Investigations into aspects of nitrogen and carbon dynamics in grassland used for dairy production on a clay loam soil

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By

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Declaration

I declare that thesis has not been previously submitted for a degree to this or any other institution and I further declare that the work is entirely my own work.

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Abstract

Increasing concentrations of nitrogen (N) in the waterbodies along with increasing concentrations of nitrous oxide (N_2O) and carbon dioxide in the atmosphere have become an international environmental concern. Permanent grasslands are important sources of feed for intensively managed dairy and beef farming systems in North West Europe and represent around 90% of agricultural land in Ireland. However, there is a potential for substantial N losses following grazing during the winter when a significant effective rainfall occurs. In addition, ploughing and reseeding of grassland in order to increase its productivity may lead to a substantial decrease in soil organic matter (SOM) followed by an increase in soil inorganic N. This two year study investigated (i) the environmental impact of a dairy production system involving grazing over the winter through calculations of soil surface N balances and its effect on soil N dynamics and N loses to groundwater; (ii) the impact of permanent grassland renovation on soil N, N_2O emissions, N leaching and soil organic carbon (SOC) in a poorly drained clay-loam soil at Solohead Research Farm. The correlations between grazing management and soil N dynamics in the soil profile or N concentrations in the groundwater were difficult due to high natural buffering capacity of the soils associated with heavy texture, high SOC, high soil pH, anaerobic conditions and presence of shallow groundwater. For this reason, grazing over the winter period had no effect on soil N dynamics and groundwater quality on this site. In contrast, grassland renovation decreased topsoil SOC and total N, increased oxidized N leaching to groundwater and N_2O emissions from the soil surface as a result of soil disturbance, enhanced decomposition of SOM followed by nitrification and denitrification. Although, the overall losses due to net SOM mineralisation were high (3 t N and 32 t C ha^{-1}), the proportion lost via N leaching and direct N_2O emissions was low (27 kg N ha^{-1} y^{-1}) suggesting that nitrate were instantaneously reduced by dissimilatory nitrate reduction to ammonium or complete denitrification.

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Contents

List of tables

List of figures

List of abbreviations

AEC – Anion Exchange Capacity

AOD – Above Ordnance Datum

ANAMMOX – ANaerobic AMMonium OXidation

BD – Bulk Density

bgl – below ground level

BNF – Biological Nitrogen Fixation

C – Carbon

CAN – Calcium Ammonium Nitrate

CEC – Cation Exchange Capacity

Cl – Chloride

CO_2 –Carbon dioxide

CP – Crude Protein

d –diameter

DIN – Dissolved Inorganic Nitrogen

DM –Dry Matter

DNRA –Dissimilatory Nitrate Reduction to Ammonium

DOC –Dissolved Organic Carbon

DON –Dissolved Organic Nitrogen

DRP – Dissolved Reactive Phosphorus

ER –Effective Rainfall

EU – European

FYM –Farmyard Manure

GC – Gas Chromatograph

GHG – Greenhouse Gas

GPS – Global Positioning System

GW – Groundwater

GWD – Groundwater Directive

HMW-DON – High Molecular Weight Dissolved Organic Nitrogen

KCl – potassium chloride

ks – saturated hydraulic conductivity

L – Length

LMW-DON – Low Molecular Weight Dissolved Organic Nitrogen

LU – Livestock Unit

MAC – Maximum Admissible Concentration

N – Nitrogen

ne – effective porosity

NH_4^+ – Ammonium

NH_3 – Ammonia

NO_x – Oxides of nitrogen

NO – Nitric oxide

N_2O – Nitrous oxide

NO_2^- – Nitrite

NO_3^- – Nitrate

NUE – Nitrogen Use Efficiency

OECD – Organisation for Economic Co-operation and Development

OM – Organic Matter

P – Phosphorus

PG – Permanent Grassland

POM – Programs Of Measures

RG – Renovated Grassland

SD – Standard Deviation

SE – Standard Error

SI – Statutory Instrument

SIN – Soluble Inorganic Nitrogen

SMD – Soil Moisture Deficit

SOC – Soil Organic Carbon

SOM – Soil Organic Matter

SON – Soluble Organic Nitrogen

SSB – Soil Surface Balance

TC – Total Carbon

TDN – Total Dissolved Nitrogen

TIC – Total Inorganic Carbon

TN – Total Nitrogen

TON – Total Oxidised Nitrogen

TSN – Total Soluble Nitrogen

Tt – vertical travel time

WFD –Water Framework Directive

WFPS – Water Filled Pore Space

1. Introduction

1.1 General Introduction

Increasing concentrations of nitrogen (N) in the waterbodies along with increasing concentrations of nitrous oxide (N_2O) and carbon dioxide (CO_2) in the atmosphere have become an international environmental concern. Implementation of the European Union Water Framework Directive (WFD; European Parliament and Council, 2000) is aiming to constrain N fluxes to the groundwaters and surface waters with an attempt to achieve at least ‘good ecological status’ for all waterbodies by 2015 with implementation of programmes of measures (POM) by 2012. The main POM currently in place to achieve the goals of the WFD in Ireland is the Nitrates Directive (European Council, 1991), enacted in 2006 under Statutory Instrument (SI) 378, 2006, subsequently replaced by SI 610 in 2010. By signing the Kyoto Protocol in 1997, governments of 37 industrialized countries agreed to reduce the emissions of the greenhouse gases (GHG) on average by 5% against the levels from 1990 over a five years period (2008-12). Ireland is committed to limit GHG emissions by 13% in the period 2008 to 2012, and by 25 to 30% in the period 2012 to 2020 compared with 1990 levels. To ensure compliance with the WFD and Kyoto protocol it is essential to identify major sources and practices that lead to pollution. Furthermore, as part of the international efforts to stabilize atmospheric GHG concentrations, signatories of the Kyoto protocol are also committed to establish national inventories of soil organic carbon (SOC) content and its changes in relation to specific land use or climatic effects.

Permanent grasslands are important sources of feed for intensively managed dairy and beef farming systems in North West Europe (Velthof et al. 2010). About 90% of agricultural land in Ireland (4 million ha) is devoted to grassland production (Richards et al. 2009). Irish dairy farming systems are primary based on grazed grassland with spring calving pattern. Organic dairy production systems generally operate at low stocking densities relative to conventional dairy systems. Low stocking densities offer a potential to extend the grazing season throughout the autumn and winter. In addition, there is a price premium in Ireland for organic milk if 55% of the milk on the farm is produced between September to March. While animal excreta are a valuable source of N and other nutrients for plants (Silva et al., 1999), high quantities of N in urine and dung (typically equivalent to over 200 and 2000 kg N ha^{-1}; Haynes and Williams, 1993, Jarvis et al., 1995; Dai, 2000; ten Berge et al., 2002) deposited in small area patches (Lantinga et al., 1987; Bakker et al., 2004) result in high N concentrations both in time and space (Decau et al., 2004; Hutchings et al., 2007). These greatly exceed plant requirements (Steele, 1982; Ball and Ryden, 1984), mainly during the months, when grass growth and thus N uptake is temperature limited. Consequently, there is a potential for substantial N losses following grazing, albeit at low stocking rates, particularly during the winter months when a significant effective rainfall occurs (Francis, 1995; Hack-ten Broeke and Van der Putten, 1997, Jewkes et al., 2007). There is limited information on the impact of such grazing system on the environment.

The yields and quality of permanent grassland decrease during ageing, because of sward deterioration (i.e. compaction, poor drainage, sward composition, weed invasion, soil acidification or erosion) following extreme weather conditions and/or bad management (Velthof and Oenema 2001). For this reason, the managed grasslands are occasionally renovated (ploughed up and reseeded) in order to maintain or increase the sward productivity (Velthof et al. 2010), reduce weeds and maintain the clover content (Humphreys and Lawless 2008). Ploughing of grassland leads to physical disruption of aggregates, increased soil aeration and consequently exposure of stable and adsorbed soil organic matter within micro- and macro- aggregates to rapid microbial respiration (Six et al. 2004; Buss et al. 2005; Velthof et al. 2010). In addition, the disruption also decreases soil moisture, increases maximum soil temperature and thus accelerates mineralisation process (Lal 2004). For this reason ploughing of grassland, particularly of long term grassland with substantial soil organic pools may temporarily lead to important increase in soil inorganic N content and CO_2 emissions. The studies on the effect of ploughing and reseeding of long term permanent grassland on soil N dynamics, N leaching, N_2O emissions, SOC, and its potential contribution to CO_2 emissions under humid Irish conditions are lacking.

1.2 Aims and Objectives

1. Soil surface N balances and soil N dynamics in a clay-loam soil under Irish dairy production systems (Chapter 3)

i. Quantification of N losses from a soil component of dairy production system involving grazing over the winter compared to conventional dairy production through calculation of soil surface balances.
ii. Evaluation of the effect of this grassland N management practice on soil soluble inorganic and organic N content down to 0.9 m depth.
iii. Determination of management and climatic factors affecting soil soluble N dynamics in a clay loam soil profile.

2. N leaching to groundwater from dairy production involving grazing over the winter on a clay-loam soil (Chapter 4)

i. Installation of a high density monitoring network on a dairy farm to investigate the effect of a system of dairy production involving grazing over the winter on a clay loam soil on concentrations of various N species in shallow groundwater and N losses over a two year period.
ii. Identification of spatial and temporal patterns in N concentrations and elucidation of groundwater flow direction.
iii. Investigation of chloride anion (Cl^-) and nitrate/Cl^- ratios in order to determine the level of dilution and proximity to sources of contamination on site.

3. Effect of ploughing and reseeding of permanent grassland on soil N, N leaching and nitrous oxide emissions from a clay-loam soil (Chapter 5)

i. Quantification of the environmental consequences and exploring the fate of N in grass-clover permanent grassland on a clay-loam soil being ploughed and reseeded on a dairy farm in southern Ireland with an emphasis on:

    a) Total N content and soluble N dynamics in the soil profile down to 0.9 m depth,
    b) N leaching to shallow groundwater (<2.2 m below ground level; bgl) and
    c) N_2O emissions.

ii. Comparison of the contents of soil soluble N at 0.3 to 0.9 m depth with N concentrations in groundwater during the study period in order to find out if soil extraction is an equivalent indicator of N leaching from clay loam soils to shallow groundwater.

4. Changes in soil organic carbon in a clay-loam soil following ploughing and reseeding of permanent grassland under temperate moist climatic conditions (Chapter 6)

i. Quantification of changes in SOC content on a poorly drained clay-loam soil under
    a) permanent grassland used for dairy farming in southern Ireland over seven years and
    b) after ploughing and reseeding of permanent grassland over two and a half years.

ii. Comparison of the levels of carbon inputs and losses in permanent and renovated grassland through investigation of above-ground phytomass productivity, root standing phytomass and dissolved organic carbon leaching.

