubation. The highest denitrification rate of 30μg N_2O-N kg^{-1}dry soil h^{-1} was observed following 6h of incubation from the highest soil moisture treatment (45%). Table 5.3 illustrates a 2-way analysis of variance of soil denitrification rate as influenced by soil moisture. A Bonferroni post-test revealed that moisture, time and interaction were all significant and denitrification rates were significantly increased with soil moisture content.

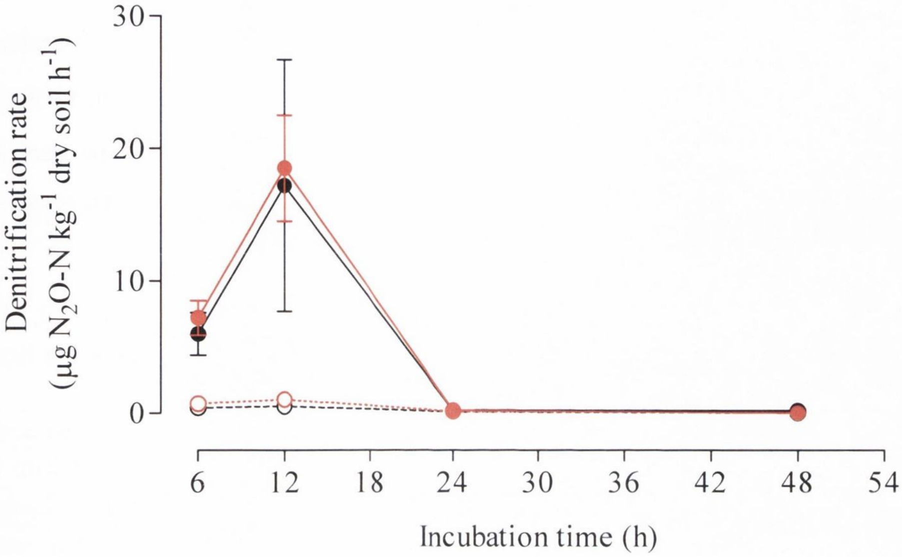

Figure 5.1: Change in denitrification rate with time. Symbols indicate: control (○), 175μg CAN g^{-1} dry soil (○), 175μg CAN + 2.5mg glucose g^{-1} dry soil (●) and 175μg CAN + 5mg glucose g^{-1} dry soil (●). Each point represents the mean ± se of six measurements.

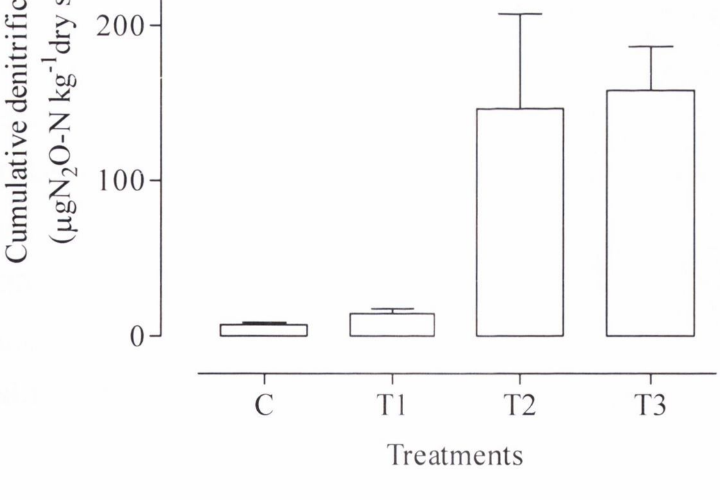

Figure 5.2: Cumulative denitrification over 48h of incubation. C = control, T_1 = 175 μg CAN g^{-1}dry soil, T_2= 175 μg CAN +2.5mg C g^{-1}dry soil, T_3 = 175 μg CAN + 5mg C g^{-1}dry soil. Each value represents the mean ± se of six measurements.

Denitrification rate at a moisture content of 40 % was significantly higher than at moisture contents of either 30 % or 35 % at 6 h ($P<0.001$), 12 h ($P<0.001$) and 24 h ($P<0.01$) respectively. The denitrification rate at a moisture content of 45% was significantly higher than those at 30% and 35% after 6h ($P<0.001$), 12h ($P<0.001$), 24 h ($P<0.001$) and 48h ($P<0.01$). Moreover, the denitrification rate at a moisture content of 45% was significantly higher than that at 40 % after 6 h ($P<0.001$), 12 h ($P<0.001$) and 24 h ($P<0.01$).

Table 5.3: Summary of 2-way ANOVA statistics for the denitrification rate as influenced by soil moisture content

Source of variation	DF	Sum of squares	Mean of square	F	Probability
Soil moisture	3	3867	1289	244	<0.0001
Incubation time	3	1324	441.3	83.53	<0.0001
Interaction	9	1579	175.4	33.2	<0.0001
Residual (error)	80	422.7	5.284		
Total	95				

5.3.2.2 Cumulative denitrification as influenced by soil moisture

Figure 5.4 illustrates the cumulative denitrification over 48 h of incubation. The cumulative denitrification at moisture content of 30 % was 32 μg N_2O-N kg^{-1} dry soil h^{-1}. This value was increased with increasing soil moisture to reach 47, 270 and 533 μg N_2O-N kg^{-1} dry soil h^{-1} at 35, 40 and 45% soil moisture respectively.

Table 5.4 illustrates a one-way analysis of variance for the cumulative denitrification as influenced by soil moisture content where moisture was found to be a significant factor. A Tuke post test revealed that the mean cumulative denitrification values from bottles incubated at soil moisture contents of 40 % and 45 % were significantly higher ($P<0.001$, <0.001) than those at soil moisture contents of 30 % and 35 %. Moreover, the mean cumulative denitrification for bottles incubated at a soil moisture content of 45% was significantly higher ($P<0.001$) than that at a soil moisture content of 40%.

Table 5.4: Summary of one-way ANOVA statistics for the mean cumulative denitrification as influenced by soil moisture content

Source of variation	Degree of freedom	Sum of squares	Mean square	P value
Soil moisture (between columns)	3	993900	331300	<0.0136
Residual (within columns)	20	111700	5585	
Total	23	1106000		

A positive exponential correlation was found between soil moisture and cumulative denitrification which accounted for 97% of the variations in the data.

5.3.3 Experiment 3: Effects of incubation temperature on soil denitrification

5.3.3.1 *Soil denitrification as influenced by soil temperature*

Figure 5.5 illustrates the change in denitrification rate over 48 h of incubation as a function of temperature. Denitrification rates from bottles incubated at 10 and 15°C were low throughout the incubation period and ranged from 1.8 to 7.3 μg N_2O-N kg^{-1}dry soil $h^{-1}$and from 4.9 to 12 μg N_2O-N kg^{-1}dry soils h^{-1} respectively. Denitrification rates from bottles incubated at 20°C ranged from 13.7 to 24.3 μg N_2O-N kg^{-1}dry soil h^{-1}, whereas that from bottles incubated at 25°C ranged from 35.9 to 65.4 μg N_2O-N kg^{-1}dry soils h^{-1}. The highest denitrification rates were observed following 24 hours of incubation.

Table 5.5 illustrates a 2-way analysis of variance for denitrification as influenced by incubation temperature. A Bonferroni post test revealed that treatment, time and interaction were all significant. Significantly higher denitrification rates were observed from bottles incubated at 20°C than for those incubated at 10°C at 24h ($P<0.001$) and 48 h ($P<0.01$). Similarly, significantly higher rates ($P<0.001$) were observed at 25°C than at 10°C throughout the experimental period. Denitrification rates from bottles incubated at 20°C was significantly higher ($P<0.01$) than that at 15°C at 24 h, but significantly lower from that at 25°C ($P<0.001$) throughout the experimental period. Moreover, the mean denitrification rate from bottles incubated at 25°C was significantly higher than that at 15°C throughout the experimental period.

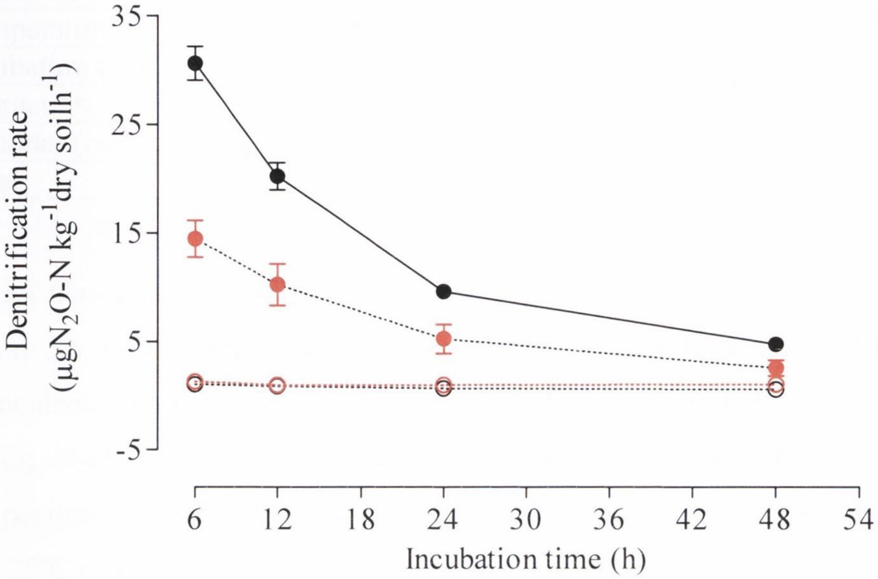

Figure 5.3: Denitrification rates at different soil moistures throughout the experimental time. Symbols indicate denitrification at soil moisture content: 30 % (○), 35 % (○), 40% (●) and 45% (●). Each point represents the mean ± se of six measurements.

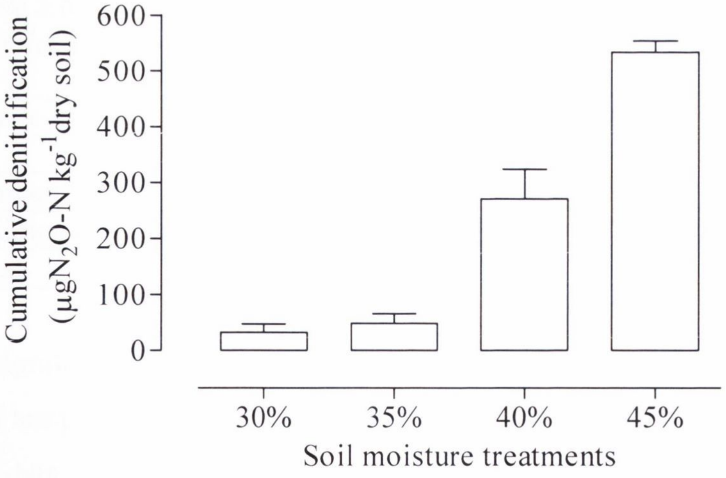

Figure 5.4: Cumulative denitrification as influenced by soil moisture content over 48h of incubation. Each value represents the mean ± se of six measurements. $y = 0.213*\exp(0.174*x)$, $r^2 = 0.97$

Table 5.5: Summary of 2-way ANOVA statistics for the denitrification rate as influenced by incubation temperature

Source of variation	DF	Sum of squares	Mean of square	F	Probability
Temperature	3	31380	10460	125	<0.0001
Incubation time	3	1743	580.9	6.941	0.0003
Interaction	9	2005	222.7	2.661	0.0094
Residual (error)	80	6695	83.69		
Total	95	41830			

5.3.3.2 Cumulative denitrification as influenced by soil temperature

Figure 5.6 illustrates the cumulative denitrification after 48 hours incubation as a function of incubation temperature. Cumulative denitrification from bottles incubated at 10°C was 235µg N_2O-N kg^{-1} dry soil. This value was increased with increasing incubation temperature to reach 408, 1027 and1525 µg N_2O-N kg^{-1} dry soil at temperature of 15, 20 and 25°C respectively.

Table 5.6 illustrates a one-way analysis of variance for the cumulative denitrification over 48 h as influenced by incubation temperature where temperature was significant. A Tuke post test revealed that cumulative denitrification from bottles incubated at 25°C was significantly higher than that at 10°C (P<0.001), 15°C (P<0.001) and 20°C (P<0.001).

Table 5.6: Summary of one-way ANOVA statistics for the mean cumulative denitrification as influenced by incubation temperature

Source of variation	Degree of freedom	Sum of squares	Mean square	P value
Temperature (between columns)	3	19500000	6502000	<0.0001
Residual (within columns)	20	4824000	241200	
Total	23	24330000		

A significantly positive exponential correlation between cumulative denitrification and soil temperature, where the equation for the line accounted for 100% of the variations in the data was found. The calculated Q_{10} for this data set between the temperature range 10° and 20°C was 4.4, whilst between the temperature range 15° to 25°C was 6.2. Using the exponential equation, $y = 30.2*\exp(0.177*x)$, it is possible to calculate an overall Q_{10} value where $\ln(Q_{10}) = 1.77$. Thus an overall Q10 value of 5.8 was calculated.

Figure 5.7 illustrates an Arrhenius plot for the calculation of the activation energy for soil denitrification. The equation for the line accounted for 98% of the variance of the data, and by multiplying the slope by the negative value of the molar gas constant, 8.314 kJmol^{-1}, gave an activation energy value of 47 kJmol^{-1}.

5.3.4 Experiment 4: Effects of nitrogen fertilization

5.3.4.1 Soil denitrification as influenced by N fertilizer

Figure 5.8 illustrates the change in denitrification rate over 48 h of incubation as a function of N fertilizer application rate. Denitrification rates for all treatments were highest following 6 h of incubation and then decreased with time. The mean denitrification rate from control bottles was low and ranged from 0.2 to 0.7μg N_2O-N kg^{-1} dry soil h^{-1}, whereas that from the highest fertilizer treatment ranged from 2.6 to 23.4μg N_2O-N kg^{-1} dry soil h^{-1}.

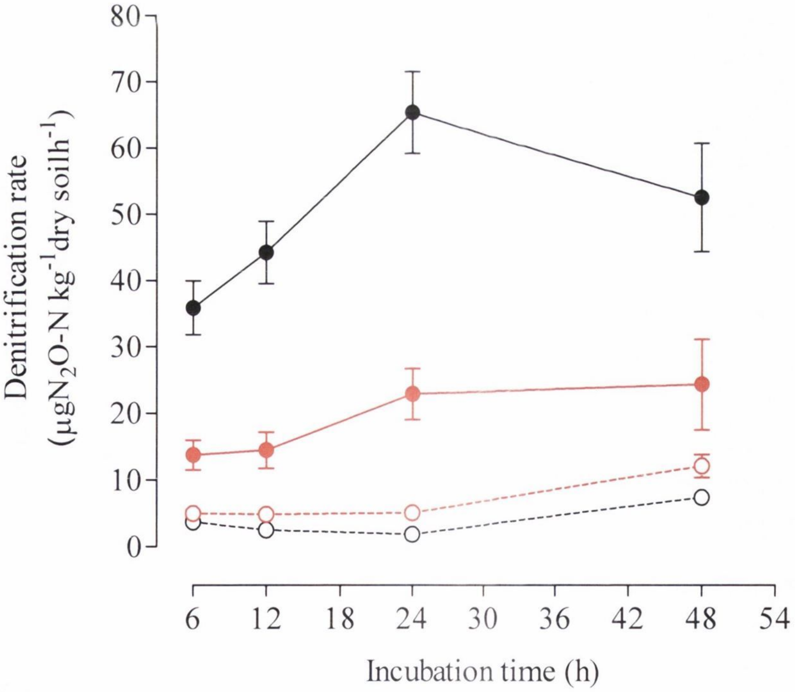

Figure 5.5: Denitrification rate as influenced by incubation temperature. Symbols indicate denitrification at soil temperature: 10°C (○), 15°C (○), 20°C (●) and 25°C (●). Each point is the mean ± se of six measurements.