1.3 Thesis layout

The thesis contains seven chapters including list of references at the end of each chapter. Following an introduction, Chapter 2 contains a literature review explaining N cycling in the grassland soils. Chapter 3 assesses the impact of a dairy system involving grazing over the winter on soil surface N balances and soil N dynamics. Chapter 4 investigates N leaching to groundwater from dairy production involving grazing over the winter and local hydrological settings. Chapter 5 assesses the impact of ploughing and reseeding of permanent grassland on soil N, N leaching and N_2O emissions. Chapter 6 focuses on quantifying the changes in SOC following ploughing and reseeding of permanent grassland and Chapter 7 presents the general discussion of the thesis and provides recommendations for future research.

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2. Literature review

2.1 Grazing and dairy production systems

There is a diversity of dairy production systems in northwest Europe largely determined by differences in climate, soil type, altitude, landscape and socio-economic circumstances (Gibon et al., 1999; Humphreys et al., 2009). Managed grasslands occupy more than 33 million square kilometres or 25% of the global land surface area, making it the single most extensive form of land use on the planet. Grasslands and their managements (e.g. dairy production systems) influence landscape, soil, air and water quality and therefore have been considered as a contributor to global environmental change (Asner et al., 2004).

The dairy systems in temperate regions such as north-western Europe, New-Zealand or the southern part of Latin America are based on grass, which is the main feed for the dairy cattle. Grass is fed either fresh – predominantly through grazing – or in a preserved form as silage or hay. The dry matter (DM) production of grassland depends on soil factors, climatic factors, fertilization, species composition, and grassland use. To ensure an adequate supply of energy and nutrients, different grazing systems have been developed. A grazing system represents a systematic methodology of allotting pasture and ensuring delivery of high-quality forage feed stuffs. This includes pasture system design such as fencing and water delivery systems, appropriate rotations with variable recovery periods, and silage management. Grazing management requires a high degree of observation and adaptive management, as pasture quality and quantity change with given rainfall, day length and temperature. Three systems of grazing and feeding management can be distinguished: (a) unrestricted stocking, (b) restricted stocking, usually only during the day and (c) zero-grazing, ration of fresh grass (Van Vuuren and Van den Pol-van Dasselaar, 2006).

The climate of Ireland is subject to a maritime influence and is characterized by mild temperatures ranging between 5.1 ºC in January and 14.7 ºC in July, annual rainfall generally in the range of 800 to 1200 mm and distributed throughout the year (Humphreys, 2008d). High rainfall and high soil moisture retention capacity of the soils result in moist soil conditions in summer and wet conditions in the winter (Humphreys, 2008d). These soil and climatic conditions favour grassland farming as soil temperatures are generally sufficient to allow grass growth throughout the year, albeit at low rates during the winter, and soil moisture deficit (SMD) generally does not impede grass growth during the summer (Humphreys et al., 2009). This environmental advantage resulted in the fact that 90% of the Irish agricultural land (4.4 million ha) is under grassland; mostly permanent grassland (Humphreys, 2008b, 2008d, 2009).

The typical system of dairy production in Ireland is unique. It has been evolved as a seasonal production system that makes maximum use of grazed grass in the diet of the dairy cows (Humphreys et al., 2009). Cows are generally calved within a three month period in spring to coincide with the commencement of grass growth and dried off in December (Humphreys et al., 2009). During the main grazing season (April to October), grazing represents the cheapest way of converting grass into milk and therefore grazed grass typically accounts for 60 to 75% of the diet of the dairy cows (Humphreys et al., 2009). As milk is produced primarily from grazed grass, the average annual concentrate supplementation is only 0.75 t per cow. However, the high moisture content of the grazed grass does not ensure sufficient DM intake for cows with a genetic potential for higher production. Therefore, the cows have relatively low milk production potential and generally produce between 3500 and 6500 kg milk cow^{-1} annually. Irish grasslands are also used for grass-silage production. Silage supplemented with minerals represents the sole feed during the non-lactating winter period (Humphreys et al., 2009).

Organic systems of dairy production operate on grass-clover grassland (Weller and Cooper, 2001; Weller et al., 2006a, 2006b) and at low stocking rates compared with conventional dairy production systems. The savings in synthetic fertilizer nitrogen (N) costs associated with biological N fixation (BNF) by clover allows dairy farmers to achieve the same net income at a lower stocking density compared with a higher stocked system reliant on high inputs of synthetic fertilizer N (Treacy et al., 2008; Humphreys et al., 2009). Andrews et al. (2007) concluded that N fixed in association with white clover is replacing an equivalent quantity of synthetic fertilizer N and does not cause differences in N surplus generated by the production systems or in N use efficiency. In contrast, Humphreys at al. (2009) reported that a lower stocked clover based grassland system provides an environmental benefit by generating lower N surpluses due to less N cycling within the system, lower urine deposition under grazing and consequently lower N losses compared with higher stocked production systems. Using clover also offers the potential of lowering nitrous oxide (N_2O) emissions (de Klein et al., 2001; Schils et al., 2005). In terms of nitrate (NO_3^-) losses to groundwater, clover-based grasslands have been found no better or worse than fertilized grassland at the same level of productivity (Scholefield and Tyson, 1992).

Manufacturers of fresh organic dairy products in Ireland offer a 157% price premium for organic milk to dairy producers that supply more than 55% of their milk during the winter period. The prohibitive cost of feed, particularly concentrates produced to organic standards for milk production during the winter is an obstacle for farmers converting to organic dairy production. On the other hand, Ireland’s climate is conducive to production from grass-clover grassland over a long growing season (Humphreys, 2007). Grazing grass-clover swards during the winter season as a large (>50%) component of the diet has the potential to supply a very cost effective and highly nutritive feed for dairy organic winter production. Although the low stocking rates offer a potential to extend the grazing season throughout the autumn, winter and early spring, grazing over the winter, albeit at low stocking rates, carries a considerable risk of N losses to groundwater (Humphreys, 2007) for these reasons:

(i) High quantities of N in urine and dung (typically equivalent to over 200 and 2000 kg N ha^{-1}; Haynes and Williams, 1993, Jarvis et al., 1995; Dai, 2000; ten Berge et al., 2002) deposited in small area patches (Lantinga et al., 1987; Bakker et al., 2004) result in high N concentrations both in time and space (Decau et al., 2004; Hutchings et al., 2007). These greatly exceed plant requirements (Steele, 1982; Ball and Ryden, 1984), mostly during the months, when grass growth and thus N uptake is temperature limited. (iii) Long grazing seasons lead to greater volumes of urine being deposited per ha. (iv) In addition, the autumn-winter period in Ireland is considered as a high-risk time of the year characterised by high rainfall washing out solubilised N from the soil profile. Hence, all these factors have led to a concern about the environmental impact of the grazing over the winter on the groundwater and air quality (Strebel et al., 1989; Aulakh et al., 1992; Sutton et al., 1993; Humphreys et al., 2008b).

2.2 Terrestrial nitrogen cycle

2.2.1 Main biochemical processes of N cycle

Nitrogen is a crucial nutrient for life on Earth; essential for many processes. Although the Earth's atmosphere is an abundant source of N (approximately 78%), most of it is relatively unavailable for use by organisms, leading to a scarcity of usable N in many types of ecosystems (Jarvis et al., 1995; Galloway et al., 2004). This is because the strong triple bond between N atoms in N_2 molecules makes it relatively inert. In order for plants and animals to be able to use N, N_2 gas must first be converted to more a chemically available form such as ammonium (NH_4^+), NO_3^-, or organic N (Galloway et al., 2004). In the organisms, N forms molecular structures as a component of all amino acids incorporated into proteins and nucleic acids, such as DNA and RNA (McDonald et al., 1995). In plants, much of the N is used in chlorophyll molecules, which are essential for photosynthesis and further growth (Parsons and Chapman, 2000; Smil, 2000). Consequently, N represents the major limiting factor for plant growth in most ecosystems (Ammann et al., 2009).

The movement of N between atmosphere, biosphere, and geosphere describes one of the major biogeochemical cycles. It consists of various storage pools of N and processes by which the pools exchange N. As it moves through the cycle, the atom of N occurs in many different organic and inorganic chemical forms, i.e. organic N or NH_4^+, nitrite (NO_2^-), NO_3^-, N_2O, nitric oxide (NO) or dinitrogen gas (N_2), each performing an essential role in the ecosystem. The cycle consists of five main processes: N fixation, N uptake (organismal growth), N mineralisation (decay), nitrification, and denitrification, which transform N from one form to another one. Microorganisms, particularly bacteria, play major roles in all of the principal N transformations, either in their effort to harvest energy or to accumulate N in a form needed for their growth. The rates of these microbially mediated processes are affected by environmental factors that influence microbial activity, such as temperature, moisture, and resource availability (Brady and Weil, 2002). As the single transformations of N are influenced by many factors, some intervening in one way may affect transformations elsewhere in the cycle (Davidson and Mosier, 2004). Up to now, the various N fluxes/pathways were investigated by different objectives (focusing either on air pollution, greenhouse gases (GHGs), water pollution, plant nutrition, etc.) and the budgets with all relevant import and export fluxes have been quite well investigated on a farm or field scale; however they have been rarely measured on the ecosystem scale (Ammann et al., 2009).

Nitrogen fixation ($N_2 \rightarrow NH_4^+$)

Nitrogen fixation is a process wherein N_2 is converted to NH_4^+, essential because it is the only way that organisms can attain N directly from the atmosphere (Harrison, 2003).

(i) Biological fixation (BNF)

Nitrogen fixing bacteria are the only organisms that fix N through metabolic processes, i.e. the nitrogenase enzyme combines gaseous N with hydrogen to produce NH_4^+, which is then further converted by the bacteria to make their own organic compounds. Most BNF occurs by the activity of mo-nitrogenase, found in a wide variety of bacteria and some *Archaea*. Some N fixing bacteria, such as *Rhizobium*, live in the root nodules of the family *Fabaceae* (legumes such as peas or beans), where they form a symbiotic relationship with the host plant, producing NH_4^+ in exchange for carbohydrates. There are also N fixing bacteria (e.g. *Rhodospirillium, Azotobacter, Bejerinckia, Derxia, Clostridium)* that exist without plant hosts, known as free-living N fixers (Stark and Richards, 2008a). In aquatic environments, blue-green algae (*Cyanobacteria*) are important free-living N fixers.