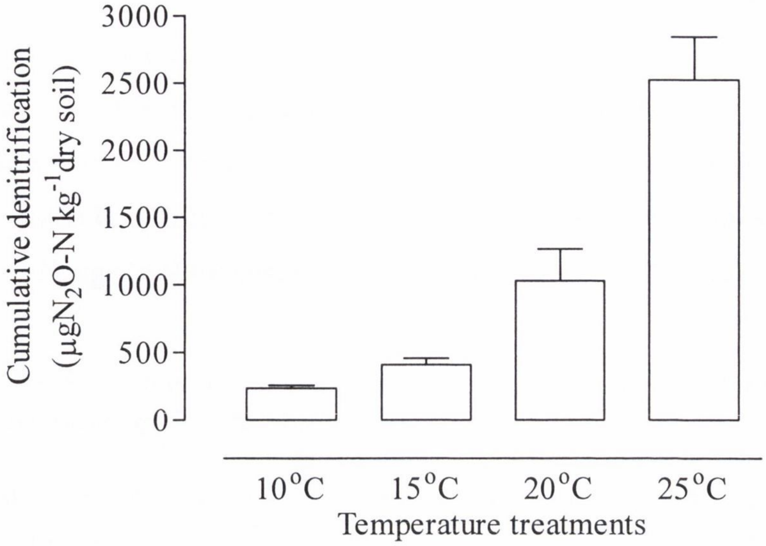

Figure 5.6: Cumulative denitrification as influenced by temperature. Each value represents the mean ± se of six measurements. $y = 30.2*\exp(0.177*x)$, $r^2 = 1.0$.

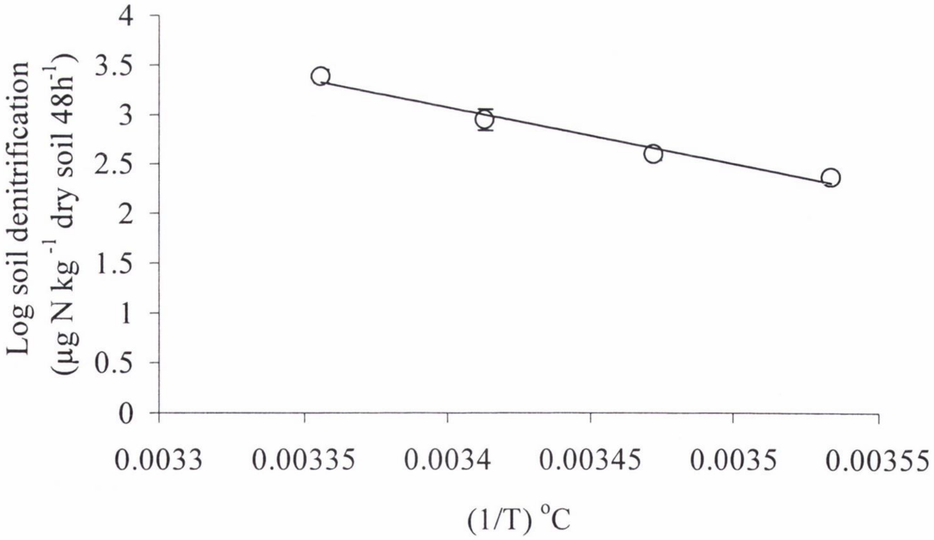

Figure 5.7: Arrhenius plot for calculation of activation energy showing correlation between cumulative denitrification and (1/T)°C. Each point represents the mean ± se of six measurements. $y = -5.724x + 22.533$, $r^2 = 0.98$

Table 5.7 illustrates a 2-way analysis of variance for denitrification rate as a function of fertilizer application rate. A Bonferroni post test revealed that treatment, time and interaction were all significant. The mean denitrification rate from the 175 μg CAN treatment was significantly higher than the control after 6 and 12 hours incubation respectively ($P<0.001$, <0.01), as were the 350μg and 525μg CAN treatments. Moreover, the mean denitrification rate for the 525 μg CAN treatment was significantly higher than the 175 μg CAN treatment after 6 hours incubation ($P<0.05$).

Table 5.7: Summary of 2-way ANOVA statistics for the denitrification rate as influenced by fertilizer application rate

Source of variation	DF	Sum of squares	Mean of square	F	Probability
Fertilizer rate	3	1666	555.2	28.17	<0.0001
Incubation time	3	2883	961.1	48.76	<0.0001
Interaction	9	990.9	110.1	5.586	<0.0001
Residual	80	1577	19.71		
Total	95	7117			

5.3.4.2 Cumulative denitrification as influenced by N fertilizer

Figure 5.9 illustrates the cumulative denitrification over 48 h as influenced by N fertilizer application rate where increasing N fertilizer has clearly increased the cumulative amount of N_2O emitted. A one-way analysis of variance of the data, illustrated in Table 5.8, revealed that fertilizer application was significant ($P = 0.0092$).

A Tuke posttest revealed that cumulative denitrification from the 175, 350 and 525 μg CAN treatments were significantly higher than the control ($P<0.01$, <0.001, and <0.001 respectively).

Table 5.8: Summary of one-way ANOVA statistics for cumulative denitrification as influenced by N fertilizer rate.

Source of variation	Degree of freedom	Sum of squares	Mean square	P value
N-fertilizer (between columns)	3	382600	127500	0.0092
Residual (within columns)	20	176300	8817	
Total	23	559000		

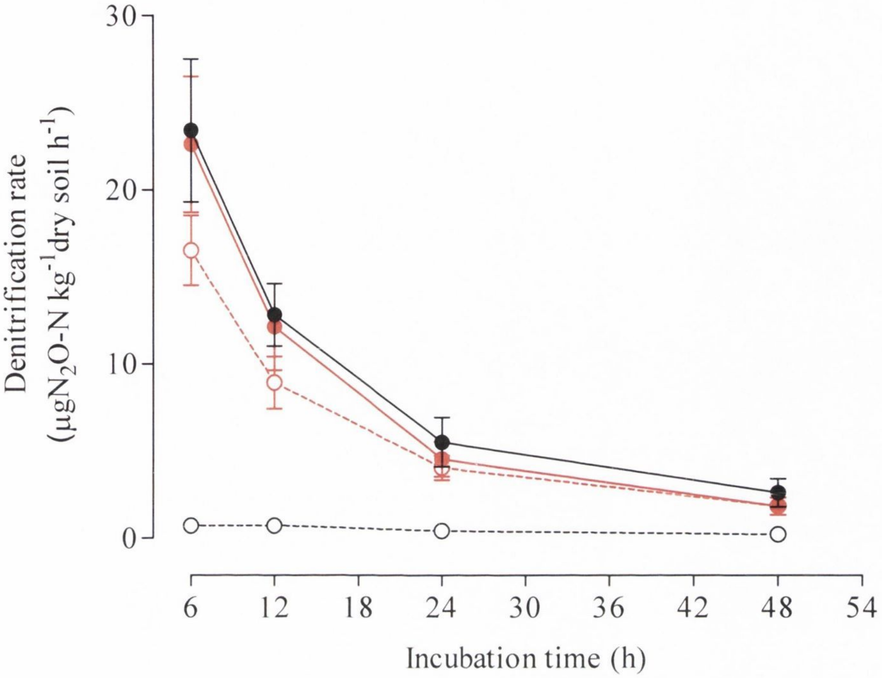

Figure 5.8: Denitrification rates during the experimental time. Symbols indicate denitrification at N fertilizer rate: 0 μg CAN g^{-1} dry soil (○), 175μg CAN g^{-1} dry soil (○), 350 μg CAN g^{-1} dry soil (●) and 525 μg CAN g^{-1} dry soil (●). Each point represents the mean ± se of six measurements.

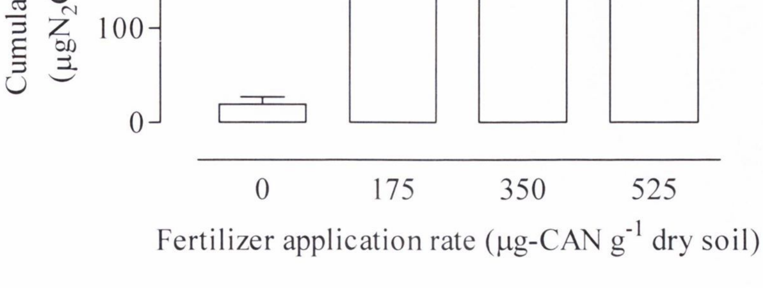

Figure 5.9: Cumulative denitrification over 48 hours incubation as influenced by N fertilizer application rate. Each value represents the mean ± se of six measurements. . $y = 435.8*x/(141.4+x)$, $r^2 = 0.99$.

A positive correlation was found between fertilizer rate and cumulative denitrification of which the line of best fit was a hyperbola, the equation for which accounted for 99% of the variation in the data.

5.3.4.3 Correlation between soil nitrate and cumulative denitrification

Figure 5.10 illustrates a linear correlation between soil nitrate and cumulative denitrification, the equation for which accounting for 82% of the variation in the data.

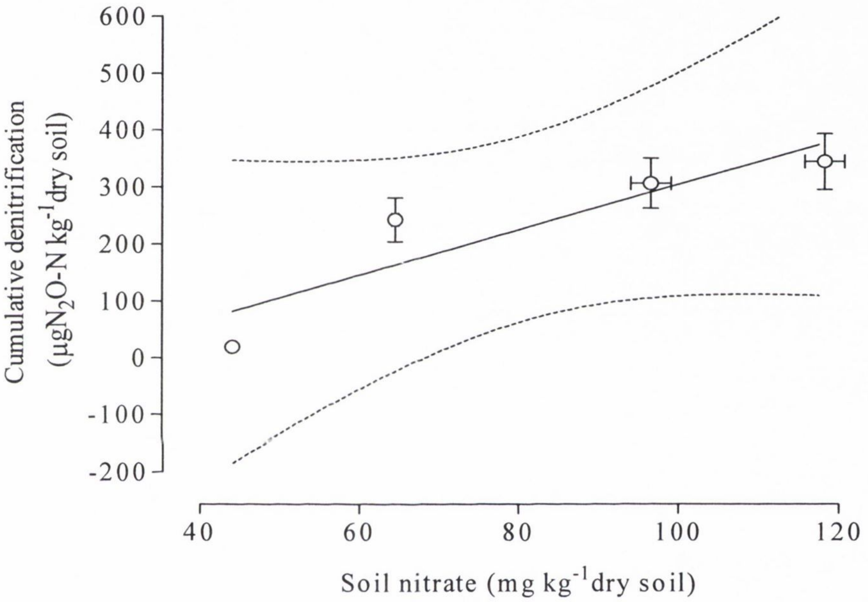

Figure 5.10: Correlation between soil nitrate and cumulative denitrification over 48h of incubation. Each point represents the mean ± se. $y = 4x - 95.41$ $(r^2 = 0.82)$. *The dotted lines representing the 95% confidence interval.*

5.4. Discussion

The aim of experiments described in this Chapter was to investigate the effects, in isolation, of soil organic carbon, soil moisture, temperature and applied N fertilizer on denitrification in the grassland soil. Here the acetylene inhibition technique was employed. Peak rates of denitrification needed to be supported by the addition of carbon as D-glucose, and for the majority of experiments the N induced peaks in denitrification lasted for less than 48 hours. However, in one important exception, induced rates of denitrification continued for more than 48 hours resulting in significantly higher cumulative emissions. This was seen for the experiment where temperature was varied. The only difference here was that the soil was stored for two weeks following collection at approximately 7°C before use. For all other experiments described in this Chapter the soil was used directly after collection. This increase in denitrification may be due to an increase in microbial activity during storage due to either an increase in N mineralization and/or an increase in the microbial pool. Either way, cumulative emissions of N_2O at 20°C and 40% soil moisture (the temperature and moisture content that all the other experiment were carried out at) ranged from 158 to 1027μg N_2O-N kg^{-1} dry soil. Hence absolute comparison of rates of denitrification between experiments is not valid, but the pattern of response to each variable is. However, in stating this, the range of denitrification rates obtained for all the experiments, when converted to kg N_2O-N ha^{-1} d^{-1} was 0.07 to 0.5 kg N_2O-N ha^{-1} d^{-1} which agrees with the published data set of Ryan *et al.* (1998) for denitrification of mineral soils in Co. Wexford (0.04 to 0.6 kg N_2O-N ha^{-1} d^{-1}).

5.4.1 Effects of organic carbon

Clearly, adding organic carbon in the readily utilized form of D-glucose to the soil, in the presence of added nitrate, has stimulated denitrification (Figure 5.1), hence denitrifcation in the field-collected soil was C limited. Here, carbon limitation may be short-term in the form of providing reducing equivalents for the partial reactions of denitrification, or long-term in which the microbial pool increases. Certainly the availability of readily oxidizable pools of organic carbon in the soil may be limited with respect to the denitrifying population of microorganisms (Pattern *et al.*, 1980). Similar evidence to this study exists in the scientific literature for the limitation of denitrification by organic carbon. Weier *et al.* (1993) and Stevens and Laughlin, (1998) have also reported a stimulation of denitrification on the addition of organic carbon, and De Wever *et al.* (2002) has shown high levels of soil carbon to be correlated with high levels of denitrification. However, the relationship is not straight forward. Doubling the amount of glucose added has had no further effect on denitrification, as illustrated in Figure 5.2. The reason here may be a significant increase in the C/N ratio of the soil on the addition of glucose, where increasing the quotient of carbon compared to nitrogen has been shown to inhibit denitrification in forest soils (Hwang *et al.*, 2006).

5.4.2 Effects of soil moisture

By varying the soil moisture content but keeping soil N, soil carbon and incubation temperature constant, denitrification has been shown to significantly increase with increasing soil moisture (Figure 5.3 and 5.4), an observation that was not possible in the field due to limiting rainfall and/or other limiting factors such as soil nitrogen and organic carbon. Similar results for soil moisture have been shown by Goodroad and Keeney, (1984), Klemedtsson *et al.* (1988), Stevens *et al.*, (1997) and Ryan *et al.* (1998). Here denitrification rate depends on the degree of water saturation and thus the development of aerobic and anaerobic micro-sites (hot spots). Hence increasing water saturation increases the number of hot spots and therefore promotes N_2O emissions via denitrification (Russow *et al.*, 2000).

The strong correlation between soil moisture and cumulative denitrification illustrated in Figure 5.4 underlines the fact that soil moisture is one of the main limiting factors that can affect N_2O flux in the field (Linn and Doran, 1984; Stevens *et al.*, 1998; Mathieu *et al.*, 2006). The exponential relationship was such that there was no significant difference between the cumulative amount of N_2O emitted over 48 hours from the 30% and 35% soil moisture treatments. Certainly in the grassland field (from where the soil was taken for the laboratory incubations), soil moisture values only approached 40% for one sampling week in April 2005. This may account for soil moisture not correlating directly with N_2O flux for the field measurements but only in its interaction with soil nitrate (Chapter 2, 3 and 4).

5.4.3 Effects of incubation temperature

Temperature can influence denitrification both positively and negatively where denitrification has an optimum temperature, above and below which rates decrease (Addiscott, 1983; Scott *et al.,* 1986; Beauchamp *et al*., 1989; Flessa *et al*., 2002). In this experiment the maximum incubation temperature was only 25°C so no calculation of optimum temperature is possible. Here the rate of denitrification increased exponentially with increasing the temperature from 10°C to 25°C. Q_{10} values for cumulative N_2O emissions over the 48 h incubation were approximately 4 to 6 depending upon what temperature comparison was made. Using the exponential equation an overall Q_{10} of 5.8 was calculated, where $\ln(Q_{10}) = 10 \times$ constant $K = 0.177$. The calculated Q_{10} value of 5.8 is high. What this signifies is that for an increase in temperature of 10°C, the cumulative amount of N_2O produced through denitrification increases almost 6 fold. Typical Q_{10} values in the literature for denitrification in soils range from 1.7 to 3 (McKenney, 1984; Peterjohn, 1991; Ambus, 1993; Scholefield *et al*., 1997). However, in the lab' incubation described in this chapter all variables other than temperature have been optimized. Under such conditions in the field, where other factors such as moisture and nitrate are not limited, denitrification is extremely sensitive to temperature and Q_{10} values as high as 8 have been recorded (Dobbie *et al.,* 1999). This would also account for the lack of effect of temperature on N_2O flux in the grassland field. As discussed for soil moisture, the limiting effects of soil nitrate may have masked any possible influence of temperature.

Whilst the Q_{10} values obtained were high, the activation energy for denitrification of 47 $kJmol^{-1}$ was well within the range of literature values for denitrification in soils of approximately 40 to 85 $kJmol^{-1}$ (McKenny *et al*., 1984; Peterjohn, 1991; Ambus, 1993).

5.4.4 Effects of N fertilizer

In agricultural soils nitrate originates from fertilizer application or is produced by chemoautotrophic nitrifying bacteria that oxidize ammonium under aerobic conditions. Thus the application of CAN significantly affects soil denitrification by increasing the concentration of soil nitrate substrate (Burford and Bremner, 1975; Tiedje, 1982; Carter *et al.,* 1995; Wagner *et al.,* 1996; Hofstra and Bouwman, 2005). In this experiment a positive correlation between denitrification and soil nitrate, derived from fertilizer application was observed (Figure 5.9 and 5.10), not surprisingly given the limiting effects of soil nitrate on the measured field rates of N_2O flux (Chapters 2, 3 and 4). However, although a high correlation coefficient was obtained for denitrification vs soil nitrate ($r^2 = 0.86$), the slope was not significantly different from zero. As Luo *et al.* (2000) has found that such correlations may involve an interaction with soil moisture, and that higher correlations could be obtained at higher soil moisture contents, then may be increasing the soil moisture content above 45% would have improved the results obtained.