(ii) Industrial N fixation (the Haber-Bosch process)

Early in the 20th century, a German scientist named Fritz Haber discovered how to short circuit the N cycle by fixing N chemically that could be added directly to the soil (Stark and Richards, 2008a). Under great pressure, at a temperature of 600°C and with the use of an iron catalyst, an atom of hydrogen (usually derived from natural gas or petroleum) and atmospheric N can be combined to form NH_4^+ (Harrison, 2003). This technology has spread rapidly over the past century and along with the advent of new crop varieties, the use of synthetic N fertilizers has led to an enormous boom in agricultural productivity which has helped to feed a rapidly growing world population (FAO, 2002; Galloway et al., 2004).

Nitrogen uptake-assimilation ($NH_4^+ \rightarrow$ Organic N)

The NH_4^+ produced by N fixing bacteria is usually quickly incorporated into protein and other organic N compounds, either by a host plant, the bacteria itself, or another soil organism (Harrison, 2003). Plants (autotrophs) absorb N from the soil solution through root hairs in the form of either NO_3^- or NH_4^+ ions. If NO_3^- is absorbed, it is first reduced to NO_2^- ions and then NH_4^+ ions for incorporation into amino acids, nucleic acids, enzymes and chlorophyll (Smil, 2000; Stark and Richards, 2008a). In plants that have a symbiotic relationship with rhizobia, some N is assimilated in the form of NH_4^+ ions directly from the nodules. It typically comprises 1 to 5% of plant DM. Animals, fungi, and other heterotrophic organisms obtain N by ingestion of amino acids, nucleotides and other small organic molecules.

Nitrogen mineralisation –ammonification (Organic N $\rightarrow NH_4^+$)

After N is incorporated into organic matter, it is often converted back into inorganic N by a process called N mineralisation, otherwise known as decay. When organisms die, decomposers (such as bacteria and fungi) consume the organic matter and lead to the process of decomposition. During this process, a significant amount of the N contained within the dead organism is converted to NH_4^+. Once in the form of NH_4^+, N is available for use by plants or for further transformation into NO_3^- through the process called nitrification (Harrison, 2003).

Nitrification ($NH_4^+ \rightarrow NO_3^-$)

Some of the NH_4^+ produced by decomposition is converted to NO_3^- via a process called nitrification. The conversion is performed primarily by soil-living bacteria and other nitrifying bacteria that gain energy from it. Nitrification requires the presence of oxygen (O_2), so nitrification can happen only in O_2-rich environments like circulating or flowing waters and the very surface layers of soils and sediments (Harrison, 2003). In the primary stage of nitrification, the oxidation of NH_4^+ is performed by bacteria such as the *Nitrosomonas* species, which converts NH_4^+ to NO_2^-. Other bacterial species, such as the *Nitrobacter*, are responsible for the oxidation of the NO_2^- into NO_3^- (Smil, 2000).

Denitrification ($NO_3^- \rightarrow N_2 + N_2O$)

Denitrification is an anaerobic process that is carried out by denitrifying bacteria (*Pseudomonas and Clostridium*; Smil, 2000), which convert NO_3^- to N_2 in anaerobic conditions (described in Chapter 2.5). Once converted to N_2, N is unlikely to be reconverted to a biologically available form because it is rapidly lost to the atmosphere as an inert gas. Denitrification is N transformation that removes N from the ecosystems, irreversibly, and it roughly balances the amount of N fixed by the N fixers described above (Ammann et al., 2009).

Anaerobic ammonium oxidation - anammox ($NH_4^+ \rightarrow N_2$)

Anammox is a biological process, in which NO_3^- and NH_4^+ are converted directly into N_2. Current findings suggest that it is an ubiquitous process that occurs in all N-containing ecosystems with suboxic conditions (Francis et al., 2007), however the magnitude of contribution of the process to the terrestrial cycle is still unclear and only a few measurements have been made in soil systems. In the oceans it makes up a major proportion (50%) of N_2 conversion thus, represents a major sink for fixed N and so limits oceanic primary productivity. The overall catabolic reaction is (Francis et al., 2007):

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$

The bacteria that perform the anammox process belong to the bacterial *Phylum Planctomycetes*, which are characterized by unique cytology: (i) they all possess one anammoxosome, a membrane bound compartment inside the cytoplasm which is the locus of anammox catabolism; (ii) extremely slow growth rate; the doubling time is nearly two weeks. The anammox process was originally found to occur only from 20 °C to 85 °C (Strous et al., 1999; Byrne et al., 2008; Jaeschke et al. 2009).

2.2.2 Nitrogen cycle in the grassland

The N dynamics (Fig. 2.1) in grassland soil is complex (Shepherd et al., 1996; Stark and Richards, 2008a) and strongly influenced by local edaphic, climatic and site history factors (Ledgard et al., 1998). In managed grasslands used for livestock production, the N cycle has been also affected by anthropogenic activities which are mostly associated with fertilizer use (Galloway et al., 2004). Unmanaged grasslands receive most of the N from BNF (Galloway et al., 2003) and senescent plant material (Vertes et al., 2007). Nitrogen fixing bacteria in symbiotic relationships with leguminous plants (e.g. white clover) have the ability to fix substantial quantities of N (100 to 300 kg N ha^{-1} yr^{-1}; Masterson and Murphy, 1983; Ledgard, 1991; Ledgard et al., 1998; Eriksen et al., 2004; Humphreys et al., 2008b). For this reason, legumes are an important component of many grasslands (Jarvis et al., 1995). Another source of N is wet and dry atmospheric deposition of N, which could amount up to around 12 kg N ha^{-1} yr^{-1} in Ireland (Sherwood and Tunney, 1991; Jordan, 1997; Watson, 2007). It originates from a variety of natural and anthropogenic sources and mainly consists of NH_3, NO_2^- and HNO_3 (Ammann et al., 2009). Natural sources include lightning and natural NH_3 emissions from rotting vegetation and manure (Whitehead, 1995; Jordan, 1997). Anthropogenic atmospheric N is derived mainly from agricultural sources (volatilisation from manure stores), industry, and fossil fuel combustion (Whitehead, 1995; Buss et al., 2005).

In managed grasslands (pastures), large inputs of N fertiliser increase the amount of N cycling within the system. This N has been used as the main driver to produce sufficient DM production to sustain high milk or meat production per hectare at economically attractive levels (Jarvis et al., 1996). Fertiliser recommendations have been established and have been based on the economic optimum levels with little regard for the efficiency of utilisation (Jarvis, 1998; The Fertiliser Manual RB209).

The grass produced from the N input to the soil is subsequently consumed by farm animals as grazed grass or as stored winter forage (silage and hay). Ruminants do not utilize the N that they ingested very efficiently. Transfer of N into milk and meat, or wool is very low (Van der Meer and Van Uum-van Lohuyzen, 1986; Jarvis et al., 1995; Grignani and Laidlaw, 2002, Raison et al., 2006) as the animal utilises only approximately 15 to 25% of the N ingested to produce the product (milk or meat) (Van Vuuren and Meijs, 1987; Smith et al., 1995; Whitehead, 1995; Pakrou and Dillon, 2000; Watson et al., 2007). Under ideal conditions, an efficiency of utilization of dietary N of 43% can be achieved (Jarvis et al., 1995). However, in practice, low forage digestabilities and imperfectly balanced amino acids reduce the efficiency level (Van Vuuren and Meijs, 1987).

The remainder (75 to 85%) of the N ingested is excreted as dung and urine (Van der Meer, 1983; Whitehead, 1995; Verite and Delaby, 2000; Soegaard et al., 2001, Eriksen et al., 2004). These N excretions are either directly deposited onto the soil by the grazing animal or returned to the soil mechanically as slurry and solid manure accumulated during housing periods. Whereas much of the dung N content is in an organic form and relatively immobile, urinary N can be readily converted into mobile inorganic N (Jarvis et al., 1995). Apart from urea, which represents the dominant proportion; i.e. 65 to 90% (Lantinga et al., 1987; Whitehead et al., 1989; Bristow et al., 1992), it contains allantoin, hippuric acid, creatinine and creatine, which are less available, but still relatively labile and may contribute to mobile available N over a relatively short term. Excreta, especially urinary N, returned to the swards result in a substantial recycling of N (Jarvis et al., 1995). Some of it may be volatilised as NH_3, but the remainder is present in a mobile form available for plant uptake or other transformations. A typical urination represents an input of 200 to 2000 kg N ha^{-1} over an area of 0.4 m^2 (Addiscott et al., 1991; Haynes and Williams, 1993; Jarvis et al., 1995; Hack-ten Broeke et al., 1996; Dai, 2000; ten Berge et al., 2002). This hotspot is in almost all circumstances likely to exceed the demand of the sward for N (Steele, 1982; Ball and Ryden, 1984) and so is available for transfer into another component of the cycle or possible loss (Ball et al., 1979; Carran et al., 1982; Sugimoto and Ball, 1989), particularly when grass growth and its demand is limited by other factor. Furthermore, the pattern of urine and dung returns introduces an enormous degree of heterogeneity in time and space. Cattle tend to urinate and defecate 9 and 12 times per day, respectively (Lantinga et al., 1987). These estimates indicate that after a single grazing, 4 to 9% of the paddock surface would be affected by urine and 0.6 to 1.2% by dung (Jarvis et al., 1995). For these reasons, N returns to the soil may cause N surplus, which is susceptible to loss through NH_3 volatilisation, leaching or denitrification, or may in fact be incorporated into the soil organic matter (SOM; Watson et al., 1992; Jarvis, 1993; Jarvis et al., 1995; Jarvis, 1998, 1999; Stark and Richards, 2008a, 2008b).