Using the fertilizer application data, it is possible, as with the field data, to calculate an emission factor (EF) for denitrification, and to compare this with EFs for N_2O flux from the grassland field where the soil samples for the lab' incubation were sampled. If, as argued in Chapter 2 by the non-correlation of soil ammonium with N_2O flux, that such emissions in the field are mostly due to denitrification, the EFs for denitrification and N_2O flux from the field should be similar. As the soil was sampled in 2005, it is the 2005 field data set that should be used. Table 5.9 illustrates this comparison. Here, for the lab' incubations, the EF decreases with increasing fertilizer application rate. Plotting this data and calculating an equation for the line, as illustrated in Figure 5.11, gives an estimate of the EF for denitrification at 100 kg CAN-N ha^{-1} of 0.61%, which is exactly the same value for the EF for the grassland soil that was determined for the third application of fertilizer of 100 kg CAN-N ha^{-1}.

The decline in EF with increasing fertilizer concentration is of interest. It implies that a greater proportion of added fertilizer is converted to N_2O at the lower application rates, and may suggest a saturation of maximum denitrification within the closed system of the incubation bottles. This has also been seen by Scholefield *et al.* (1997), using an open incubation system in which N_2O and N_2 are continuously removed in stream of Helium. Here increasing the amount of added nitrate from 25 to 200 kg N ha^{-1} decreased the proportion of added N that was denitrified by 50%.

Table 5.9: Comparison of emission factors (EFs) for denitrification and field measurements of total N_2O flux.

Applied fertilizer (kg CAN-N ha^{-1})	EF (denitrification as determined in the laboratory)	se	EF (total N_2O emissions in the field)	se
47	0.94	0.16		
95	0.61	0.09		
142	0.46	0.07		
100			0.61	0.03

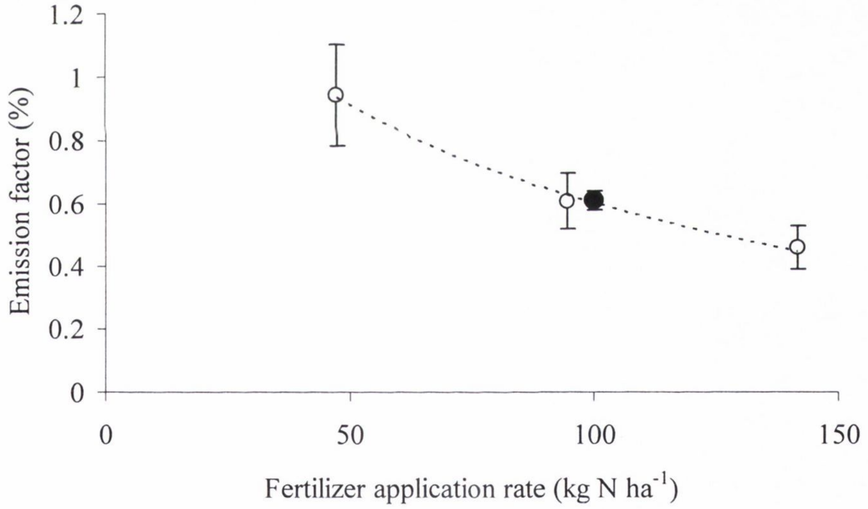

Figure 5.11: Relationship between emission factor and increasing N fertilizer application rate. Symbols indicate: denitrification (○) and field measurement of total N_2O flux (●). Each point represents the mean ± se. $y = -0.4456 \ln(x) + 2.6551$, $r^2 = 0.995$.

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Chapter 6: Field validations of DNDC-model for N_2O emissions from the cut and grazed pasture and the spring barley field

6.1 Introduction

The estimation of nitrous oxide emissions from agricultural soils is of considerable interest because of the importance of fertilized agriculture as a source of N_2O to the atmosphere (Davidson, 1991). Variations in soil moisture, soil temperature, carbon and nitrogen substrate for microbial nitrification and denitrification are critical to the determination of N_2O emissions (Leffelaar and Wessel, 1988; Tanji, 1982; Frissel and Van Veen, 1981; Batlach and Tiedje, 1981; Cho *et al.*, 1979). In a literature review on N_2O emissions from agriculture Williams *et al.*, (1992), documented the considerable variations in temporal and spatial variability in emission data. They concluded that linkage among microbial, physical and chemical variables that influence nitrification, denitrification, decomposition and N_2O transport in soils occur over many temporal and spatial scales which makes interpretation of the available data difficult. To overcome this they recommended that models be developed which can simulate the processes responsible for production, consumption and transport of N_2O at all relevant temporal and spatial scales for developing emission inventories.

Recently, the use of different kinds of model has become popular to estimate N_2O emissions from cropping systems. This allows the development of mitigation strategies, the extrapolation of results from small scale experimental plots to the regional and global scale and to overcome the laborious field work.

Numerous simulation models have been developed to estimate denitrification rates and processes in soils like DNDC, CENTURY, ExpertN and NASA-Ames model. These models include similar components (soil physics, decomposition, plant growth and N transformations), but in some cases use different algorithms for these processes. The simulated N_2O fluxes using these models were within a factor of 2 of the observed annual fluxes, but even when models produced similar N_2O fluxes they often produced very different estimate of gaseous N loss as nitric oxide (NO), dinitrogen (N_2) and ammonia (NH_3) (Frolking *et al.*, 1998).

The DeNitrification DeComposition (DNDC) model is a process oriented model of soil carbon and nitrogen biogeochemistry for agricultural soils (Li *et al.*, 1992a, 1994). This model was later expanded to simulate NO, N_2O, CH_4, CO_2 and NH_3 emissions (Li, 2000). The model consists of two components. The first component, consisting of the soil climate, crop growth and decomposition sub-models, predicts soil temperature, moisture, pH, redox potential and substrate concentration profiles driven by ecological drivers. The second component, consisting of nitrification, denitrification and fermentation sub-models predicts NO, N_2O, N_2, CH_4 and NH_3 fluxes based on the modeled soil environment factors. The advantage of the DNDC-model is that it has been extensively tested and showed reasonable agreement between measurements and model results for many different ecosystems (Li, 2000; Stange *et al.*, 2000; Brown *et al.*, 2001; Smith *et al.*, 2002; Li *et al.*, 2004; Kesik *et al.*, 2005). However, validation of the model does not always work well. For example the deviation between model and measurements for the annual N_2O emissions from managed grassland in Dutch and Flemish grasslands was approximately 100% (De Vries *et al.*, 2005).

The aim of this modeling process is to assess the reliability of the DNDC-model for estimating N_2O from the grass and arable fields by validating it against field measurements of N_2O. In addition to this, the model was used to calculate the emission factors for N_2O emissions and to predict possible scenarios for N_2O mitigation strategies.

6.2 Materials and Methods

6.2.1 DNDC-model validations

In this Chapter validations of the DNDC model were implemented with the data sets collected from the cut and grazed pasture and the small plots of the arable field in addition to climate variables from the Teagasc Research Centre weather station in Carlow. Daily mean maximum and minimum temperature and daily precipitation were prepared for the model. For the arable field, model validation was possible only for the vegetation period, hence measurements were lacking for the rest of the year.

The validation of DNDC model was carried out by 1) comparing the measured and modeled temporal pattern of N_2O flux and 2) comparing the measured and modeled cumulative N_2O emissions and EFs. The relative deviation (y) of simulated emissions from those observed was calculated by the following equation:

$$Y = (X_S - X_O)/X_O \times 100,$$

Where X_O is the observed emission and X_S is the simulated emission. DNDC annual and seasonal emissions were the sum of simulated daily fluxes (Cai *et al.*, 2003).

6.2.2 N_2O emissions from the arable field

Measurements of N_2O emissions from the arable spring barley field (small plots) were carried out for two consecutive seasons on a weekly basis as mentioned in Chapter 4. Field site description and management is also as described in Chapter 4.

6.2.3 N_2O emissions from the grazed pasture

Measurements of N_2O emissions from the cut and grazed pasture were carried on a weekly basis as mentioned in Chapter 2. Field site description and management is also as described in Chapter 2.

6.2.4 Calculation of emission factor

The N_2O emission factors were calculated by subtracting the model N_2O emissions of unfertilized soils from the model N_2O emission of fertilized soils divided by the N fertilizer input corrected for ammonia volatilization.

6.2.5 Model sensitivity

The response of sub models and the complete model to variations of relevant parameters from baseline conditions was tested by varying one parameter and fixing others during one cycle of the model. This sensitivity analysis demonstrates that the model behavior is consistent with its structure and assumptions (Li, 1992).

6.3. Results

6.3.1 Simulation of N_2O emissions from the barley field (small plots)

Emissions of N_2O from the fertilized conventional and reduced tillage plots were described well by the DNDC-model. Differences between simulated and observed seasonal emissions for all fertilizer treatments ranged from -0.38 to 0.12 kg N ha^{-1} (Table 6.1). The simulation of N_2O at high N fertilizer rates (140 and 159 kg N ha^{-1}) gave relative deviations from the observed of -1.4 and 13% for conventional tillage and -16 and -39% for reduced tillage respectively (Figures 6.1 and 6.2). However, simulation of N_2O at medium N fertilizer (70 and 79 kg N ha^{-1}) gave the best fit for conventional tillage with relative deviations of -15.9 and 30%, but less satisfactory results for reduced tillage with relative deviation of -24 and -55% (Figures 6.3 and 6.4). The average relative variation for all fertilized treatments was 24%. Emissions from the zero fertilizer plots of both the conventional and reduced tillage treatments were poorly described by the DNDC-model, with relative deviations of the simulated from the observed ranging from -33% to 10 times the measured flux values (Figures 6.5 and 6.6). However these differences are associated with a small range emissions of N_2O (-0.12 to 0.10 kg N ha^{-1}).

Table 6.1: Observed and modeled seasonal N_2O emissions from conventional and reduced tillage plots.

		Seasonal emissions (kg N ha^{-1})		
2004 season	Treatment	Observation	Model	Difference
Conventional tillage	140 kg N ha^{-1}	0.79	0.78	-0.008
	70 kg N ha^{-1}	0.26	0.35	-0.08
	0 kg N ha^{-1}	0.01	0.11	+0.10
Reduced tillage	140 kg N ha^{-1}	0.99	0.59	-0.38
	70 kg N ha^{-1}	0.49	0.22	-0.27
	0 kg N ha^{-1}	0.09	0.03	-0.06
2005 season				
Conventional tillage	159 kg N ha^{-1}	0.87	0.99	+0.12
	79 kg N ha^{-1}	0.39	0.45	+0.06
	0 kg N ha^{-1}	0.16	0.11	-0.05
Reduced tillage	159 kg N ha^{-1}	0.94	0.79	-0.15
	79 kg N ha^{-1}	0.42	0.32	-0.10
	0 kg N ha^{-1}	0.13	0.10	-0.12

Figure 6.7 illustrates a positive linear correlation between the simulated and measured N_2O emissions. The correlation between them is significant with an r^2 value of 0.8, the regression equation: $y = 0.81x + 0.034$, indicating that the DNDC-model generally underestimates N_2O emissions compared with the field collected measurements.

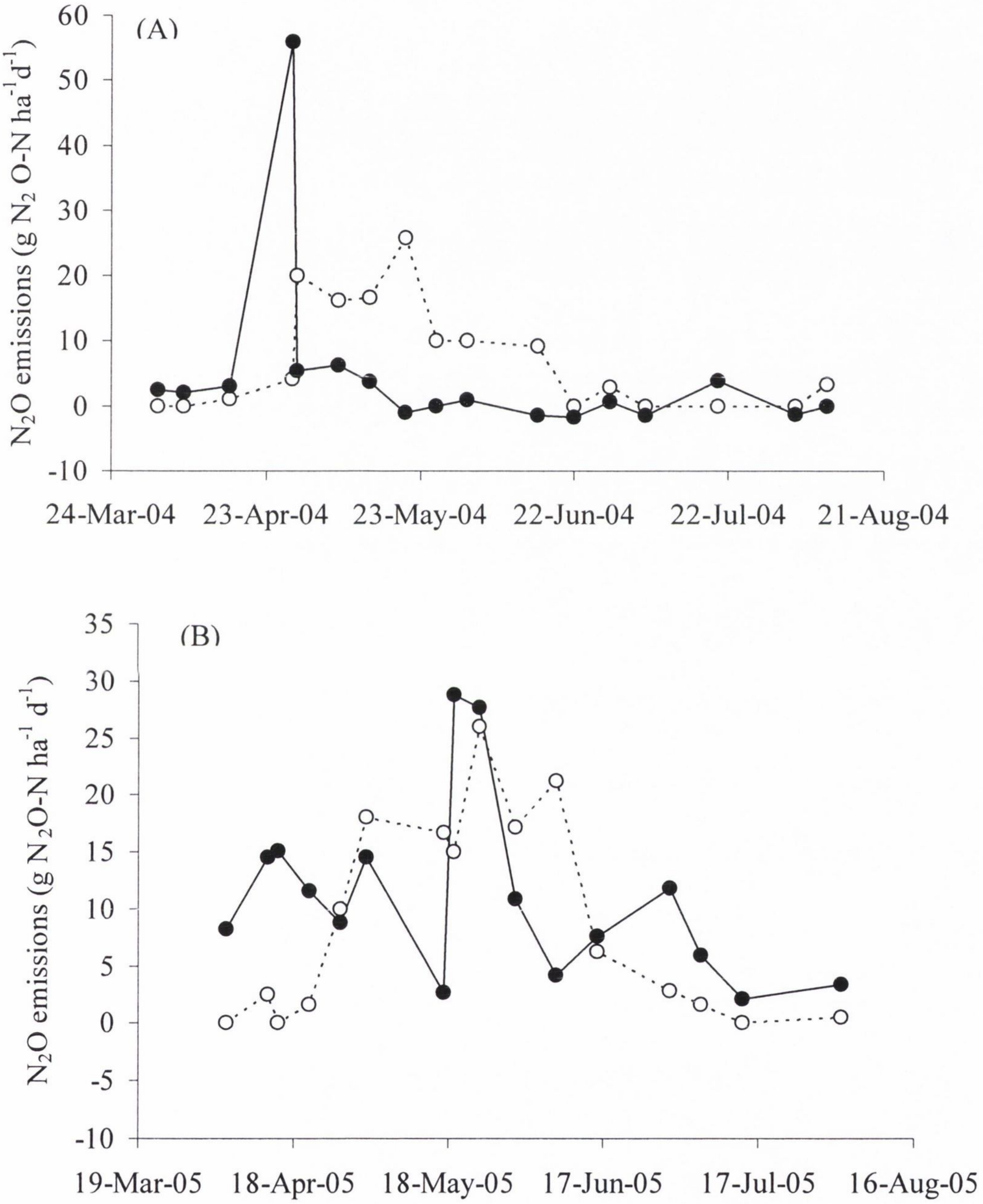


Figure 6.1: Comparison of model-simulated N_2O (○) and field measured N_2O (●) from the high fertilized, (140 and 159 kg N ha^{-1}), conventional tillage in 2004 (A) and 2005 (B).