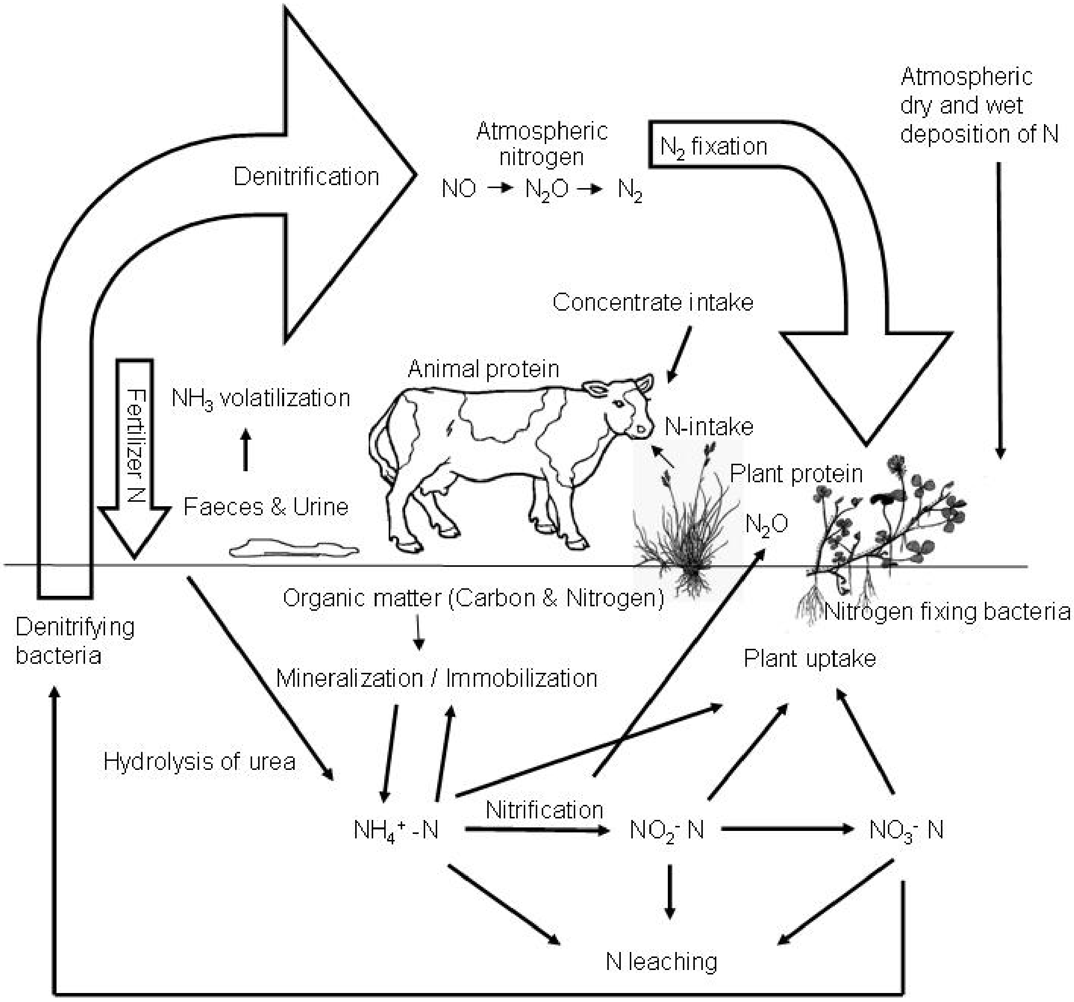

Fig. 2.1 Schematic representation of the N cycle in a grassland system.

Under low stocking rates, NO_3^- pollution decreases, SOM increases and physical parameters such as soil infiltration and soil aggregation stability improve (Hubbard et al., 2004; Saggar et al., 2007). However, under high stocking rates, N can become a pollutant source for drinking water, air and soil, because of high N surpluses and low N use efficiency during grazing. As the cost of fertiliser increases, and negative environmental effects are linked with excessive usage, the efficiency of N use is becoming more important (Jarvis, 1999; Marks et al., 1999; Stevens, 1999; Grignani and Zavattaro, 2000; Grignani and Laidlaw, 2002; Galloway et al., 2008).

An escaped N may have the capacity to disturb physiochemical and biological balances on local, regional, national or global scale (Jarvis et al., 1995) Animal production systems are major contributors to increasing concentrations of N trace gases, especially ammonia (NH_3) and N_2O in the atmosphere (Jarvis et al., 1995). Ammonia has attracted a considerable attention because it is the most alkaline trace gas and interacts with acidic species with a marked influence on atmospheric chemistry and the acidity of precipitation. Fruhermore, a short time after release it is returned back to the land (Sutton et al., 1993; Fangmeier et al, 1994). This causes acidification in poorly buffered soils after nitrification and release protons. Nitrous oxide is a potent GHG contributing to climate change. The fourth assessment report of the Intergovernmental Panel on Climate Change reported that N_2O on a per-molecule basis is 298 times more effective than carbon dioxide (CO_2) at absorbing long –wave radiation over a 100 year period and thus contributes to the radiative forcing of the atmosphere (Forster et al., 2007). The major source of N_2O is the biological reduction of excess NO_3^- under anaerobic conditions. However, nitrification (i.e. microbial oxidation of NH_4^+) may also act as a significant source of N_2O (Jarvis et al., 1995).

2.3 Losses of N by leaching

Nitrogen leaching is a natural process, occurring even in uncultivated systems (Havlin et al., 2005). It takes place when soil reaches the field capacity point, when no more water can be retained by its structure. The field capacity point represents the maximum amount of water that can be held by capillarity, before the water is drawn away by gravity. The surplus (excess) water moves downwards, transporting soluble N species below the rooting zone, where plants can no longer utilise them (Stark and Richards, 2008b). In most temperate regions, leaching occurs most frequently during the winter, when rainfall is high, evapotranspiration and grass or crop uptake is low (Whitehead, 1995). However, there are exceptions to this general seasonal pattern. One exception occurs in the soils with well-developed macropores, as these may allow some N leaching to occur in the autumn before the field capacity has been attained. A second exception to the normal seasonal pattern occurs in dry winters (and in normal winters in dry areas) when some N may remain throughout the winter in the non-mobile phase of the soil water (Whitehead, 1995).

2.3.1 Factors affecting N leaching

The amount of N leached during the winter season as a whole is usually determined mainly by two factors: (i) the total quantity of water passing through the soil profile (Shepherd et al., 2001; Stark and Richards, 2008a, 2008b), and (ii) the concentration of the soluble N in the topsoil at the onset of leaching or at the end of the growing season. The total amount of water passing through the soil profile (drainage) is influenced by the quantity, pattern, and time of rainfall and supplemental irrigation (Havlin et al., 2005), by temperature which directly affects evaporation and by the presence of vegetation on the soil surface, which takes up some water for the growth. Low evapotranspiration, low crop water and N demand in coincidence with periods of high rainfall, soil water content, and drainage water may increase the N leaching potential during cold winter periods (Havlin et al., 2005).

Irrigation generally increases the volume of drainage and thereby decreases the overall concentration of the solute in the soil water or groundwater as a result of dilution (Burden, 1982; Ledgard et al., 1998). In addition, the irrigation applied during the growing season tends to reduce the amount of N that is leached during the following winter by increasing the grass growth and thus N uptake (Whitehead, 1995). Conversely, when N uptake during the growing season is seriously restricted by drought, the amount of N leached subsequently is usually high (Jordan and Smith., 1985).

The size of the potential leachable N pool may be determined by the soil N balance between N inputs from synthetic and organic fertilizers, urine, dung deposition, SOM mineralisation, atmospheric deposition and N removal by immobilization (accumulation) into SOM, denitrification, NH_3 volatilization and plant uptake (Jarvis et al., 1995).

The extent to which N is carried out of the soil is controlled by the soil texture. Soil texture is represented by the proportion of soil particles of different sizes in the soil horizons. These are according to the international classification (Table 2.1) classified as sand, silt and clay particles. With a uniform input of water, the downward movement is two to three times greater in a sandy soil than in a clay soil (Whitehead, 1995).

The structural arrangement of these soil particles represents the physical structure of the soils, which has a considerable effect on the depth to which the existing (resident) soil water is displaced by additional water (Goss et al., 1998). The degree of the aggregation of the soil constituents depends on the nature of the soil. In general, the more clay the soil contains, the more aggregated it will be (Addiscott et al., 1991). This is because clay acts as a cement that holds other particles together and thereby has a strong influence on the structure of the soils. In addition, soils, in particular topsoils, contain another cementing material, which is soil organic matter (SOM). This comprises of matter from generations of plant residues that have been decomposed by microbes in the soil and converted to a form in which it is able to coat individual clay particles and also the fragments produced by various shattering processes. In doing so, it cements the fragments together and stabilizes them against being broken into smaller and smaller fragments.

The simplest way of explaining the process of leaching from the soil is by describing the concept of piston flow in homogeneous soils (coarse-textured soils) i.e. water entering the soil moves downwards, pushing in front of it the water containing soluble N that was previously in the same body of the soil. Thus, ten millimetres of rain or additional water displaces an equivalent volume of the soil water. However, because the soil has a solid phase that does not move, the distance moved in the liquid phase is more than ten millimetres. This scenario would only happen if the soil was completely uniform, but this is rarely the case (Addiscott et al., 1991).

The transport process of water applied to the surface of a well-structured soil is more complex; i.e. drainage water moves rapidly down through large pores (macropores) or fractures, which act as flow conduits. If these are continuous in the vertical direction, they form a preferential flow (Addiscott et al., 1991). The aggregates themselves contain numerous micropores through which water moves slowly and form a matrix flow. For these reasons, the existing soil water can be categorized broadly into mobile and non-mobile phases (in macropores and micropores, respectively), with the mobile phase being displaced much more readily by additional water (Whitehead, 1995). The micropores act as stores and secondary sources of solute. Consequently, the soluble N species in the mobile phase are highly susceptible to leaching whereas soluble N species in the non-mobile phase are much less susceptible. The interaction between mobile and non-mobile resident water in well structured soils is minimal (Addiscott et al., 1991). Thus, the concentration of N in the mobile phase, as well as the size of this phase, and therefore the size, shape and distribution of the pores making up this phase, have a large influence on the extent to which leaching occurs after a period of heavy rainfall (Jarvis et al., 1995; Whitehead, 1995).

Table 2.1 The International Soil Science Society's classification of particle sizes. Larger particles classified in order of increased size as gravel, cobbles, stones and boulders are not considered to be soil material (Addiscott et al., 1991)

Fraction	Particle diameter (μm)
Coarse sand	2.0-0.2
Fine sand	0.2-0.02
Silt	0.02-0.0002
Clay	<0.002

The presence of water and its movement through the soil profile is crucial for leaching to occur. Soil becomes saturated when water fills up the soil pores completely. If there is a substantial proportion of pores containing air, the soil is unsaturated. Water flows in both saturated and unsaturated soils in response to a force of some kind (Addiscott et al., 1991). The downward movement of water (and solutes) in a partially saturated or unsaturated soil decreases rapidly relative to that in fully saturated soil. Although the pattern of the solute transport and groundwater movement is complex, it can be described by partial flows as follows:

Diffusion

Diffusion represents movements of solute in the water from an area of greater concentration towards an area where it is less concentrated. It occurs as long as a concentration gradient exists, even if the water is not moving (Fetter, 1999). Thus, soluble N diffuses from non-mobile phase to mobile phase and vice-versa (e.g. after the application of fertilizer N). On one hand, the diffusion in the soil water is an important phenomenon securing plant nutrition; on the other hand, it is one of the main factors that determines where soluble N is or is not protected from the leaching (Addiscott et al., 1991).

Advection

Advection is a movement of solute within the water in which it is dissolved. The mean advective velocity of solute in flowing water is typically predicted by Darcy's Law, or by the Richards Equation in the unsaturated zone. The amount of solute that has been transported is a function of its concentration in the water and the quantity of the water flowing (Fetter, 1999).

Dispersion

If there is a high initial concentration of soluble N in the surface soil, its movement down the soil profile following the addition of water is inevitably accompanied by some vertical dispersion (Addiscott et al., 1991). This is a process of solute spreading by mixing that occurs at the moving front of a solute plume at all scales. There are three basic causes of this phenomenon: (i) at the pore scale, fluid travels faster through the centre of the pores than along the edges (Bear, 1972; Fetter, 1999); (ii) some of the fluid particles travel along longer flow paths in the porous medium than others; (iii) some pores are larger than others, which allows the fluid flowing through these pores to move faster. Consequently, the solute-containing water, in this case soil water is not all travelling at the same velocity (Fetter, 1999). In general the greater the average depth of leaching, the greater the vertical distance over which the solute is dispersed (Addiscott et al., 1991). The effect of dispersion in long term reduces the concentration of N leaching to groundwater and eventually it prolongs its overall impact (Buss et al., 2005).

Soil drainage systems increase the rate of water movement through the soil profile. The installation of the system lowers the groundwater table which subsequently reduces the period during which the soil is fully saturated and waterlogged in the winter. This leads to a considerable reduction in the denitrification process simultaneously with an increase in N leaching (Scholefield et al., 1993). Additionally, an improvement in drainage and aeration in the soil may increase the amount of N mineralised from the SOM. Thus, the losses via leaching are likely to be greater compared to previous losses via denitrification (Scholefield et al., 1988; Whitehead, 1995). In general, the ratio of NO_3^- leaching to denitrification is greater if the soil is well-drained due to more aerobic conditions.

The quantification of N leaching, particularly NO_3^- leaching, is important for the following reasons: (i) it represents a loss of plant-available N from the soil; (ii) leached N enters groundwater, streams and surface waters causing pollution and its eutrophication (Whitehead, 1995); (iii) leached NO_3^- is an indirect source of N_2O; and (iv) in an economic context, any N lost from the agricultural system signifies a financial loss to the farmer (Stark and Richards, 2008b).

2.3.2 Leaching of inorganic N

2.3.2.1 Ammonium (NH_4^+)

Ammonium in the soil may result from the application of synthetic fertilizers, from the hydrolysis of livestock urea or from the mineralisation of SOM (Whitehead, 1995). It is usually produced in the litter zone, and then leached down the profile to be nitrified at depth. It can be also produced by dissimilatory NO_3^- reduction to NH_4^+ (DNRA; Gardner et al., 2006; Francis et al., 2007; Kartal et al., 2007, Stark and Richards, 2008a). This biochemical process is mainly carried out by bacteria that are obligate and facultative anaerobes (bacteria that are capable of surviving with or without O_2) with fermentative metabolism (Koike and Sorenson, 1988) and is enhanced in highly anaerobic soils with high C content (Buresh and Patrick, 1978; Sorenson, 1978). Although it occurs in the same habitat as denitrification (Tiedje et al., 1981; Hill, 1996), its ecological significance is not very well understood (Sorensen 1987). Ammonium was proved to be highly soluble and mobile when aminization and ammonification are inhibited by low temperatures or at very high concentrations such as beneath urine patches. On the other hand, NH_4^+ ion is positively charged and therefore can be bound to negative exchange sites of SOM or clay particles (Feigenbaum et al., 1994; Whitehead, 1995; Stark and Richards, 2008b). This provides some degree of protection against rapid nitrification and subsequent leaching, particularly from highly concentrated spots (e.g. in urine patches). Certain clay minerals, particularly vermiculite and mica, are capable of fixing NH_4^+ by replacement with cations in the expanded lattices of clay minerals. It is believed that coarse clay (0.2 to 2 µm) and fine silt (2 to 5 µm) are the most important fractions in fixing added NH_4^+, however the extent of the process of fixation is affected by the soil moisture content and soil temperature. For this reason, the stability of fixed NH_4^+ is controlled by alternate cycles of wetting-drying and freezing-thawing. The presence of potassium (K^+) often restricts NH_4^+ fixation since K^+ can also fill fixation sites. Consequently, K fertilization before NH_4^+ application reduces the NH_4^+ fixation. Although the agricultural significance of NH_4^+ fixation is not great, it is very important in certain soils (Walsh et al., 1960; Havlin et al., 2005).

2.3.2.2 Nitrite (NO_2^-)

Nitrite is an intermediate product in many N transformations. It is produced by the oxidation of NH_4^+ in the first stage of nitrification (*Nitrosomonas bacteria*) and by the reduction of NO_3^- in the first stage of denitrification (Buss et al., 2005). Since NO_2^- is significantly more reactive than NO_3^- in the soil, there is only a limited range of redox conditions under which it is stable (Buss et al., 2005). Although NO_2^- is negatively charged, its sorption (retention) in the soil is commonly observed (Davidson et al., 2003; Fitzhugh et al., 2003). There is a hypothesis that NO_2^- reacts with the aromatic ring structures of dissolved organic matter to produce dissolved organic N (DON) compounds, especially in low pH environments where nitrous acid (HNO_2) is the key reactant. The final organic N compounds may be adsorbed to soil particles or taken up by the plants and bacteria

(Davidson et al., 2003). Due to its highly reactive nature in the soils, NO_2^- rarely occur in natural waters at concentrations comparable to those of NO_3^-, except temporarily under reducing conditions (Buss et al., 2005).

2.3.2.3 Nitrate (NO_3^-)

Nitrate is a stable anion, under aerobic conditions; however, under anaerobic conditions it can be converted to other oxides of N and to N_2 by the process of denitrification (Korom, 1992; Burt et al., 1999; Buss et al., 2005). The NO_3^- in the soils may be derived either from direct application of synthetic fertilizers or from percolation of urine through macropores in the dry soil followed by the hydrolysis of urea and nitrification of the resultant NH_4^+. This possibility is supported by the presence of NH_4^+ with a peak concentration at a slightly shallower depth in the soil profile (about 1m) than, that of NO_3^- (Ryden et al., 1984). Experiments on concentration of NO_3^--N draining through the soil from cattle urine patches resulted in concentrations ranging from 52 to 176 mg NO_3^--N L^{-1}, depending on the year and the season (Stout et al., 1997). Although agriculture is usually considered to be the main source of NO_3^- in the soils, there may be some NO_3^- derived from natural processes as well. Organic matter-rich sediments contain relatively high concentrations of organically bound N, which is mineralised to NH_4^+ as the sediment undergoes diagenesis to form a sedimentary rock (Rodvang and Simpkins, 2001). The nitrification of this NH_4^+ produces high levels of natural NO_3^-.

The NO_3^- is very soluble in water and due to its negative charge it is not adsorbed by the clay and organic colloids which are also negatively charged (Whitehead, 1995). Consequently, it is highly mobile in the soil solution and subject to leaching losses when water movement is high (Havlin, et al., 2005; Stark and Richards, 2008b). Due to insufficient water content and water movement through the soil profile during the summer months, NO_3^- is likely to remain in the soil until it is lost during the autumn and winter through a combination of leaching and denitrification (Whitehead, 1995).

2.3.3 Leaching of organic N

Organic N includes all substances in which N is bonded to carbon (C). It occurs in both soluble and particulate form. Soil organic matter content in the soils is highly dependent upon soil texture, structure and soil depth. It is always higher in the topsoil and decreases with the soil depth (Ros et al., 2009) and may be 40–50% higher in non-sandy soils, than in sandy soils; its content does not differ between silt and clay soils too much.

2.3.3.1 Dissolved organic N (DON)

Dissolved organic N (DON) is defined as organic N present in a dissolved form in soil solution (Murphy et al., 2000). It has been referred to a fraction of soil organic N which is collected in situ using a lysimeter or suction cup among other devices, and where no extractant is used (Murphy et al., 2000). The DON originates from plant litter leachates, microbial and root exudates, and hydrolysis of insoluble SOM (Haynes, 2005). There are two distinct functional DON pools in soil (Yu et al., 2002; Jones et al., 2004): (i) The first labile DON pool comprises low molecular weight DON (LMW-DON); i.e. mainly free amino acids, amino sugars and proteins (Stevenson, 1982; Antia et al., 1991). As it is turned over very rapidly by the microbial community, it does not accumulate in the soil. (ii) The second pool is a high molecular weight pool (HMW-DON) rich in complex humic substances (polyphenol-bound N), which are resistant to microbial attack (Peierls and Paerl, 1997; Stepanauskas et al., 1999, 2002; Marschner and Kalbitz, 2003; Jones et al., 2004). Consequently, it turns over slowly and represents the major DON loss to freshwaters. The low molecular weight (LMW) component of DON represents an important source of N for microorganisms and can also be utilised directly by some plants. Therefore, low concentration of amino acids in the soil solution indicates that labile DON in the soil is rapidly removed from solution by either roots or microorganisms preventing its accumulation (Jones et al., 2004). Due to rapid removal, rapidly mineralising LMW organic acids are capable of migrating only a few millimetres in acid forest soils (e.g. citrate and oxalate; Van Hees et al., 2005).

Dissolved organic N represents a significant pool of soluble N in many soils and freshwaters (Jones et al., 2004), and is present in appreciable quantities in all agricultural land use types, even in highly intensive agricultural systems where the residue quality is good and microbial activity is known to be high (Christou et al., 2005). In general, DON concentrations vary between 25 µg N L^{-1} and 10 mg N L^{-1} (Lawes and Gilbert, 1881; Watson et al., 2000a; Perakis and Hedin, 2002; Siemens and Kaupenjohann, 2002; Jones et al., 2004; Vinther et al., 2006), and account for 0.1 to 3.0% of total soil N (Haynes, 2005). In a grassland soil, a high release of root exudates increases the rate of DON immobilization compared to arable soils, leading to a decrease in the concentration of DON (Khalid et al., 2007), although there may be no difference in DON concentration between high and low intensity grasslands (Christou et al., 2005).

The DON plays an important role in ecological processes such as N leaching, mineralisation and plant uptake (Ros et al., 2009), and is increasingly being recognised as a major component of the terrestrial and marine N cycles (Antia et al., 1991; Chapin, 1995; Nasholm et al., 2000; Neff et al., 2002; Christou et al., 2005). For these reasons, it needs to be included in ecosystem N budgets and N cycling studies (Murphy et al., 2000; Siemens and Kaupenjohann, 2002; Jones et al., 2004).

2.3.3.2 Soluble (extractable) organic N (SON, EON)

Soluble (extractable) organic N (SON) is soil N that is extracted from the field moist or dried soils by shaking with water or a salt solution at a high soil-solution ratio (KCl, K_2SO_4, $CaCl_2$) for short periods of time, followed by centrifugation or filtering to separate the solution phase from the solid phase or by electro ultrafiltration (EUF) (Murphy et al., 2000; Jones and Willet, 2006). The size and characteristics of the SON pool is strongly influenced by methodology (Ros et al., 2009). The amount of SON in the soil can range from less than 5% of total soil N by mild salt solution (e.g. $CaCl_2$, diluted acids, etc.) to more than 50% by strong extraction methods such as acid hydrolysis (Stevenson, 1994; Matsumoto and Ae, 2004).