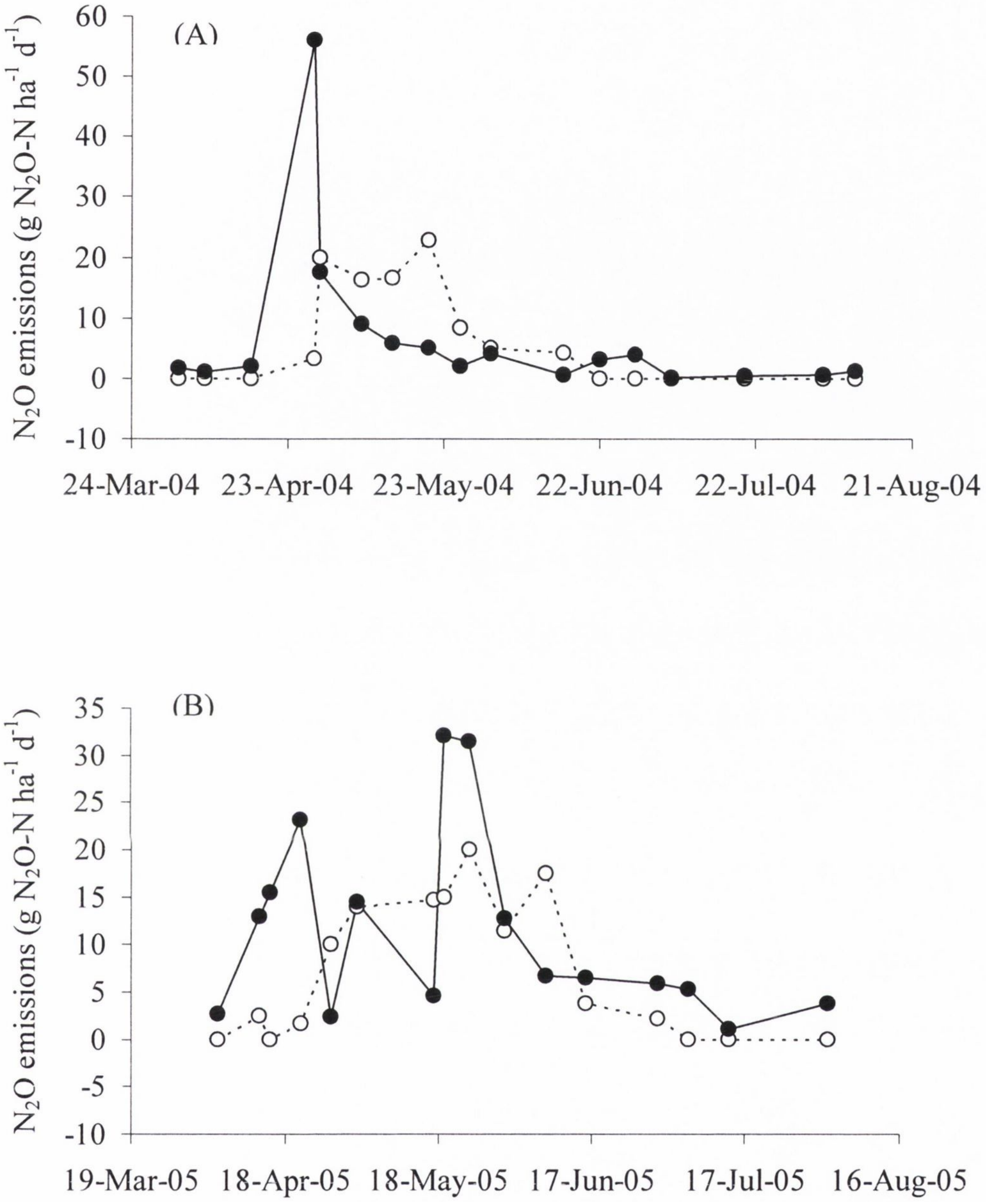


Figure 6.2: Comparison of model-simulated N_2O (○) and field measured N_2O (●) from the high fertilized, (140 and 159 kg N ha^{-1}), reduced tillage in 2004 (A) and 2005 (B).

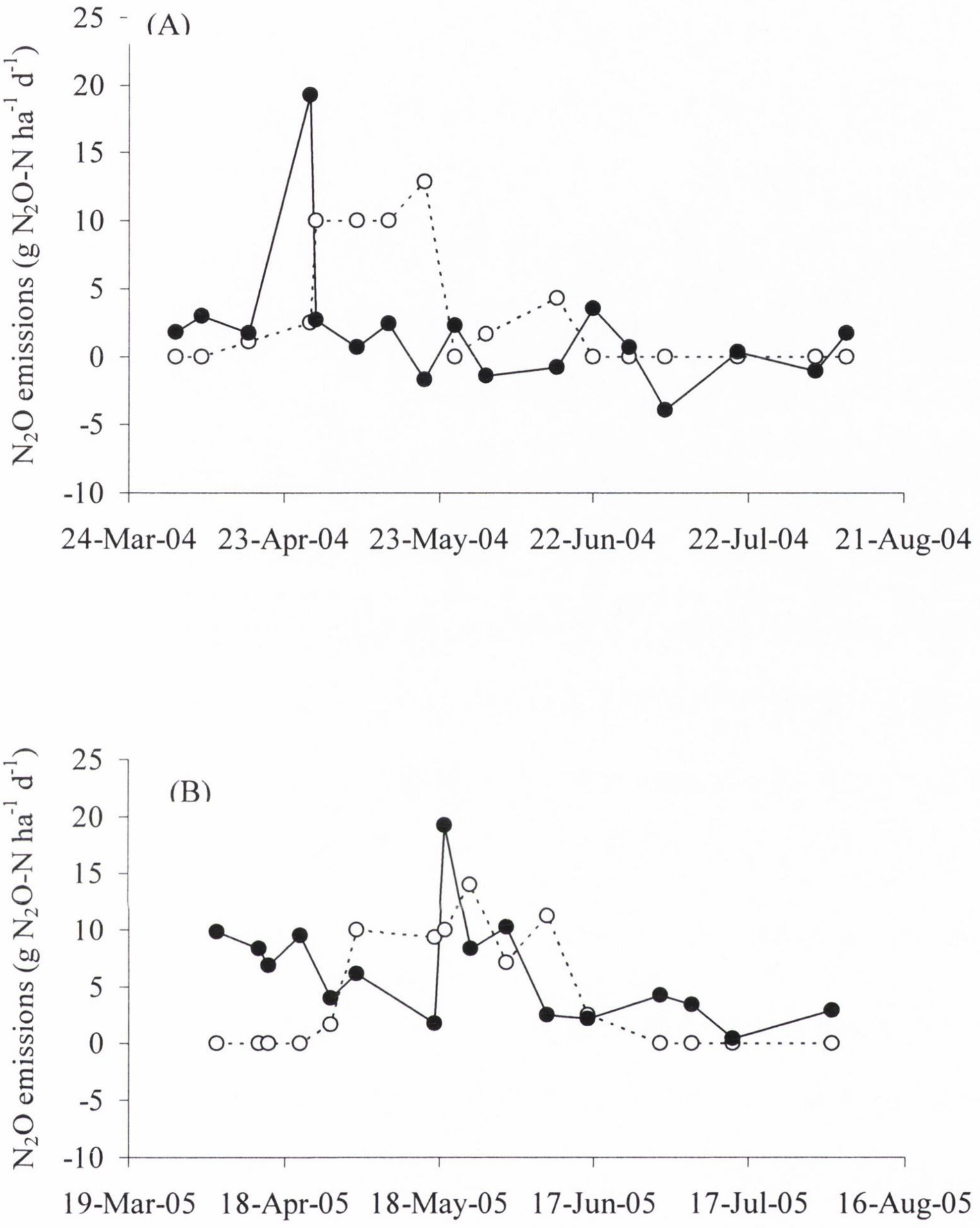
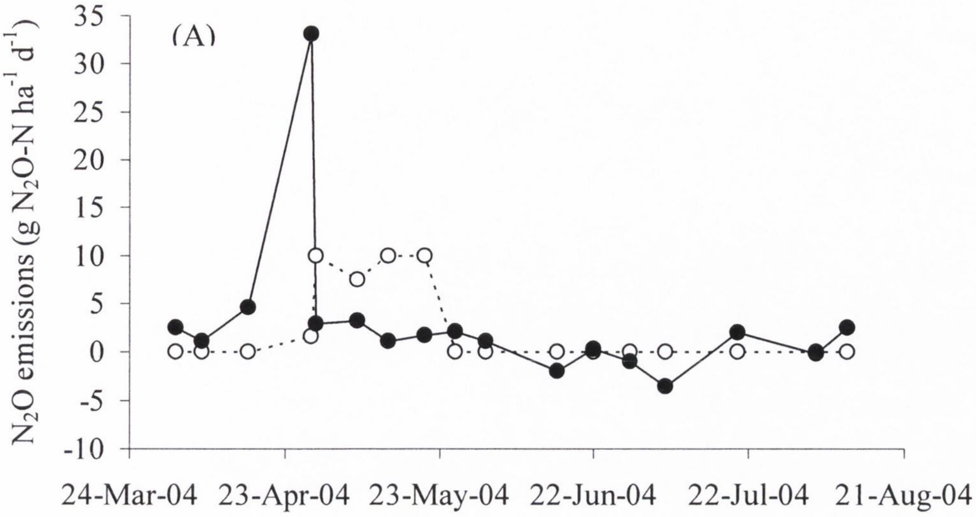


Figure 6.3: Comparison of model-simulated N_2O (○) and field measured N_2O (●) from the medium fertilized, (70 and 79 kg N ha^{-1}), conventional tillage in 2004 (A) and 2005 (B).



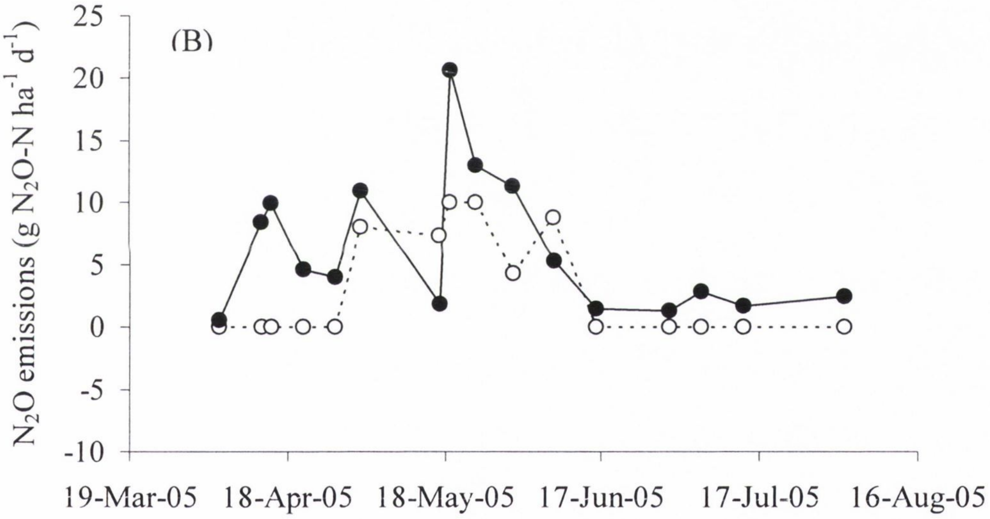
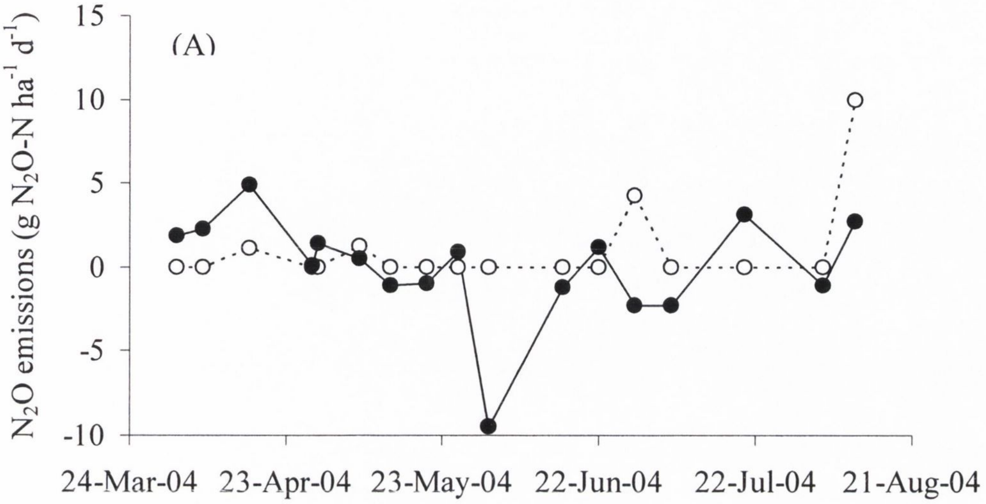


Figure 6.4: Comparison of model-simulated N$_2$O (○) and field measured N$_2$O (●) from the medium fertilized, (70 and 79 kg N ha^{-1}), reduced tillage plots in 2004 (A) and 2005 (B).



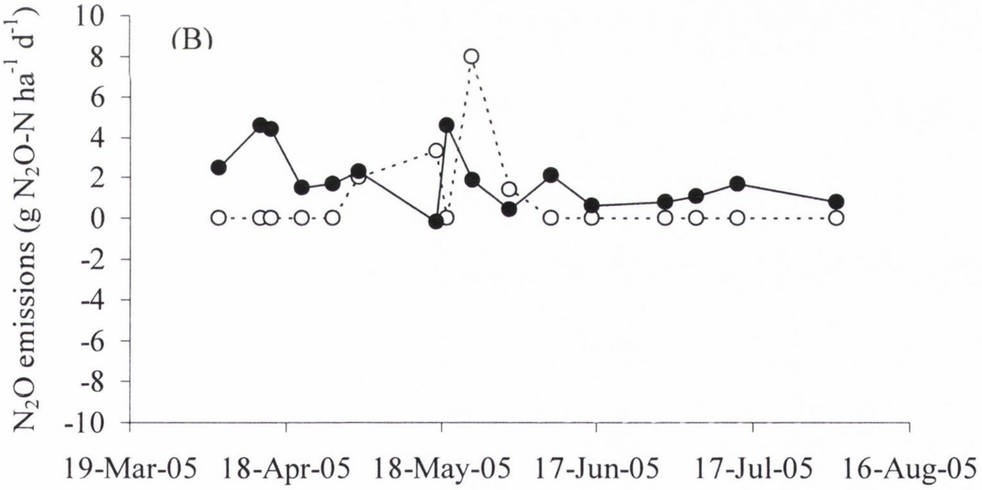
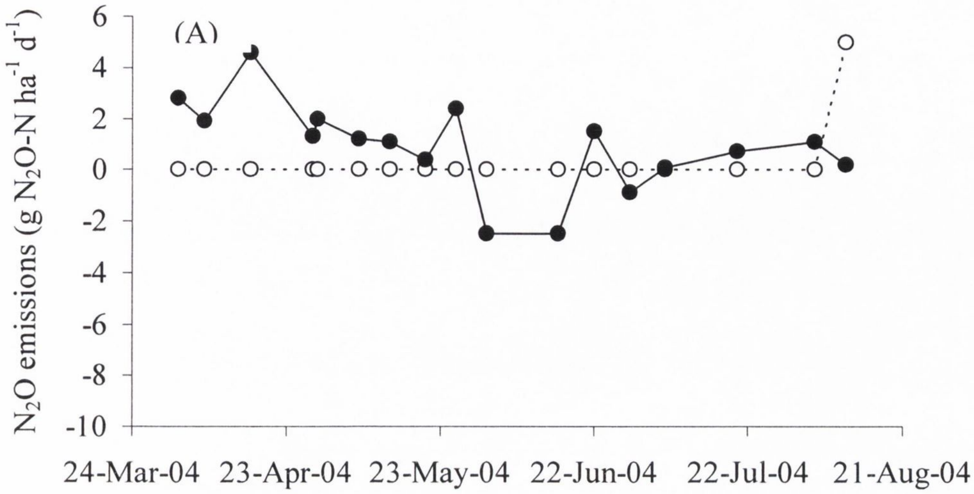


Figure 6.5: Comparison of model-simulated N_2O (○) and field measured N_2O (●) from the control (0 N kg ha^{-1}) conventional tillage in 2004 (A) and 2005 (B).