The DON is considered as a sub-pool of SON that exists as a part of soil organic matter N. Thus, SON represents the sum of DON plus extra organic compounds that solubilise during extraction, originating from soil biomass and particular organic N (Ros et al., 2009). The extra solubilised compounds in SON are considered as organic N that potentially dissolves over time, having a lower turnover rate than DON (Tipping, 1998; Kalbitz et al., 2000; Zsolnay, 2003).

Soluble organic N pools are composed, partially at least, of easily mineralisable N, and so have an impact on the usually very small but rapidly cycling N pools such as NH_4^+ (Mengel et al., 1999). As a result, SON is likely to be an important pool in N transformation pathways and plant uptake (Németh et al., 1988; Yu et al., 1994; Murphy et al., 1999). In soils, SON pool can arise by several processes: substrate fragmentation, depolymerisation and solubilisation, microbial lysis, faunal grazing of soil microbes and freeze/thawing (Wang and Bettany 1994). There is an opinion that there is a relatively constant pool of SON (related to SOM content and soil texture) and a more dynamic pool of SON, which reflects current plant dynamics (Murphy et al., 2000). These two fractions of SON are likely to vary greatly in their chemical composition, stability and transformation rates (Murphy et al., 2000).

The SON has been identified as a key pool in soil-plant N cycling in forest system (Qualls and Haines 1991), arctic tundra (Atkin, 1996) and subtropical wet heathland (Schmidt and Stewardt 1997). The quantities of SON are usually higher under grassland and forest, and the proportion of amino compounds is greater than in arable soils (Nemeth et al., 1988; Mengel et al., 1999). Although SON is a clearly significant pool within agricultural soils (Murphy et al., 2000), its measurement has largely been overlooked (Bhogal et al., 2000).

The size of the SON pool is of the same magnitude as inorganic N, and of equal size in many cases. For a wide range of arable agricultural soils types, extractable SON content varies generally between 20 and 45 kg SON ha^{-1} and comprises about 40 to 60% of total soluble N (TSN) (Murphy et al., 1999, 2000). There is likely to be a constant ratio between inorganic N and SON in these soils (Murphy et al., 2000). In the grassland soils, the concentrations of SON in the soil profile range from 20 to 90% of the TSN pool (Bhogal et al., 2000), increasing with the number of previous years under grass/clover ley (Murphy et al., 2000). The size of this pool under grasslands is influenced by N mineralisation (Appel and Mengel, 1998; Mulvaney et al., 2001), total soil N content (Ros et al., 2009), soil pH, land use changes and agricultural management practices (Haynes, 2005).

Both DON and SON are influenced by similar processes and in the same way as inorganic N pools, but these pools are more constant than inorganic ones (Murphy et al., 2000).

Compared to DON, the content of SON is more prone to changes in seasons, soil depth and pH (Ros et al., 2009); i.e. while no influence of different seasons was observed on DON concentrations, SON concentrations were different between summer and winter periods, and also between autumn and winter periods with the minimum occurring during the winter and the maximum in the late summer (Jensen at el., 1997; Ros et al., 2009). Changes in the seasonal concentrations of SON are attributed to differences in the temperature and soil moisture, which are important factors controlling microbial activity and its adaptation (Schmidt et al., 2007). The SON concentration in the soil usually decreases (22%) as a result of an increase in soil pH (pH > 6) (Ros et al., 2009), which may be explained by its increasing solubility (Andersson et al., 1994) or by increased microbial activity and the consumption of soluble molecules (Karlik, 1995).

Conversely, DON concentrations are primarily controlled by management factors (i.e. different land use and fertilisation; Ros et al., 2009). Although the total dissolved N (TDN) pool is dominated by DON in less intensive agricultural systems, the concentration of DON in soil solution is dependent upon the land use and generally follows the series from citrus farm > vegetable farm > forest = arable farming > grassland = wetland > heathland (Christou et al., 2005). Larger variations in DON compared to SON were also observed as a response to synthetic N fertilisation. It is known that the concentration of DON increases, as the application of synthetic N fertilizer changes the microbial community structure and solubilises soil organic N due to its pH effect (Chantigny, 2003). While the increase in SON content following the application of synthetic fertilizer N may be only minor (ca. 10%), DON may increase by up to 50% (Ros et al., 2009). Despite these findings, the grassland management or land use change has been shown to have a proportionally lesser impact on the amount of DON present compared to inorganic N (Christou et al., 2005).

The extent of organic N leaching is dependent on its retention by clay minerals. Ligand exchange between dissolved organic matter and carboxyl (Kaiser et al., 1997) or hydroxyl groups (Shen, 1999) on the surface of soil minerals is considered to be an important mechanism for sorption (Chiou et al., 1983). Sorption capacity of the soil is influenced by soil pH (maximal at pH 4 to 5 and decreasing with pH>5) (Shen, 1999), clay content (through its relationship with the amount of mineral surface), the ionic strength of the soil solution and the ion species present in the soil solution (e.g. Ca^{2+} binding to mineral sites or complexing with dissolved organic matter). Thus management practices in agricultural systems such as manure application and liming change the sorption capacity of the soil and the resulting composition of the dissolved organic matter in the solution.

Although the flux of organic compounds through both DON and SON pools is affected by changes in biophysical conditions and management practices (Ros et al., 2009), organic N losses via leaching are more likely to be related to water fluxes through the soil profile (Van Kessel et al., 2009). There has not been clear evidence of movement of DON down the profile (Bhogal et al., 2000); however there has been a number of studies reporting considerable DON leaching from the soils. In the past, it was believed that organic forms of N are unlikely to be leached below the root zone, although some organic N from slurry may be leached through vertical cracks or large-diameter pores (macropores; Whitehead, 1995). It has been discovered only recently, that considerable amounts of N from faeces or organic manures are being leached in organic form. Lysimeter studies have shown that land application of livestock manure can result in a concentration of up to 600 mg of DON L^{-1} in a leachate (Elrashidi et al., 1999). In another study, quantities of DON leached from plots receiving farmyard manure (FYM) were considerably higher compared to inorganic N losses. Loss of DON increased in order from non-fertilized plots < synthetic fertilizer plots < FYM plots (Murphy et al., 2000). Since SOM blocks active sites on soil minerals and thus reduces the sorption of dissolved organic matter (Murphy et al., 2000), an increase in DON leaching from the FYM treatment may be explained by a greater amount of N in the soil along with reduced sorption of DON on soil particles in the FYM plots.

Quite large pools of DON have been also measured in leachates from forest floors (Yavitt and Fahey 1986; Stevens and Wannop 1987; Qualls and Haines, 1991; Currie et al., 1996). Since the concentration of DON in forest floor leachates exceeded the concentration of inorganic N (up to 94% of the total N leached; Yu et al., 1994), DON has been found to be a dominant source of N leached into surface water in forested watersheds (Wissmar 1991, Hedin et al., 1995). The DON leached has been considered to comprise only about one-tenth of the SON extracted from the same soil (Murphy et al., 2000). Hence, the SON content of the soil water extracts are likely to be several orders of magnitude greater than inorganic N content (Emmett et al., 1991; Yu et al., 1994). This suggests that the leaching of organic N could be a major pathway for N loss from at least some soils. In other soils, DON may be mineralised to NO_3^--N during the percolation through the soil profile (Stevens and Wannop, 1987) and then may be included in measured losses (as NH_4^+ and NO_3^-).

Dissolved organic N (DON) leached from the soil may carry nutrient cations such as Ca^{2+} and Mg^{2+} and pollutants such as toxic complexed metals (low affinity for DON e.g. Cd, Zn, or high affinity for DON e.g. Cu, Cr, Hg) and pesticides (Chiou et al., 1986; Berggren et al., 1990, Wissmar, 1991, Liu and Gary 1993; Murphy et al., 2000). This makes the study of dissolved organic matter/heavy metal reactions even more important (Murphy et al., 2000). Heavy metals such as Copper (Cu), originating from animal manure in agricultural systems (Romkens and Dolfing 1998) form potentially highly mobile complexes with DON (Temminghoff et al., 1997; Kalbitz and Wennrich 1998; Romkens and Dolfing 1998) which may result in higher concentration of Cu in the drainage solution (Murphy et al.,2000).

2.3.4 Environmental consequences of N leaching

Nitrogen lost from the farming systems either in an inorganic or organic form is likely to contribute to water pollution. Over-enrichment of aquatic environments leads to changes in primary production, biological structure and turnover resulting in a higher trophic state of waterbodies (Stark and Richards, 2008b). This process is generally known as an eutrophication. The full impact of eutrophication depends primarily on the balance between N and phosphorus (P) concentrations in waterbody. Where there is an excess of P but only little N, a small addition of NO_3^- can lead to significant changes in the trophic status. For this reason, in the freshwater environment, an excess of N particularly affects oligotrophic waters (i.e. nutrient-poor and rich in O_2; Mason, 2002).

High nutrient levels affect biodiversity by favouring plants which prefer or can survive in nutrient-rich environments. Consequently, this leads to excessive plant growth (typically algal; WHO, 1999). Subsequent death of algae and its decomposition leads to increased O_2 consumption by aerobic bacteria resulting in low dissolved O_2 concentrations in waters and sediments of aquatic systems. This can result in hypoxic (low O_2) or anoxic (O_2 depleted) conditions in the waterbodies (Stark and Richards, 2008b). Insufficient concentrations of dissolved O_2 can not support marine life and subsequently leads to death of invertebrates and fish. The most affected areas (O_2 concentration < 2 ppm) are commonly called dead zones for as long as O_2 consumption exceeds replenishment (Stark and Richards, 2008b). In temperate climates eutrophication in affected areas appears annually during summer time (Stark and Richards, 2008b). In addition, algae are likely to cause fish asphyxiation by physically clogging or damaging their gills (www.fwr.org). Certain algal species, such as freshwater *cyanobacteria* and marine *dinoflagellates* produce toxins that can seriously affect the health of mammals, birds and fish (World Heath Organisation, 1999).

Excessive concentrations of NO_3^- in drinking water have been associated with adverse health effects in humans (Buss, et al., 2005). Although NO_3^- is not directly toxic to humans, under strongly reducing conditions, such as those in the human gut, it is transformed to NO_2^-. Nitrite ions pass from the gut into the blood stream and bond to haemoglobin molecules, converting them to a form that cannot transport O_2 (methaemoglobin). Therefore, excessive consumption of NO_3^- in drinking water has been associated with a risk of methaemoglobinaemia or ‘blue baby syndrome’ (Fan and Steinberg, 1996). Additionally, high concentrations of NO_3^- (> 23 mg N L^{-1}) have been shown to induce stomach cancer in animals, including mice and rats. However, epidemiological studies have not yet identified a causal link between exposure to NO_3^- and cancer in humans (Mason, 2002; World Heath Organisation, 2004). In other studies, there have been reported carcinogenic and terratogenic effects of other N compounds in humans (Ia GarcRoché et al., 1987).

Under current legislation (European Parliament and Council, 2000, 2006) all EU countries are required to monitor water quality with regard to NO_3^- concentration and trophic status. According to a recent report for the period 2004-2007, 34% of the groundwaters within EU had an average NO_3^- concentrations above 25 mg NO_3^--N L^{-1} and 33% of surface waters were defined as eutrophic or hypertrophic (European Commission, 2010).

2.3.5 Measurements of N leaching and their limitations

Measurements of N leaching involve analyses of water which drains from the soil at the base of the root zone, as this is the zone below which the NO_3^- is considered to have escaped. The concentrations of N species leaving the soil in a given area and the quantity of water in which it is carried are crucial for estimating the fluxes of N from the soil. Fluxes of water through the soil may be calculated from the water balance by subtracting an estimate of the amount of water evaporating from the soil from a measured amount of rainfall with irrigation. Due to high variation in the concentrations of N and the fluxes of water from point to point, there is a weakness in this approach as the mean concentration of N multiplied by the mean flux of water (drainage) is not likely to be the true mean of the leached fluxes (Addiscott et al., 1991).

2.3.5.1 Extracting the soil solution by suction: Porous ceramic cup

This approach has a long history. The first device described as an ‘artificial root’ was constructed in 1904. This root was represented by a porous tube through which water could be drawn from the soil under suction (Briggs and McCall, 1904). Nowadays, the porous ceramic cups made of a hydrophilic material (typically kaolin clay) containing small pores (Grossmann and Udluft, 1991) are fitted to plastic or metal tubes, which are inserted at various depths in the soil. The samples of soil solution withdrawn into a collector are obtained by applying suction to the tubes (Addiscott et al., 1991; Whitehead, 1995). The sampling units are installed in carefully prepared holes in the soil. If the units are installed vertically, there is a risk that rain water, irrigation water or urine will be channelled down the remaining small gap around the sampling unit. Various approaches have been used to avoid this problem. Some researchers sieve the soil and use it to back-fill the hole, while others back-fill the hole with silica flour. The other option to overcome this problem is to plug the top of the hole with bentonite which has the ability to expand greatly when it is wetted and seals the gap around the sampling unit. Installation of the ceramic cups at an angle of 45° or less to the soil surface decreases the risk of channelling; however for this the cups need to be longer (Addiscott et al., 1991).

There must be a proper contact between the porous cup and the soil around it. Filling the gap with soil or silica flour may help but pouring the slurry of the soil taken from the hole round the sampling unit is another way (Addiscott et al., 1991). A further problem arises when the pores of the porous cups become plugged with soil materials. This may affect the N concentration which is measured and cause variability of ± 30% or more (Hansen and Harris, 1975). It is believed that the porous cup draws water from a sphere of about 0.6 m^2. Although the representation of a large volume might be seen as an advantage, samples are drawn from a wide variety of pores, not all of which may contribute to the flow. This is because the suction applied through the porous cup distorts patterns of flow through the soil (Van der Ploeg and Beese, 1977). Additionally, the N concentration in the sample is influenced by the performance of the sampling procedure (speed, created pressure). The faster water is drawn out of the soil through the porous ceramic cups, the smaller its NO_3^- concentration tends to be (Hansen and Harris, 1975). This fact reflects the relative concentration of N in larger and smaller pores. This results in unsatisfactory reproducibility of both the volume of the water removed and the concentration of solutes in it. The main interest of the sampling is in the water that carries soluble N species through, and out of the soil, which is mobile water; the porous ceramic cups draw water from a wide range of pores (Addiscott et al., 1991).

Nevertheless, the ceramic cups are most effective on sandy and other unstructured or homogenous soils in which water moves fairly uniformly down the profile (piston flow) but they may underestimate the amount of leaching in structured soils (Goulding and Webster, 1992; Hatch et al., 1997; Goulding 2000; Murphy et al., 2000). As they have been found to preferentially sample immobile water from soil pads, they do not work well on poorly drained heavy clay soils (Goulding and Webster, 1992; Hatch et al., 1997), where macropores are the dominant drainage route, especially after heavy rain (Grossmann and Udluft 1991) or irrigation. Another limitation is associated with measuring the DON, since it contains molecules with high sorption potential (Murphy et al., 2000). Despite all their limitations, they are relatively cheap and allow considerable flexibility although much depends on the care with which they are installed and used (Addiscott et al., 1991).

2.3.5.2 Lysimeters

The first lysimeters were constructed in Paris in 1688 by the mathematician and meteorologist De la Hire, who worked for Louis XIV (Addiscott et al., 1991). Lysimeters are blocks of soil, usually in cylindrical containers or simply held by the soil around it. However, they can differ in shape and size; i.e. field scale lysimeters in Rothamsted are rectangular blocks greater than 5 ha in size. The lysimeter upper surface is exposed to rain and evaporation in the usual way and may have plants growing on it. At the base of the soil, there is a system for collecting water that passed through the soil. Ideally, they should be installed in the field so that the soil surface is at ground level, and soil temperatures within each lysimeter are close to those occurring naturally (Addiscott et al., 1991; Goulding and Webster, 1992).

There are two ways of constructing a lysimeter containing undisturbed soil: (i) to leave the soil where it is and dig a trench beside it and insert a collector to catch the water passing down through the soil; and (ii) to remove the soil ‘en bloc’, with the minimum disturbance, and attach a collecting system to the base of the returning column of soil. The first approach leads to an Ebermayer lysimeter named after a Bavarian meteorologist, the second leads to intact monolith or block lysimeter (Addiscott et al., 1991). The key difference between the two categories is that of lateral constraint. An Ebermayer lysimeter has no side walls, except possibly where the trench is, whereas a monolith lysimeter does have some form of a side wall. As there are no walls around the Ebermayer lysimeter, any lateral flow of water that occurs in the natural soil is retained. On the other hand, there is no way of knowing exactly from what area the water and soluble N collected come from (Addiscott et al., 1991).

The surface tension at the resulting air-water interface holds back drainage of water from the soil. This means that water drains from the soil above the interface only when the soil becomes saturated (Richards et al., 1939). This problem can be avoided by applying suction to the base of the soil, which controls both the rate at which water drains from the soil and the amount of water held in the soil at the base (Coleman, 1946). As a result, suction determines which particular suite of pores is releasing water. This could influence both the quantity and the concentration of N in water leaving the soil (Haines et al., 1982). In the Ebermayer lysimeters, this can be overcome by placing a porous ceramic plate firmly in contact with the base of the soil and applying the suction to this. Similarly in monolith lysimeter, suction can be applied through porous candles at the base of the soil (Belford, 1979). In lysimeters which have no suction applied to the base, the amount of water draining through the soil is less than in the field, and consequently conditions are more anaerobic, and likely to increase denitrification and reduce NO_3^- leaching (Addiscott et al., 1991).

The main advantage of the lysimeters is that their soil volume is easily defined and that the inputs and outputs of water and N (other than gaseous forms of N) can be measured accurately (Goulding and Webster, 1992). However some disadvantages have been identified as well. Soil may be compressed vertically and also laterally next to the pipe that forms the casing. Soils with unstable structure may collapse during the installation and collection of the monolith. Disturbance to the soil may increase the mineralisation of soil N and hence the amount of NO_3^- leached. There may be a serious problem with a clay soil that shrinks away from the wall of the lysimeter during dry weather (Addiscott et al., 1991). Developing cracks at the inside edge of the lysimeter, particularly with clay soils, may allow water to by-pass the bulk of the soil. For this reason, lysimeters are most effective with freely-draining soils and highly textured soils (Goulding and Webster, 1992).

These various disadvantages are overcome in large monolith lysimeters by applying suction at the base to match the surface tension lost by breaking the vertical pores in the soil (Belford, 1979). Such monolith lysimeters generally provide the most effective method for assessing N leaching from many soil types, although they are expensive and time-consuming to install (Whitehead, 1995). In general, lysimeters are in the middle of price range, at approximately one-tenth of the cost of a field drainage system but 10 times the cost of porous cups. Despite the fact that they may be subject to soil shrinkage problems, they are the most reliable and economic tools for measuring total water and solute loss from the soil, and are large enough to minimise spatial variation and allow management practices almost as normal (Murphy et al., 2000).

2.3.5.3 Groundwater sampling

Installed monitoring wells collect representative samples of water from the aquifer. Wells and sampling devices can be constructed of materials that have the minimum tendency to leach materials into and sorb compounds from the water sample. Monitoring wells can be installed for a number of different purposes beside N chemistry investigation, which are: (i) measuring the elevation of watertable; (ii) collecting of water sample for a broad range of chemical analysis; (iii) testing the permeability of an aquifer; and (iv) collecting a sample of soil gases etc. (Fetter, 1999).

The design of the well is dictated by its use. The factors that should be included in the design of a monitoring well include: type of casing material, its diameter, if there will be a well screen or an open borehole, length of the casing, depth of the well, setting and length of the well screen, its diameter, the type of material, slot openings, whether gravel pack is necessary, method of installation, material used to seal annular space between the casing and the borehole wall (Fetter, 1999).

The casing is a piece of solid pipe that leads from the ground surface to the well screen or open borehole and is intended to keep both soil and water from the entering the well other than through the screen or open borehole. If the well will be used to collect groundwater samples, the diameter of the casing needs to be such that standard well-sampling equipment can fit inside. The common standard for a variety of pumps is 5 cm (Fetter, 1999). Casing diameter can also be influenced by the depth of the well. The deeper the well, the stronger the casing and screen must be to resist the lateral pressure. Larger diameter casing can be made with thicker walls to have greater strength. There are a number of materials used to make well casings and screens, e.g., polytetrafluoroethylene (PTFE), mild steel, galvanized steel, stainless steel, polyvinyl chloride (PVC), acrylonitrile butadiene styrene (ABS), fluorinated ethylene propylene (FEP) etc. These materials vary in their chemical inertness, strength, durability, ease of handling and cost. The ideal casing material is inexpensive, strong, not subjected to degradation in the environment, and will not affect water- quality samples by either leaching chemicals into or sorbing them from the groundwater (Ranney and Packer, 1997).