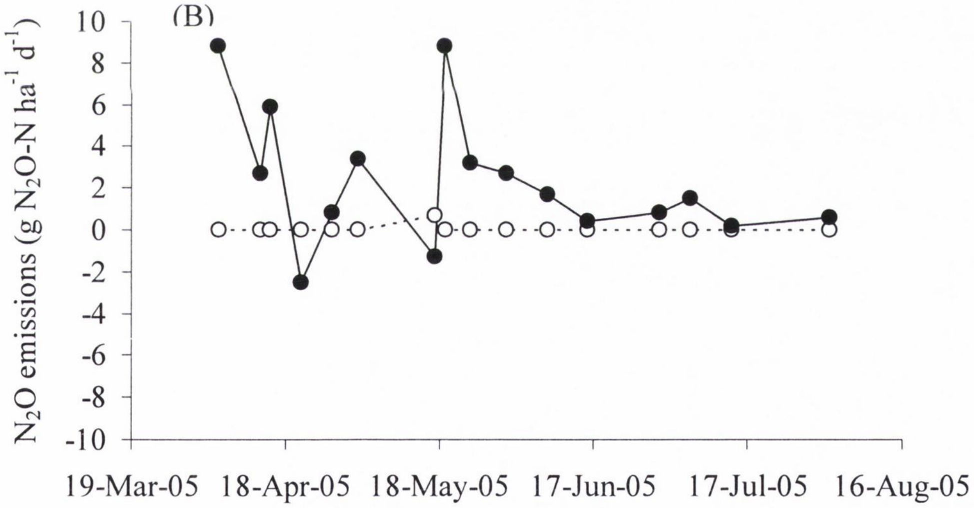


Figure 6.6: Comparison of model-simulated N_2O *(○) and field measured* N_2O *(●) from the control (0 N kg* ha^{-1}*) reduced tillage in 2004 (A) and 2005 (B).*

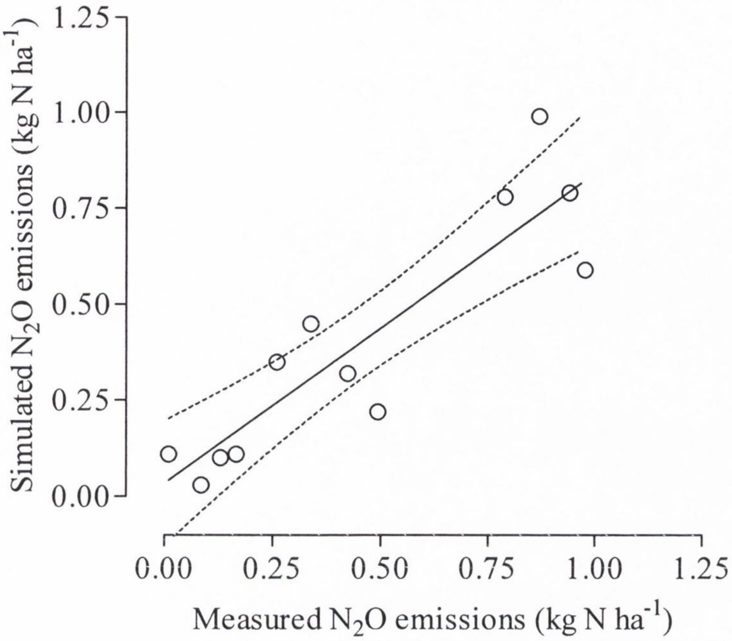


Figure 6.7: Comparison of simulated emissions using the DNDC with measured seasonal fluxes of N_2O *from the spring barley field.* $y = 0.81x + 0.034$ $(r^2 = 0.8)$*. The dotted lines representing the 95% confidence interval.*

6.3.2 Simulation of N_2O *emissions from the pasture field*

Figure 6.8 illustrates a comparison between model-simulated and field measured N_2O fluxes from the fertilized and control pasture plots from October 2003 to November 2004 respectively. With the exception of a few high peaks in N_2O emissions which were observed from both the fertilized and control plots, the simulated emissions of N_2O flux by DNDC-model showed almost the same seasonal patterns as the field measured flux. These higher peaks resulted in an annual cumulative N_2O flux of 6.04 and 3.58 kg N_2O-N ha^{-1} , with annual differences of 3.55 and 2.65 kg N_2O-N ha^{-1}, for fertilized and control plots respectively (Figures 6.8 and 6.9). Therefore the estimation of seasonal emissions was very poor with relative variations of 151% (for fertilized plots) and 284% (for the control plots) from the measured flux.

For 2005, the DNDC-model was used to estimate N_2O flux from the fertilized plots, as the N_2O flux from the control plots was measured for a short period only. Here the model also produced similar patterns as the observed flux (Figure 6.9), but in contrast to the 2004 data, underestimated N_2O emissions from the fertilized plots and gave 1.27 kg N_2O-N ha^{-1} with a relative difference of 56% from the measured flux.

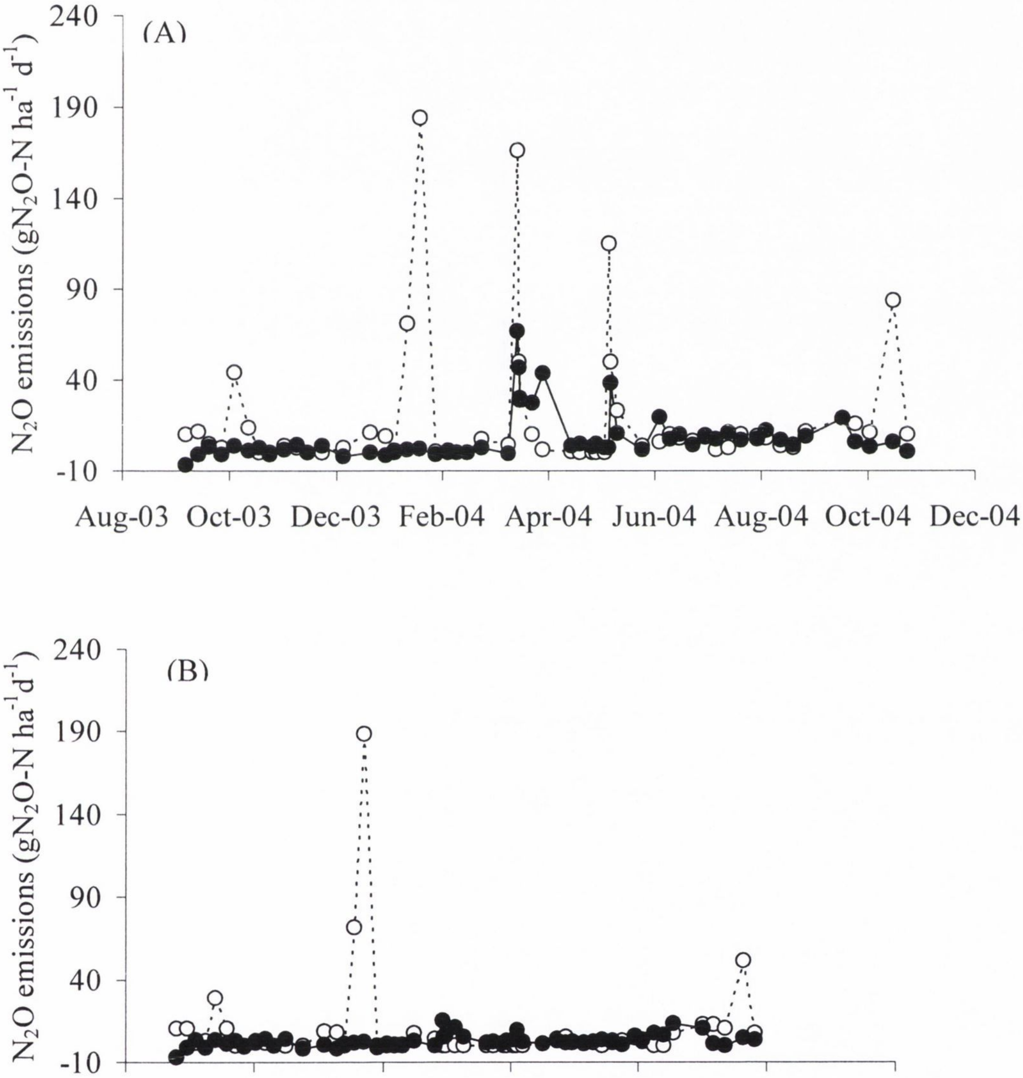


Figure 6.8: Comparison of model-simulated N_2O (○) and field measured N_2O (●) fluxes from the fertilized (A) and control (B) pasture plots in 2003-2004.

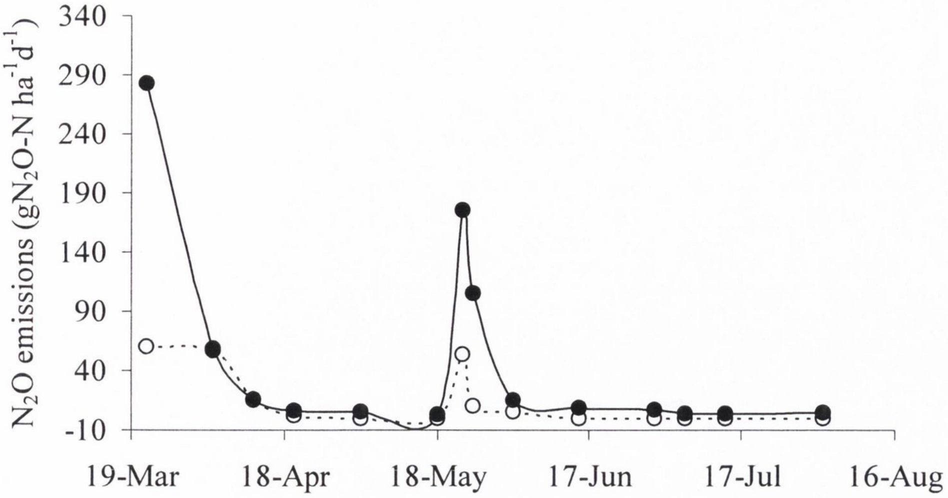


Figure 6.9: Comparison of model-simulated N_2O (○) and field measured N_2O (●) from the fertilized pasture plots in 2005.

6.3.3 Emission factors

Emission factors for the simulated seasonal N_2O emissions from the conventional and reduced tillage plots ranged from 0.4 to 0.6% and 0.3 to 0.5% of the applied N fertilizer for 2004 and 2005 respectively. For the cut and grazed pasture, an emission factor of 1.37% was calculated for the period, November 2003 to November 2004.

6.3.4 Sensitivity to agricultural practices

Tables 6.2 and 6.3 illustrate the sensitivity of the DNDC-model to changes in soil characteristics, management and climate for the arable field, conventional and reduced tillage respectively. For the conventional tillage, increasing soil bulk density to 1.8g cm^{-3} increased predicted soil N mineralization by 26% and N_2O fluxes to the atmosphere by 66%. A lower soil pH of 4 decreased N_2O flux with 94% however, a higher soil pH of 8 also decreased N_2O flux by 38%. A 20% increase in initial soil organic carbon resulted in 19% increase in N mineralization and 62% increase in N_2O emissions. The increasing of the fertilizer amount by 50% increased the flux by 51% and affects the ratio of N_2O/N_2O+N_2. Moreover, varying fertilizer application time had less effect on N_2O emissions; however application of different fertilizer type like urea and ammonium sulphate gave 54 and 59% more N_2O emissions respectively and showed more pronounced influence N_2O/N_2O+N_2. A 20% increase in daily rainfall resulted in a 10% increase in the flux however a 20% increase in air temperature resulted in 66% more flux.

Table 6.2: Sensitivity of the DNDC-model to change in soil characteristics, management and climate at the spring barley field (conventional tillage, 2004).

Scenario	Mineralization Rate kg N $ha^{-1}y^{-1}$	Annual flux (kg N $ha^{-1}y^{-1}$) N_2O	N_2	N_2O+N_2	Ratio (N_2O/N_2O+N_2)
**Baseline*	257.4	*1.6*	*2.4*	*4*	*0.4*
Bulk density(g cm^{-1})					
1	194	0.67	1.00	1.67	0.40
1.6	290.8	2.11	2.22	4.33	0.45
1.8	324.2	2.65	3.48	6.13	0.43
Soil pH					
4	257.4	0.09	0.18	0.27	0.33
6	257.4	1.62	2.05	3.67	0.44
8	257.4	1	1.76	2.76	0.36
Initial soil organic carbon					
+20%	305.8	2.59	3.51	6.1	0.42
-20%	211.1	0.69	1.05	1.74	0.40
Fertilizer amount (kg N ha/y)					
210	259.8	2.41	2.46	4.87	0.49
70	257.4	1.03	2.06	3.09	0.33
Fertilizer type					
Urea	257.4	2.46	2.35	4.81	0.51
Ammonium bicarbonate	257.2	1.4	2.06	3.46	0.40
Ammonium sulphate	257.4	2.54	2.36	4.9	0.52
Fertilizing timing					
15th of April	257.4	1.53	2.34	3.87	0.40
15th of May	257.4	1.65	2.4	4.05	0.41
27th of May	257.2	1.6	2.45	4.05	0.40
Rainfall					
+20%	267.1	1.76	2.75	4.51	0.39
-20%	244.5	1.41	1.57	2.98	0.47
Air temperature					
+20%	269.6	2.65	4.27	6.92	0.38
-20%	243.2	0.93	1.41	2.34	0.40

**Baseline scenario: Bulk density 1.4g/cm^3, soil pH 7.0, SOC 0.0194 kg C/kg, fertilizer applied and timing (140kg N/ha CAN, on the 27th of April), annual average max. and min. air temperature 13.7 and 4.8°C and average daily precipitation 2.2cm and soil tillage to 22cm depth carried in March five weeks before planting.*

Table 6.3: Sensitivity of the DNDC-model to change in soil characteristics, management and climate at the spring barley field (reduced tillage)

Scenario	Mineralization Rate kg N $ha^{-1}y^{-1}$	Annual flux (kg N $ha^{-1}y^{-1}$)			Ratio (N_2O/N_2O+N_2)
		N_2O	N_2	N_2O+N_2	
**Baseline*	303.8	*4.74*	*1.74*	*6.48*	*0.73*
Bulk density(g cm^{-3})					
1	249.3	2.67	0.71	3.38	0.79
1.6	335	5.41	1.81	7.22	0.75
1.8	366.8	6.1	3.43	9.53	0.64
Soil pH					
4	303.8	0.56	0.15	0.71	0.79
6	303.8	4.51	1.47	5.98	0.75
8	303.8	3.2	1.36	4.56	0.70
Initial soil organic carbon					
+20%	351.7	6.11	3.12	9.23	0.66
-20%	257.6	3.14	1.17	4.31	0.73
Fertilizer amount (kg N ha/y)					
210	304.1	5.98	2.27	8.25	0.72
70	310	4.22	1.87	6.09	0.69
Fertilizer type					
Urea	303.8	5.4	1.79	7.19	0.75
Ammonium bicarbonate	303.7	4.17	1.75	5.92	0.70
Ammonium sulphate	303.8	5.52	1.77	7.29	0.76
Fertilizing timing					
15th of April	303.8	4.62	1.76	6.38	0.72
15th of May	303.8	4.7	1.74	6.44	0.73
27th of May	303.8	4.63	1.77	6.4	0.72
Rainfall					
+20%	316.6	4.96	2.26	7.22	0.69
-20%	287.1	4.3	1.19	5.49	0.78
Air temperature					
+20%	323.2	6.72	2.9	9.62	0.70
-20%	286.7	2.96	1.19	4.15	0.71

**Baseline scenario: Bulk density 1.4g cm^{-3}, soil pH 7.0, SOC 0.0194 kg C/kg, fertilizer applied and timing (140kg N/ha CAN, on the 27th of April), annual average max. and min. air temperature 13.7 and 4.8°C, average daily precipitation 2.2cm, soil tillage to 15cm depth carried in September of the year before planting.*

For the reduced tillage, increasing soil bulk density to 1.8g cm^{-3} increased predicted soil N mineralization with 21% and N_2O fluxes to the atmosphere by 29%. A lower soil pH of 4 decreased N_2O flux by 88% however, a higher soil pH of 8 also decreased N_2O flux by 32%. Unlike the conventional tillage soil organic carbon had less effect, a 20% increase in initial soil organic carbon resulted in only16% increase in N mineralization and 29% increase in N_2O emissions. The increasing of the fertilizer amount by 50% increased the flux by 26%. Moreover, varying fertilizer application time and application of different fertilizer type like urea and ammonium sulphate had less effect on N_2O emissions and N mineralization. A 20% increase in daily rainfall had less effect on the flux however, a 20% increase or decrease in air temperature resulted in 42% more flux or 38% less flux respectively.

6.4 Discussion

Results described in this Chapter assess the reliability of the DNDC-model for estimating N_2O flux from the spring barley small plots field and the cut and grazed pasture field by validating it against field measurements of N_2O. In addition the model was used to estimate the impact on N_2O emissions of changes in agricultural management practices, soil and climatic change and to calculate emission factors. Here several management practices were examined including conventional tillage, reduced tillage and variable rates of N-fertilizer application.

For the arable field, a comparison between measured and simulated annual N_2O fluxes is not possible because N_2O fluxes in 2004/2005 were measured from April to August only. In addition, an estimation of annual emissions using the background emissions and EF is not valid for this experiment as discussed in Chapter 4. Therefore comparison on a seasonal basis is the only way which can be used for this experiment. However for the pasture field the model was validated using the annual flux, as full annual measurements from the pasture field are available. The DNDC-model was found to be valid for the estimation of N_2O flux from the arable small plot trial soil (sandy loam to loam), but poorly estimated the flux from the grassland (sandy clay loam). Similar results were found for managed Dutch and Flemish grasslands where the difference of the predicted flux using the DNDC from the measured flux was approximately 100% (De Vries *et al.*, 2005).

Seasonal emissions of N_2O from the arable field for the fertilized conventional and reduced tillage plots, were described well by the DNDC-model, with some small differences of -0.38 to 0.12 kg N ha^{-1} where the model under or over-estimated emissions (Table 6.1). Here an average relative variation of 24%, between simulated and measured flux, was calculated. This is excellent in comparisons with published N_2O emission data for grass and arable soils using the DNDC-model (see Table 1.5). In most of the cases the model was able to capture N_2O peaks, however the modelled peaks sometimes occurred later than the observed and in place of giving one sharp peak, some peaks continued for some time before returning back to background level. A comparison between the model output and measured data in 2004, revealed that the model overestimated the WFPS in some parts of the season. For example the maximum measured WFPS for conventional tillage in 2004, was 57%, whereas the estimated WFPS was 67%. This overestimation of WFPS may be behind the observed discrepancies at some times in the season.

However, the correlation between the seasonal simulated and observed N_2O flux from the arable plots illustrated in Figure 6.7, which included data from two years, different fertilization rates and different tillage systems, was extremely significant, the linear equation accounting for 80% of the variations in the data. This strong correlation between simulated and measured flux shows that the DNDC-model can be used for the estimation of N_2O flux in this case. In the case of the control plots only though, the small range of emissions (-0.12 to 0.10 kg N ha^{-1}), was poorly described by DNDC. Here, relative deviations ranged from -33% to 10 times the measured flux values (Table 6.1).

As discussed in Chapters 2, 3, 4 and 5, N fertilizer application rate is a major driving force for N_2O flux from soils. This is confirmed by the outputs of the DNDC-model. Hence in 2004 annual fluxes were increased by 51 and 26% for the conventional and reduced tillage plots respectively, when N-fertilizer was doubled (Tables 6.2 and 6.3). Similar effects of N fertilizer were estimated by Crill *et al.* (2000) using data from a maize field. In 2005 seasonal N_2O fluxes simulated from all treatments were higher compared with 2004 due to higher N fertilizer application rates (Table 6.1). Here denitrification increased by 22 and 27% for the conventional and reduced tillage plots respectively.

With regards to the effect of soil tillage on N_2O emissions a significant agreement between measured and modelled data has been observed. Outputs from the DNDC showed a small difference in N_2O flux due to tillage. Here a difference of 0.2 kg N_2O-N ha^{-1} between seasonal N_2O emissions from conventional and reduced tillage for both 2004 and 2005 was calculated, where reduced tillage gave 20% less flux than the conventional tillage. However, replacing CAN with other types of fertilizer like urea and ammonium sulphate increases the flux from conventional tillage by 54 and 58% and from reduced tillage by only 14 and 16% respectively. The pronounced sensitivity of the DNDC-model to low or high pH is in agreement with Knowles, (1981) who found that the optimal pH range for denitrification is 7 – 8, and Eaton and Patriquin, (1989) who reported a decrease in denitrification rate for pH values below 6.

For the pasture field, the DNDC overestimated significantly the N_2O emissions in 2004 whilst underestimating the emissions in 2005. For both years, the model had the same pattern and was able to pick out most of the peaks. However, the presence of two high peaks from both the control and fertilized plots in the winter of 2004 led to a significant overestimation of the cumulative N_2O emissions. This may be related to a high soil organic carbon (0.038 kg C kg^{-1} dry soil) at the site as the model is very sensitive to SOC, and an increase of 20%, equivalent to 3.8g kg^{-1}, organic carbon increased both N mineralization and annual N_2O emission by 19 and 62% respectively. Similar influences of SOC were reported by Li *et al.* (1992), Brown *et al.*, (2002) and Hsieh *et al.* (2005). Because measurements in the field were made only on a weekly basis, it is also possible that the peaks predicted by the DNDC were missed. In 2005 the model had the same pattern of flux but underestimated the emissions. The reason here may be because the model underestimated the WFPS during March and early April, where higher N_2O flux peaks were measured. Here the maximum estimated WFPS was approximately 50%, whereas the measured maximum WFPS was 67%.

The calculated EFs for the arable field from the simulated emissions ranged from 0.3 to 0.6% for 2004/2005. This is comparable with the overall EF calculated from the measured data of 0.58% (Chapter 4), which is 56% less than the IPCC default value. For the pasture field an EF of 1.37% of the applied N fertilizer was calculated for 2004. This EF is 12% higher than the IPCC default EF of 1.25%.

With respect to the effect of climate change on N_2O flux, the DNDC-model showed that N_2O emissions from the soil were most sensitive to increases in air temperature. Here an increase of 1.5°C in the daily average air temperature resulted in a 66 and 42% increase in the predicted annual flux for the conventional and reduced tillage plots respectively. Similar effects of temperature were reported by Li *et al*. (1996) and Hsieh *et al*. (2005). With regard to rainfall, a reduction of 20%, equivalent to 10mm from the daily total rainfall, resulted in a 12 and 9% reduction in the predicted annual flux values for the conventional and reduced tillage plots respectively.

In conclusion, the DNDC has proven extremely useful in estimating emissions from the arable field, but more work is required to parameterize the DNDC for the grassland soil where a poor correlation between measured and predicted results was obtained. Perhaps the wider range of soil nitrate and soil ammonium values possible with the design of the arable experiment has improved the fit of the model. Certainly a wider data base is required for the grassland site including more intensive measurement periods, and better input data such as soil organic carbon.

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Chapter 7: General Discussion

The aim of this Chapter is to bring together and discuss common observations from all the separate experiments and to suggest further work that is required in determining emission factors of N_2O emissions from the Irish agricultural sector.

The adoption of reduced tillage as a means of mitigating N_2O emissions from the field was not successful in this study which may be a matter of time as discussed in Chapters 3 and 4. However, because N_2O emissions from nitrification and denitrification are closely linked to other N transformations and loss processes (Whitehead, 1995), management options to reduce one loss process could potentially enhance other environmental problems (de Klein *et al.,* 2001). Therefore to have a good mitigation system for reducing N_2O emissions, the nitrogen cycle of agricultural systems as whole should be considered (Jarvis *et al.,* 1996). Moreover, the true mitigation of greenhouse gases in general is possible only when the net Global warming potential (GWP) of the three major greenhouse gases is reduced (Six *et al.*, 2004). Here a long term study, putting these entire factors in consideration, should be carried out.

By plotting the measured N_2O fluxes against simulated fluxes of both the arable and the cut grazed pasture together as illustrated in Figure 7.1, it can be seen that the DNDC-model is valid for estimating N_2O emission from a wide range of soil, tillage and crop only when the soil organic carbon of the pasture field was reduced. Here the regression equation is: $y = 1.039x - 0.049$ and r^2 value is 0.94. However, the correlation at high soil organic carbon for the cut and grazed pasture is poor with regression equation: $y = 1.281x + 0.035$ and r^2 value of 0.45.

Using the standard format described in Chapter 2, EFs were calculated for the grassland for 2004 and 2005, the large cereal plots for 2004 and 2005, the small cereal plots including variable fertilizer application rates for 2004 and 2005, and finally for denitrification in isolation using the grassland soil. All of these EFs are listed below in Table 7.1.

As can be seen, EFs varied from 0.1 to 0.83% of applied N fertilizer. However, by plotting the cumulative N_2O fluxes due to fertilizer against applied N fertilizer corrected for ammonia volatilization, as discussed in Chapter 4, an overall emission factor can be calculated for the two field sites at Carlow. This can be seen below in Figure 7.2.

Clearly the two soils are of the same response with regard to N_2O fluxes as a function of applied fertilizer, the overall gradient giving an apparent EF of 0.61 ± 0.08 %. This is also apparent when one combines the log N_2O flux vs soil nitrate data for the arable and grassland soils as illustrated in Figure 7.3. Here individual slopes did not differ significantly from each other ($P = 0.76$), allowing an overall equation to be calculated that accounted for 48% of the variance of the data, where log N_2O flux = 0.038*(soil nitrate) + 0.019, the slope being significantly different from zero ($P < 0.0001$). This is not surprising given the similarity in soil types. What one cannot do however is apply the new overall EF value for the whole of Ireland, a problem reflected in the wide disparity in EF values given from the three other Irish data sets which range from 0.72 to 4.92% (Scanlon and Kiely, 2003; Hyde *et al.*, 2005; Hsieh *et al.*, 2005).

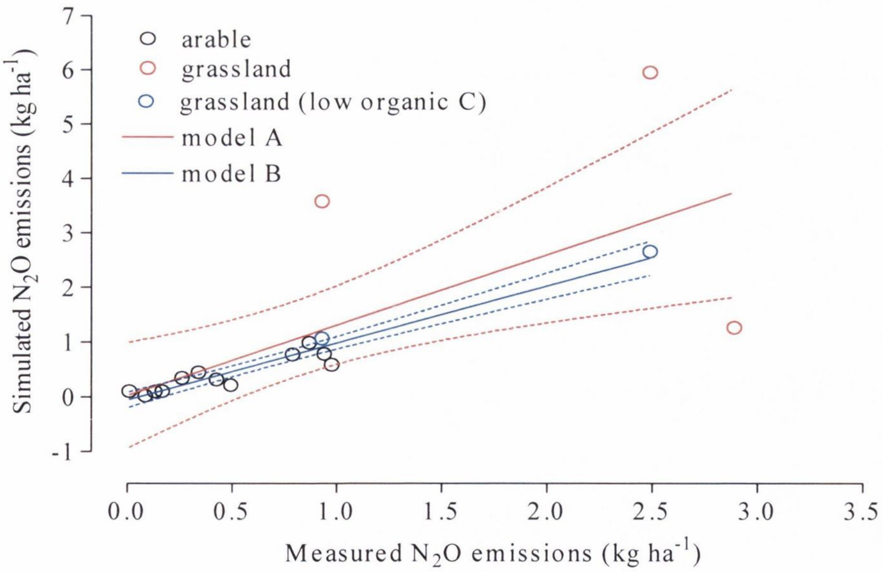

Figure 7.1: Comparison of simulated emissions using the DNDC with measured fluxes of N_2O from the spring barley field (○), the cut and grazed pasture (○) and the cut and grazed pasture at low soil organic carbon (○). Model A and B represent model results before and after SOC reduction. For A: $y = 1.281x + 0.035$, ($r^2 = 0.45$) and for B: $y =$ $1.039x - 0.049$, ($r^2 = 0.94$). *The dotted lines representing the 95% confidence interval.*

Table 7.1: Various EFs calculated for the two soils at Carlow

Crop	2004	2005
Cut and grazed pasture	0.83 ± 0.15 %	0.61 ± 0.03 %
Cut and grazed pasture – denitrification*		0.67 ± 0.14 %
Spring barley large plots Conventional Tillage	0.1 ± 0.13 %	0.6 ± 0.25 %
Spring barley large plots Reduced Tillage	0.58 ± 0.1 %	0.5 ± 0.19 %
Spring barley small plots Conventional Tillage – field rate CAN	0.63 ± 0.06 %	0.61 ± 0.03 %
Spring barley small plots Conventional Tillage – half field rate CAN	0.42 ± 0.41 %	0.54 ± 0.13 %
Spring barley small plots Reduced Tillage – field rate CAN	0.63 ± 0.2 %	0.65 ± 0.14 %
Spring barley small plots Reduced Tillage – half field rate CAN	0.65 ± 0.45 %	0.59 ± 0.03 %

* results is the mean of the 3 separate EFs determined for the 3 separate N concentrations

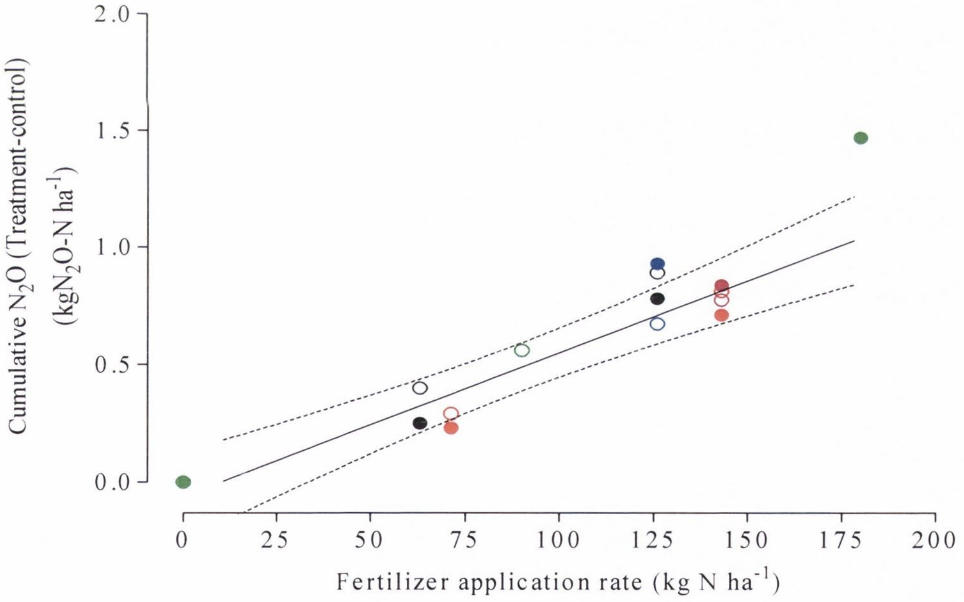

Figure 7.2: Correlation between fertilizer application rate and cumulative N_2O flux over the growing season for both the arable and grassland fields. Each point represents the mean ± se. $y = 0.0061x + 0.06$ and ($r^2 = 0.77$). Symbols indicate: Conventional mall plots 04 (●), reduced small plots 04 (○), conventional small plots 05 (●), reduced small plots 05 (○), conventional large plots 04 (●), reduced large plots 04 (○), conventional large plots 05 (●), reduced large plots 05 (○), pasture 04 (●), pasture 05(○). The dotted lines representing the 95% confidence interval.

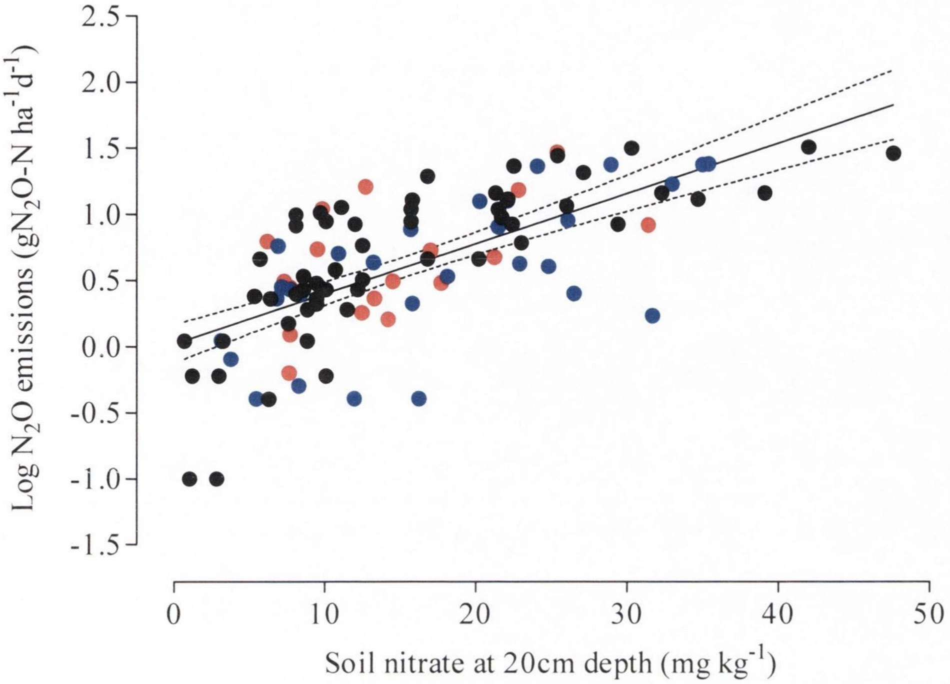

Figure 7.3: Correlation between log N_2O emissions and soil nitrate for the cut and grazed pasture (●), the arable small plots (●) and the arable large plots (●). The solid line represents the overall linear relationship for the combined data, the dotted lines representing the 95% confidence interval.

In Chapter 6 the DNDC-model gave a good estimate of N_2O fluxes from the arable site with an average relative deviation from the measured fluxes of 24%. This goodness of fit can be improved further by better input data, particularly in the case of the cut and grazed pasture where a relative deviation of more than 150% was found. As discussed in Chapter 6, this great disparity was assumed to be due to poor data on soils, in particular soil organic carbon to which the model is extremely sensitive. However, as Figures 7.2 and 7.3 reveal a similarity in response between the arable and grassland soils to fertilizer application rate and soil nitrate concentration it is possible that one could improve the goodness of fit of the DNDC-model with regard to the grassland soil by assuming the same organic carbon content as the arable soil. Using this new analysis, graphs of modeled and measured fluxes for the cut and grazed pasture are illustrated in Figure 7.4.

Here a greatly improved fit was obtained with annual relative deviations from the measured data being 10% for the fertilized plots and 15% for the control plots. Thus the model predicted an annual flux from the fertilized plots of 2.66 kg N_2O-N ha^{-1}, whereas the measured annual flux was 2.4 kg N_2O-N ha^{-1}. In the case of the control plots the modeled flux was 1.07 kg N_2O-N ha^{-1} compared to 0.93 kg N_2O-N ha^{-1} for the measured flux. Using the modelled data an EF of 0.88% is obtained, comparable to the calculated EF for the measured flux of 0.83% of the applied fertilizer. What this may imply is that the algorithm that relates organic carbon to N_2O flux in the DNDC model is significantly overestimating the actual flux; hence reducing the organic carbon of the grassland soil from 0.038 to 0.0194 kg kg^{-1} dry soil reduces the modelled annual flux from 6 to 2.66 kg N_2O-N ha^{-1}, a reduction of 56%. The other possibility is that the analysis of soil samples of the grassland field overestimated the organic carbon. Either way, the process based DNDC-model is still ideally suited to predict N_2O emissions from Irish soils. What is required though is a regional soil data base for Ireland, suitable for model inputs, which can be used in GIS maps. By superimposing fertilizer and management inputs a more reliable reporting of N_2O emissions from agriculture for Ireland could be achieved.

With regard to empirical models that have been published for estimating N_2O emissions from arable and grassland soils, such as Conen *et al.* (2000); Roelandt, *et al.* (2005) and Flechard *et al.* (2006), then these rely on soil moisture or rainfall, temperature and soil N inputs. As an example, Conen *et al.,* published in 2000 a paper where N_2O fluxes were related to three soil parameters; soil mineral N in the top soil, WFPS and soil temperature. In this model the lower limit of WFPS and soil temperature below which N_2O flux was lower than 10g N_2O-N $ha^{-1}d^{-1}$ or higher than 100g N_2O-N $ha^{-1}d^{-1}$ when mineral N was not limiting is determined. However the applicability of this model to our data is relatively poor. Here most of our data was comparable with the lower boundary. This may be due to the limited WFPS of our sites, which never exceed 70%, and poor correlation of WFPS with N_2O fluxes.

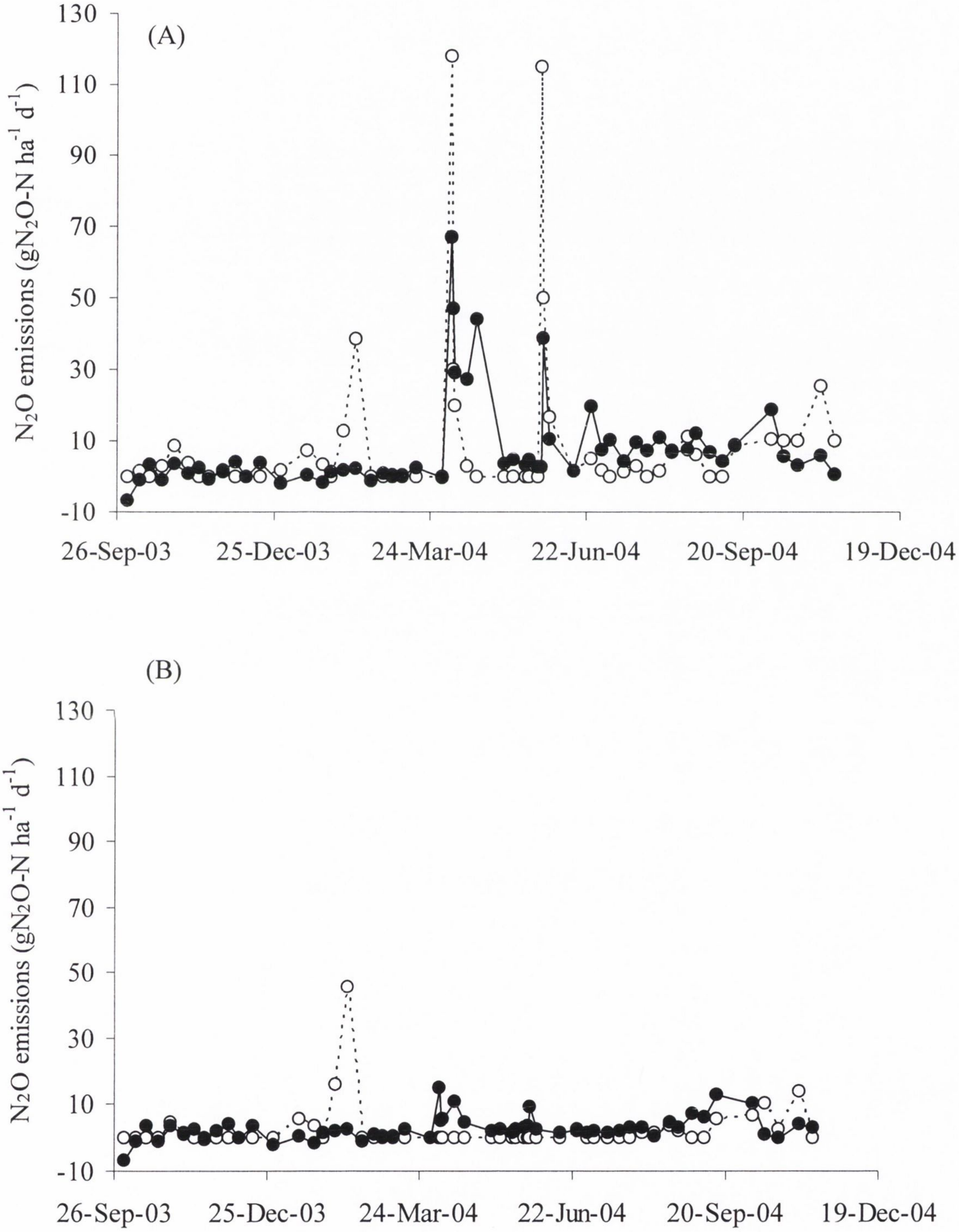

Figure 7.4: Comparison of model-simulated N_2O (○) and field measured N_2O (●) fluxes from fertilized (A) and control (B) pasture plots in 2003-2004 using the arable field SOC.

With regards to GWP in terms of CO_2-C equivalents, a comparison between annual emissions of nitrous oxide and carbon dioxide (soil respiration), measured from the same field in 2004 is illustrated in Table 7.2. Here, a N_2O GWP of 200 kg CO_2-C equivalents ha^{-1} for the cut and grazed pasture compared with 1310 kg CO_2-C equivalents ha^{-1} for soil respiration was calculated. For the arable field the N_2O GWP of 50 and 118 kg CO_2-C equivalents ha^{-1} compared with 930 and 970 kg CO_2-C equivalent ha^{-1} for soil respiration. Thus although N_2O has a higher GWP than CO_2 or CH_4 on a molecule for molecule basis, our results reveal small contributions from N_2O to the overall GWP for soil emissions of greenhouse gases. This may be influenced, as discussed in the preceding Chapters, by the soil type and low soil moisture content of our field sites.

Table 7.2: Comparison between annual emissions of nitrous oxide and carbon dioxide (soil respiration), in 2004.

	CO_2 (kg CO_2-C equivalents ha^{-1})*	N_2O (kg CO_2-C equivalents ha^{-1})
Cut and grazed pasture	1310	200
Arable field (conventional)	930	50
Arable field (reduced)	970	118

*Data kindly provided by Suresh Kumar

The method used for measuring N_2O has significant effects on the results obtained. The use of eddy covariance techniques, such as in the Cork study of Scanlon and Kiely (2003), and Hsieh *et al.* (2005), give continuous measurements and can be used on a large footprint with less labour intensity, but depending on wind speed, direction and down time of the system, significant gaps in the data have to be back filled by estimation. Moreover, the instrument installation and maintenance are expensive. On the other hand a static chamber, such as that used in the Wexford study of Hyde *et al.* (2005), or in this study, is technically simpler with less cost and can be used on a known sample area with better replication. However, the chamber used in the Wexford study was 11.5 cm diameter by 15 cm high, and is very small compared with the 50 x 50 x 30 cm chamber used in this study. The chamber size and height are required to improve gas linearity inside the chamber, although too high a chamber relative to the footprint dilutes the N_2O signal (Conen and Smith, 2000). The disadvantages of static chambers are the high labour intensity and the possibility of missing many peaks.

For better estimates of N_2O fluxes from Irish agriculture, I suggest a continuous measurement programme using an automated chamber, as a large proportion of N_2O emissions occur during short events such as those immediately following N fertilizer application and rainfall. In this study, the higher N_2O peak in the winter of 2004 shown by DNDC model for the cut and grazed pasture (Figure 6.8), has not been 'caught' by the measurement regime, and may be real in that freeze/thaw cycles produce peaks in N_2O flux (Christensen and Tiedje, 1990; Van Bochove *et al.*, 2000). Moreover, the high sensitivity of N_2O flux to soil temperature, as shown by the DNDC-model, requires taking measurements at different times during the day to pick up the diurnal effect of temperature. Such diurnal effects of temperature have been reported by Addiscott (1983); Scott *et al.* (1986) and Flessa *et al.* (2002). Furthermore, investigation of N_2O emissions from the other two main sources of animal waste management systems and N lost to the agricultural system, e.g. through leaching, runoff or atmospheric deposition in addition to more investigations to distinguish between nitrification and denitrification are required.

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Appendix 1

Ordination of the measured flux values of N_2O from the large plots with soil nitrate, ammonium, temperature and gravimetric moisture content.

Sampling date	N_2O flux (g N_2O-N $ha^{-1}d^{-1}$)	Soil nitrate (mg kg^{-1}dry soil)	Soil ammonium (mg kg^{-1}dry soil)	Soil temperature (°C)	Gravimetric soil moisture (%)
18/11/03	-2.75	5.78	19.29	10.47	18.95
27/01/04	0.43	5.48	10.85	2.61	22.88
11/05/04	2.47	8.43	2.73	12.73	19.04
17/06/04	-0.09	5.05	5.10	19.22	7.65
08/07/04	0.75	3.80	3.20	18.41	9.01
13/04/05	2.10	15.81	13.77	13.75	21.21
19/05/05	2.52	26.53	5.51	13.18	22.10
02/06/05	0.42	11.97	4.58	14.28	22.70
18/11/03	-0.73	5.56	18.70	10.17	20.38
27/01/04	1.12	3.16	8.09	2.42	23.95
11/05/04	2.82	7.16	2.26	12.39	20.39
17/06/04	-0.24	2.67	3.54	18.79	10.00
08/07/04	-0.04	2.99	4.76	18.00	17.73
13/04/05	3.36	18.12	15.87	13.50	22.27
19/05/05	1.68	31.67	6.40	13.30	22.65
02/06/05	0.42	16.25	5.89	14.28	20.51
11/05/04	8.89	26.08	13.80	11.87	19.04
17/06/04	0.46	8.31	8.50	17.92	7.65
13/04/05	12.39	20.25	23.81	13.75	21.21
03/05/05	4.20	22.90	31.16	11.40	28.51
19/05/05	16.80	33.00	8.08	13.18	22.10
24/05/05	23.52	35.00	14.62	12.63	24.77
02/06/05	7.56	15.69	5.76	14.30	22.70
11/05/04	23.47	28.92	13.38	11.63	20.39
17/06/04	2.68	7.71	4.38	17.58	10.00
08/07/04	5.67	6.93	4.80	14.42	17.73
13/04/05	12.60	22.08	22.17	13.50	22.27
03/05/05	3.99	24.80	29.67	11.50	24.70
13/05/05	23.73	35.40	8.38	13.30	22.65
24/05/05	22.89	24.07	10.39	12.80	22.63
02/06/05	7.98	21.49	7.08	14.30	20.51

Appendix 2

Ordination of the measured flux values of N_2O from the small plots conventional tillage with soil nitrate, ammonia, temperature and gravimetric moisture content

Sampling date	N_2O flux (gN_2O-N $ha^{-1}d^{-1}$)	Soil nitrate (mg kg^{-1}dry soil)	Soil ammonia (mg kg^{-1}dry soil)	Soil temperature (^{o}C)	Gravimetric soil moisture (%)
07/04/2004	2.1	9.4	11.9	23.2	7.8
13/05/2004	3.8	10.7	13.8	17.9	11.7
15/06/2004	-1.4	6.0	5.4	14.6	18.3
06/07/2004	-1.4	2.9	4.7	14.4	17.2
04/08/2004	-1.3	1.0	3.1	15.5	16.3
07/04/2004	3.0	9.4	11.9	23.2	7.6
13/05/2004	2.4	5.4	1.2	19.9	11.6
15/06/2004	-0.8	1.6	7.8	9.8	18.0
06/07/2004	-3.9	1.2	3.7	14.3	17.7
04/08/2004	-1.1	0.8	2.5	17.6	16.8
07/04/2004	2.3	9.4	11.9	23.2	7.7
13/05/2004	-1.1	4.2	3.9	21.4	11.6
15/06/2004	-1.2	0.9	2.9	12.8	18.8
06/07/2004	-2.3	0.9	2.8	17.3	18.6
04/08/2004	-1.1	0.8	3.3	17.0	17.0
05/04/2005	8.2	8.1	2.7	23.9	8.0
13/04/2005	14.5	32.3	41.2	20.9	10.9
21/04/2005	11.6	26.0	19.1	28.1	7.3
02/05/2005	14.5	39.1	26.4	26.2	14.5
19/05/2005	28.8	47.6	11.4	21.5	12.2
24/05/2005	27.7	25.4	3.9	26.0	11.2
31/05/2005	10.9	15.7	9.8	25.8	13.4
05/04/2005	9.9	8.1	2.7	23.9	8.5
13/04/2005	8.4	29.4	34.6	22.1	10.8
21/04/2005	9.5	21.7	17.0	27.0	7.3
02/05/2005	6.1	23.0	25.2	30.1	14.5
19/05/2005	19.3	16.8	7.8	21.5	12.1
24/05/2005	8.4	12.0	3.0	23.3	11.2
31/05/2005	10.3	9.7	12.9	23.8	13.7
05/04/2005	2.5	8.1	2.7	23.9	8.4
13/04/2005	4.6	16.8	3.6	19.8	10.7
21/04/2005	1.5	7.6	4.9	23.1	7.4
02/05/2005	2.3	6.4	3.2	28.4	14.3
19/05/2005	4.6	5.7	4.4	24.0	12.4
24/05/2005	1.9	11.5	3.7	24.2	11.3
31/05/2005	0.4	6.3	12.5	24.6	14.4

Appendix 3

Ordination of the measured flux values of N_2O from the small plots reduced tillage with soil nitrate, ammonia, temperature and gravimetric moisture content

Sampling date	N_2O flux (gN_2O-N $ha^{-1}d^{-1}$)	Soil nitrate (mg kg^{-1}dry soil)	Soil ammonia (mg kg^{-1}dry soil)	Soil temperature (°C)	Gravimetric soil moisture (%)
07/04/2004	1.1	8.9	12.0	22.6	7.5
13/05/2004	5.8	12.5	2.5	17.6	11.6
15/06/2004	0.6	3.0	6.8	11.7	18.1
06/07/2004	0.1	2.8	4.3	14.7	17.6
04/08/2004	0.6	1.2	2.9	15.5	16.7
07/04/2004	1.1	8.9	12.0	22.6	7.4
13/05/2004	1.1	8.8	0.5	18.8	11.5
15/06/2004	-2.0	1.6	4.7	11.9	18.0
06/07/2004	-3.5	1.0	4.9	13.4	17.9
04/08/2004	-0.2	0.9	3.8	15.3	16.9
07/04/2004	1.9	8.9	12.0	22.6	7.3
13/05/2004	1.1	3.3	1.3	18.1	11.6
15/06/2004	-2.5	1.0	4.8	11.8	18.8
06/07/2004	0.1	1.0	3.4	17.5	19.4
04/08/2004	1.1	0.7	4.2	19.4	17.5
05/04/2005	2.7	10.1	5.3	23.0	8.3
13/04/2005	13.0	34.7	52.2	18.8	11.1
21/04/2005	23.1	22.5	13.5	24.7	7.5
02/05/2005	14.5	21.3	21.1	21.8	14.7
19/05/2005	32.1	42.0	18.1	20.4	12.0
24/05/2005	31.5	30.3	2.5	22.1	11.3
31/05/2005	12.8	15.8	13.1	21.6	13.6
05/04/2005	0.6	10.1	5.3	23.0	8.4
13/04/2005	8.4	22.4	29.1	21.2	11.4
21/04/2005	4.6	20.2	13.2	24.5	7.6
02/05/2005	10.9	21.5	22.0	24.9	14.2
19/05/2005	20.6	27.1	15.1	21.6	12.1
24/05/2005	13.0	22.1	5.1	24.3	11.3
31/05/2005	11.3	11.1	10.3	24.0	14.1
05/04/2005	8.8	10.1	5.3	23.0	8.2
13/04/2005	2.7	12.2	3.9	22.8	11.0
21/04/2005	-2.5	8.9	6.7	24.6	7.4
02/05/2005	3.4	8.6	6.5	29.6	14.3
19/05/2005	8.8	15.7	10.5	23.0	12.2
24/05/2005	3.2	12.5	3.2	24.3	11.3
31/05/2005	2.7	8.6	7.9	25.4	14.4

Appendix 4

Calculation of WFPS for the cut and grazed pasture during the experimental period 2004/2005.

Date	Volumetric W.C (%)	Bulk density (g cm^{-3})	Total porosity (%)	WFPS (%)
18/11/03	24.26	1.06	59.89	40.50
03/02/04	24.89	1.06	59.89	41.56
31/03/04	24.32	1.06	59.89	40.61
07/04/04	25.57	1.06	59.89	42.69
20/04/04	25.45	1.06	59.89	42.50
06/05/04	25.87	1.06	59.89	43.19
11/05/04	23.70	1.06	59.89	39.57
18/05/04	21.10	1.06	59.89	35.22
20/05/04	17.08	1.06	59.89	28.52
25/05/04	16.99	1.06	59.89	34.47
27/05/04	18.36	1.06	59.89	30.65
28/05/04	20.88	1.06	59.89	34.87
01/06/04	18.23	1.06	59.89	30.43
15/06/04	13.95	1.06	59.89	23.29
24/06/04	22.74	1.06	59.89	37.98
25/06/04	22.62	1.06	59.89	37.78
01/07/04	20.98	1.06	59.89	35.04
06/07/04	19.24	1.06	59.89	32.12
14/07/04	18.58	1.06	59.89	31.03
21/07/04	17.58	1.06	59.89	29.36
27/07/04	15.67	1.06	59.89	26.17
03/08/04	15.28	1.06	59.89	25.52
10/08/04	20.19	1.06	59.89	33.71
19/08/04	26.04	1.06	59.89	43.48
24/08/04	24.39	1.06	59.89	40.74
01/09/04	24.74	1.06	59.89	41.30
08/09/04	22.00	1.06	59.89	36.73
15/09/04	24.14	1.06	59.89	40.32
06/10/04	25.79	1.06	59.89	43.07
13/10/04	20.19	1.06	59.89	33.71
21/10/04	26.43	1.06	59.89	44.12
03/11/04	24.53	1.06	59.89	40.96
11/11/04	24.10	1.06	59.89	40.24
22/03/05	27.48	1.06	59.89	45.89
04/04/05	28.48	1.06	59.89	47.56
12/04/05	21.75	1.06	59.89	36.32
20/04/05	26.38	1.06	59.89	44.06
03/05/05	22.15	1.06	59.89	36.99
18/05/05	21.27	1.06	59.89	35.51
25/05/05	23.03	1.06	59.89	38.45
02/06/05	23.18	1.06	59.89	38.70
15/06/05	19.65	1.06	59.89	32.81
30/06/05	17.43	1.06	59.89	29.11
06/07/05	18.00	1.06	59.89	30.06
14/07/05	17.47	1.06	59.89	29.17
06/08/05	19.50	1.06	59.89	32.56

Appendix 5

Calculation of WFPS for the arable field- Largeplot experiment for the period2003- 2004 and 2005.

Date	Treatment	Volumetric W.C (%)	Bulk density (g cm^{-3})	Total porosity (%)	WFPS (%)
18/11/03	C	15.92	1.33	49.71	32.03
	L	16.91	1.49	43.89	38.52
09/12/03	C	19.34	1.33	49.71	38.90
	L	18.77	1.49	43.89	42.77
27/01/04	C	18.61	1.33	49.71	37.44
	R	19.32	1.49	43.89	44.03
07/04/04	C	19.50	1.33	49.71	39.23
	L	18.55	1.49	43.89	42.27
20/04/04	C	18.84	1.33	49.71	37.90
	L	17.62	1.49	43.89	40.14
29/04/04	C	16.64	1.33	49.71	33.47
	L	16.16	1.49	43.89	36.82
06/05/04	C	18.05	1.33	49.71	36.30
	L	17.40	1.49	43.89	39.66
11/05/04	C	15.99	1.33	49.71	32.16
	L	16.93	1.49	43.89	38.57
18/05/04	C	14.73	1.33	49.71	29.63
	L	16.67	1.49	43.89	37.98
26/05/04	C	12.36	1.33	49.71	24.85
	L	14.41	1.49	43.89	32.83
01/06/04	C	14.35	1.33	49.71	28.87
	L	13.13	1.49	43.89	29.92
17/06/04	C	7.09	1.33	49.71	14.26
	L	9.04	1.49	43.89	20.59
24/06/04	C	15.46	1.33	49.71	31.09
	L	15.74	1.49	43.89	35.87
30/06/04	C	13.19	1.33	49.71	26.54
	L	16.45	1.49	43.89	37.49
08/07/04	C	8.27	1.33	49.71	16.63
	L	15.05	1.49	43.89	34.29
20/07/04	C	9.24	1.33	49.71	18.58
	L	12.88	1.49	43.89	29.35
04/08/04	C	11.68	1.33	49.71	23.50
	L	10.52	1.49	43.89	23.96
05/04/05	C	19.29	1.33	49.71	38.80
	L	18.67	1.49	43.89	42.55
13/04/05	C	17.45	1.33	49.71	35.10
	L	18.20	1.49	43.89	41.47
15/04/05	C	18.33	1.33	49.71	36.88
	L	17.05	1.49	43.89	38.85
20/04/05	C	21.75	1.33	49.71	43.75
	L	18.23	1.49	43.89	41.54
03/05/05	C	22.15	1.33	49.71	44.56
	L	19.80	1.49	43.89	45.11

17/05/05	C	19.03	1.33	49.71	38.29
	L	19.33	1.49	43.89	44.05
19/05/05	C	18.10	1.33	49.71	36.41
	L	18.45	1.49	43.89	42.04
24/05/05	C	19.85	1.33	49.71	39.93
	L	18.45	1.49	43.89	42.04
02/06/05	C	18.50	1.33	49.71	37.22
	L	17.02	1.49	43.89	38.77
15/06/05	C	16.13	1.33	49.71	32.45
	L	15.25	1.49	43.89	34.75
07/07/05	C	10.37	1.33	49.71	20.85
	L	10.75	1.49	43.89	24.49
22/07/05	C	8.17	1.33	49.71	16.43
	L	8.17	1.49	43.89	18.61

Appendix 6

Calculation of WFPS for the arable field- Smallplot experiment for the growing seasons 2004/2005.

Date	Treatment	Volumetric W.C (%)	Bulk density (g cm^{-3})	Total porosity (%)	WFPS (%)
07/04/04	CN1	18.80	1.54	41.74	45.04
	CN2	18.80	1.54	41.74	45.04
	CN3	18.80	1.54	41.74	45.04
	LN1	18.45	1.48	44.07	41.86
	LN2	18.45	1.48	44.07	41.86
	LN3	18.45	1.48	44.07	41.86
16/04/04	CN1	19.36	1.54	41.74	46.39
	CN2	19.36	1.54	41.74	46.39
	CN3	19.36	1.54	41.74	46.39
	LN1	20.04	1.48	44.07	45.47
	LN2	20.04	1.48	44.07	45.47
	LN3	20.04	1.48	44.07	45.47
29/04/04	CN1	17.89	1.54	41.74	42.85
	CN2	17.89	1.54	41.74	42.85
	CN3	17.89	1.54	41.74	42.85
	LN1	16.69	1.48	44.07	37.87
	LN2	16.69	1.48	44.07	37.87
	LN3	16.69	1.48	44.07	37.87
07/05/04	CN1	18.89	1.54	41.74	45.25
	CN2	18.89	1.54	41.74	45.25
	CN3	18.89	1.54	41.74	45.25
	LN1	16.71	1.48	44.07	37.92
	LN2	16.71	1.48	44.07	37.92
	LN3	16.71	1.48	44.07	37.92
13/05/04	CN1	15.13	1.54	41.74	36.24
	CN2	16.63	1.54	41.74	39.83
	CN3	17.65	1.54	41.74	42.29
	LN1	14.98	1.48	44.07	33.98
	LN2	15.83	1.48	44.07	35.91
	LN3	15.35	1.48	44.07	34.83
20/05/04	CN1	15.87	1.54	41.74	38.02
	CN2	16.42	1.54	41.74	39.35
	CN3	15.53	1.54	41.74	37.21
	LN1	15.16	1.48	44.07	34.41
	LN2	14.89	1.48	44.07	33.79
	LN3	15.09	1.48	44.07	34.23
26/05/04	CN1	14.12	1.54	41.74	33.83
	CN2	14.51	1.54	41.74	34.76
	CN3	16.57	1.54	41.74	39.71
	LN1	10.62	1.48	44.07	24.10
	LN2	14.51	1.48	44.07	32.92
	LN3	13.96	1.48	44.07	31.67
01/06/04	CN1	15.01	1.54	41.74	35.96
	CN2	14.48	1.54	41.74	34.70
	CN3	17.34	1.54	41.74	41.55

	LN1	15.22	1.48	44.07	34.53
	LN2	15.83	1.48	44.07	35.93
	LN3	16.97	1.48	44.07	38.50
15/06/04	CN1	12.73	1.54	41.74	30.49
	CN2	8.90	1.54	41.74	21.32
	CN3	11.30	1.54	41.74	27.07
	LN1	10.45	1.48	44.07	23.71
	LN2	10.65	1.48	44.07	24.16
	LN3	10.53	1.48	44.07	23.88
22/06/04	CN1	12.08	1.54	41.74	28.95
	CN2	14.85	1.54	41.74	35.57
	CN3	13.94	1.54	41.74	33.39
	LN1	10.70	1.48	44.07	24.28
	LN2	11.35	1.48	44.07	25.76
	LN3	14.99	1.48	44.07	34.02
29/06/04	CN1	15.61	1.54	41.74	37.41
	CN2	15.50	1.54	41.74	37.14
	CN3	17.13	1.54	41.74	41.03
	LN1	14.06	1.48	44.07	31.89
	LN2	16.40	1.48	44.07	37.20
	LN3	17.81	1.48	44.07	40.40
06/07/04	CN1	12.58	1.54	41.74	30.13
	CN2	12.53	1.54	41.74	30.01
	CN3	14.78	1.54	41.74	35.40
	LN1	12.78	1.48	44.07	28.99
	LN2	11.83	1.48	44.07	26.83
	LN3	14.93	1.48	44.07	33.86
20/07/04	CN1	12.27	1.54	41.74	29.39
	CN2	10.97	1.54	41.74	26.28
	CN3	14.26	1.54	41.74	34.17
	LN1	11.17	1.48	44.07	25.34
	LN2	11.14	1.48	44.07	25.27
	LN3	15.50	1.48	44.07	35.16
04/08/04	CN1	13.43	1.54	41.74	32.17
	CN2	14.98	1.54	41.74	35.88
	CN3	14.50	1.54	41.74	34.74
	LN1	13.33	1.48	44.07	30.23
	LN2	13.30	1.48	44.07	30.18
	LN3	16.23	1.48	44.07	36.81
10/08/04	CN1	15.17	1.54	41.74	36.36
	CN2	16.98	1.54	41.74	40.69
	CN3	17.67	1.54	41.74	42.33
	LN1	14.96	1.48	44.07	33.94
	LN2	16.18	1.48	44.07	36.71
	LN3	17.36	1.48	44.07	39.40
05/04/05	CN1	19.27	1.54	41.74	46.18
	CN2	19.27	1.54	41.74	46.18
	CN3	19.27	1.54	41.74	46.18
	LN1	18.67	1.48	44.07	42.37
	LN2	18.67	1.48	44.07	42.37
	LN3	18.67	1.48	44.07	42.37
13/04/05	CN1	17.28	1.54	41.74	41.39
	CN2	18.10	1.54	41.74	43.37

	CN3	16.53	1.54	41.74	39.59
	LN1	15.85	1.48	44.07	35.96
	LN2	17.45	1.48	44.07	39.59
	LN3	18.58	1.48	44.07	42.15
15/04/05	CN1	20.38	1.54	41.74	48.82
	CN2	22.50	1.54	41.74	53.91
	CN3	18.73	1.54	41.74	44.86
	LN1	19.30	1.48	44.07	43.79
	LN2	16.20	1.48	44.07	36.76
	LN3	19.13	1.48	44.07	43.39
21/04/05	CN1	21.95	1.54	41.74	52.59
	CN2	21.25	1.54	41.74	50.91
	CN3	18.75	1.54	41.74	44.92
	LN1	19.80	1.48	44.07	44.93
	LN2	19.68	1.48	44.07	44.64
	LN3	19.73	1.48	44.07	44.76
27/04/05	CN1	19.38	1.54	41.74	46.42
	CN2	18.85	1.54	41.74	45.16
	CN3	18.73	1.54	41.74	44.86
	LN1	17.28	1.48	44.07	39.20
	LN2	19.55	1.48	44.07	44.36
	LN3	18.88	1.48	44.07	42.83
02/05/05	CN1	20.78	1.54	41.74	49.78
	CN2	23.10	1.54	41.74	55.35
	CN3	22.13	1.54	41.74	53.01
	LN1	17.88	1.48	44.07	40.56
	LN2	19.95	1.48	44.07	45.27
	LN3	22.80	1.48	44.07	51.73
17/05/05	CN1	19.75	1.54	41.74	47.32
	CN2	15.18	1.54	41.74	36.36
	CN3	16.00	1.54	41.74	38.33
	LN1	19.25	1.48	44.07	43.68
	LN2	16.38	1.48	44.07	37.15
	LN3	15.78	1.48	44.07	35.79
19/05/05	CN1	17.68	1.54	41.74	42.35
	CN2	17.68	1.54	41.74	42.35
	CN3	19.38	1.54	41.74	46.42
	LN1	16.98	1.48	44.07	38.52
	LN2	17.78	1.48	44.07	40.33
	LN3	18.73	1.48	44.07	42.49
24/05/05	CN1	20.60	1.54	41.74	49.36
	CN2	18.88	1.54	41.74	45.22
	CN3	19.45	1.54	41.74	46.60
	LN1	18.10	1.48	44.07	41.07
	LN2	19.58	1.48	44.07	44.42
	LN3	19.53	1.48	44.07	44.30
31/05/05	CN1	20.48	1.54	41.74	49.06
	CN2	19.23	1.54	41.74	46.06
	CN3	19.75	1.54	41.74	47.32
	LN1	17.75	1.48	44.07	40.27
	LN2	19.38	1.48	44.07	43.96
	LN3	20.25	1.48	44.07	45.95
08/06/05	CN1	20.48	1.54	41.74	49.06

	CN2	19.68	1.54	41.74	47.14
	CN3	20.03	1.54	41.74	47.98
	LN1	18.33	1.48	44.07	41.58
	LN2	19.68	1.48	44.07	44.64
	LN3	21.15	1.48	44.07	47.99
16/06/05	CN1	15.50	1.54	41.74	37.14
	CN2	13.90	1.54	41.74	33.30
	CN3	17.13	1.54	41.74	41.03
	LN1	12.88	1.48	44.07	29.21
	LN2	15.58	1.48	44.07	35.34
	LN3	16.90	1.48	44.07	38.35
30/06/05	CN1	12.23	1.54	41.74	29.29
	CN2	9.58	1.54	41.74	22.94
	CN3	13.93	1.54	41.74	33.36
	LN1	10.05	1.48	44.07	22.80
	LN2	12.10	1.48	44.07	27.45
	LN3	13.28	1.48	44.07	30.12
06/07/05	CN1	13.40	1.54	41.74	32.11
	CN2	10.63	1.54	41.74	25.46
	CN3	13.95	1.54	41.74	33.42
	LN1	11.20	1.48	44.07	25.41
	LN2	13.05	1.48	44.07	29.61
	LN3	14.80	1.48	44.07	33.58
14/07/05	CN1	10.75	1.54	41.74	25.76
	CN2	9.62	1.54	41.74	23.06
	CN3	14.35	1.54	41.74	34.38
	LN1	10.73	1.48	44.07	24.33
	LN2	11.78	1.48	44.07	26.72
	LN3	12.18	1.48	44.07	27.62
02/08/05	CN1	15.50	1.54	41.74	37.14
	CN2	13.75	1.54	41.74	32.94
	CN3	17.50	1.54	41.74	41.93
	LN1	12.25	1.48	44.07	27.80
	LN2	13.75	1.48	44.07	31.20
	LN3	14.50	1.48	44.07	32.90