In most monitoring wells, the well screen is the same diameter and is made of the same material as the casing to which it is attached. The screen has openings to permit water to enter. Although the manufacturers offer screens in a variety of opening sizes, generally ranging from 0.02 to 0.63 cm, the openings can be done by hand cutting of slots or drilling the holes into the pipe (Fetter, 1999).

The casing and screen may be placed in the borehole and the native soil allowed to cave around the screen. This is called a naturally developed well and is often used in sandy soils with very limited amounts of silt and clay present. When water is withdrawn from such a well, it may initially be cloudy due to suspended silt and clay, but the water should eventually clears as the fines near the screen are removed by the process called well development. If the soil has a high clay or silt content, it is necessary to use an artificial filter pack. Filter pack material is medium to coarse sand that is predominately silica with no carbonates. Its purpose is to stabilize the natural formation and keep it out of the screen and reduce the amount of silt and clay that enters the well (Fetter, 1999).

The annular space in the borehole above the filter pack must be sealed to prevent the movement of surface water downward. The seal should be made of material that has a low permeability, bonds well to the natural soil and the casing, is durable, permanent and expands to ensure a tight seal. Materials typically used for an annular seal are bentonite, neat cement grout, and bentonite-sand slurry. Bentonite is clay containing at least 85% sodium montmorillonite. It swells to several times its original volume when it is hydrated. However, bentonite has a high cation-exchange capacity and can affect the chemistry of water that comes into contact with it. This problem can be avoided if fined sand is placed in annular space above the filter pack material. This keeps the annular seal material form coming into contact with the water entering the well screen (Fetter, 1999).

The length of the screen and the depth to which it is set is based on the objectives of the monitoring program. To monitor the groundwater table and its chemistry, the screen must be set, so that it intersects the water table over the whole year. It means the screen has to be deep and long enough, so that when the water table is at the greatest depth below ground level (bgl), there is enough screen remaining below the water table to contain sufficient water for the water sample (Fetter, 1999).

Because the purpose of drilling a monitoring well is to collect a sample of water and analyze it for small concentration of chemicals, the equipment and supplies that are used, have to be decontaminated prior to the installation. The groundwater sample should be representative of water in the aquifer, not of the water standing in the well casing or screen. It means that water that has been standing in the well has to be removed prior to the sampling (Fetter, 1999).

2.3.5.4 Artificial field drainage system

As heavy clay soils impede the downward flow of water (except when they dry out and form cracks), some form of artificial drainage (mole or tile) is often constructed in order to make them useful for farming (Addiscott et al., 1991). The ‘mole’ is a piece of metal that is drawn through the soil creating a drainage channel below the surface – the mole drain. For the channel to remain stable and functional the soil must have high clay content and in such conditions mole drains can be effective for up to 10 years. In the case of tile drain, the pipes are made from the porous material placed in prepared channels and covered with gravel.

Sampling and analysis of the water from drains under an individual field is applicable only when the soil beneath the drainage is almost impermeable to water; i.e. the drains collect a large proportion of the water passing through the upper part of the soil. An implementation of drainage into the soil changes the pattern of the water flows through the soil profile. As a result, there are the following main flows: (i) surface runoff that is the water movement across the surface of the soil; (ii) interflow, which is the lateral flow on the top of the impermeable subsoil beneath the plough-depth; and (iii) flow into and through the drainage systems. Downward seepage below the drain usually contributes little to water movement (Addiscott et al., 1991). The amount of N leached is estimated by combining data on N concentrations with measurements of the water flow through the drains. It is likely that field drains may intercept soil drainage only partially and the proportion that is intercepted is difficult to assess (Murphy et al., 2000).

The sampling of drainage water from an artificial field drainage system beneath grazed grassland has the advantage of overcoming the heterogeneity (spatial variability) caused by livestock (Cameron and Scotter, 1988). On the other hand, it may be difficult to prevent the lateral flows between the plots (Addiscott et al., 1991). Another disadvantage of this method is the need to relate the frequency of sampling to the rate of flow of the drainage water (Cameron and Scotter, 1988). Despite this, sampling of drainage from the artificial drainage system is the most effective method in well structured clay soils compared to the other two methods mentioned above (Cameron and Scotter, 1988).

Similarly, in small catchments areas underlined by impermeable clays, all the drainage water leaves the catchment by a single ditch or stream. Therefore this method does not require drains to be installed. By monitoring both NO_3^- concentrations in the ditch or stream and its flow rate, it is possible to estimate the amount of N leached from the catchment area (Whitehead, 1995). High resolution data may be available from fully automated systems on hydrologically isolated plots (Cannell et al., 1984; Vinten and Redman 1990). As the samples of water are taken only from a single source in the catchment area, these studies have the advantage of reduced sample replication. Despite their economical, time and labour saving advantages, these measurements are restricted to areas with impermeable soils only (Whitehead, 1995).

2.3.5.5 Soil sampling

Soil sampling involves measuring the concentration of soluble N species in soil extracts obtained by shaking with a suitable solution (Bremner, 1965). A range of salt solutions have been used, most commonly solutions of calcium chloride ($CaCl_2$), potassium chloride (KCl) and potassium sulphate (K_2SO_4) (Murphy et al., 2000). The type of extractant used has been found to affect the quantity of total soluble N (TSN) extracted. Salt solutions may disturb adsorption equilibrium on the soil exchange surfaces and release organic N, which was not originally dissolved. Additionally, strong salt solution lyses microbial cells and removes N from dying cells (Bhogal et al., 2000). The extent of extraction appears to be also influenced by soil type (Bhogal et al., 2000). Although the soil extracts cannot be analysed for SON directly, SON can be determined by subtracting the inorganic N concentration from total soluble N (TSN) concentration (Murphy et al., 2000).

Successive sampling at various depths in the soil at some intervals during the drainage season (Whitehead, 1995), may give information on changes in the N pools in the soil profile; however, these changes may not necessary arise from downward movement (Addiscott et al., 1991). Currently, this simple methodology has been routinely used to estimate soil inorganic N in the soil profile on farms to support fertilizer recommendations (Shepherd et al., 1996; Wilson et al., 1996).

2.4 Loss of N by surface runoff

The surface runoff of water occurs when the intensity of rainfall (or melting of snow) exceeds the capacity for infiltration into the soil. The water then moves laterally over the soil surface to ditches and streams, taking with it soluble and particulate material. Runoff is most likely to occur on soils that are poorly structured, have a high groundwater table, have a considerable slope, or are frozen just below the surface. Due to high rainfall and low soil temperatures, which may result in temporarily frozen ground, surface runoff is more likely to occur during the winter period. In some situations, runoff can be reduced by improving the soil porosity and in other situations by lowering the water table (Whitehead, 1995).

2.5 Losses of N by denitrification

Denitrification is the biological or chemical progressive reduction of NO_2^- or NO_3^- (Fig. 2.2). It takes place mainly under anaerobic conditions and results in the evolution of nitrogenous gases (N_2O, N_2 and NO) (Stark and Richards, 2008a), which can then be lost to the atmosphere from the system. Thus, denitrification completes the N cycle initiated by N_2 fixation by returning N to its elemental form N_2 (Seitzinger et al., 2006). Although the denitrification process has a stable endpoint at N_2, the process can be arrested at any of the intermediate stages by a number of factors. The process of denitrification was observed for the first time by Gayon and Dupetit in 1885.

$2NO_3^-$	→	$2NO_2^-$	→	2NO	→	N_2O	→	N_2
Nitrate ions		Nitrite ions		Nitric oxide		Nitrous oxide		Dinitrogen gas

Fig. 2.2 Denitrification reaction chain

2.5.1 Biological denitrification

Biological denitrification is a microbially mediated redox process in soil or groundwater and requires the presence of electron donors such as biodegradable organic C and/or sulphide minerals (Buss et al., 2005). It is a respiration process by which denitrifying microbes couple N oxide reduction with oxidation of organic matter to produce energy by phosphorylation (Firestone 1982). Denitrifying microbes can use either NO_3^- or O_2 as electron acceptors (Roberston and Kuenen, 1991). However, organic C tends to be oxidised preferentially by O_2 as it supplies more energy to the micro-organisms (Buss et al., 2005). With an excess of organic C, aerobic bacteria use dissolved O_2 until it is depleted. Once O_2 concentrations are depleted, reduction of other electron acceptors becomes energetically favourable for facultative anaerobes (i.e. bacteria that are capable of surviving with or without O_2). As O_2 levels decrease, obligate anaerobes (i.e. bacteria that survive only in the absence of O_2) begin to use the remainder of the available electron acceptors. When the NO_3^- is depleted, reduction reactions proceed through manganese and iron oxides, then sulphate (Buss et al., 2005). Conditions required for respiratory denitrification therefore include: presence of denitrifying microbes (facultative/obligate anaerobes), absence of O_2, sufficient NO_3^- (or other N oxides), organic C (or another electron donor), and other environmental conditions (e.g. soil pH and temperature) suited to soil microbes (Barton et al., 1999).

Denitrifying microorganisms (bacteria) capable of denitrification are ubiquitous and widely distributed throughout a variety of environments, and thus denitrification occurs widely throughout terrestrial, freshwater and marine ecosystems (Beauchamp et al., 1989; Seitzinger et al., 2006); e.g. some are found at great depths in aquifers (nearly 300 m below the ground; Francis et al., 1989). Although we are only beginning to understand the diversity of denitrifiers and their distribution in space and time (Wallenstein et al., 2006), the process is generally not limited by the absence of these organisms (Tiedje, 1988). The process is carried out by over 33 genera of bacteria (aid. *Agrobacterium, Bacillus, Pseudomonas and Azosplrillum*), most of which are capable of completely reducing NO_3^- to N_2, while several genera produce N_2O as a final product of denitrification (Stevenson and Cole, 1999). Most of them are facultative anaerobic heterotrophs, i.e. they obtain both their energy and cellular C from the oxidation of organic compounds (heterotrophism). However, some denitrifying bacteria are autotrophs, i.e. they obtain their energy from the oxidation of inorganic species (such as FeS_2, Fe^{2+}, Mn^{2+}) and use inorganic C (mainly from HCO_3^-) for cell construction (autotrophism; Buss et al., 2005). The denitrifying bacteria use NO_3^- and NO_2^- as electron acceptors in anaerobic conditions, though in aerobic conditions they use molecular O_2. The various species vary greatly in their sensitivity to O_2 and in the concentration of O_2 at which denitrification is induced (Lloyd, 1993). In general, the absence of O_2 and the presence of organic C reduces sulphur or iron facilitated denitrification (Buss et al., 2005; Burgin and Hamilton, 2007).

Denitrification is an enzymatic process. In general, in anaerobic conditions, denitrifying bacteria produce enzymes that catalyse all the reactions (Whitehead, 1995). Most of them produce all the enzymes in the sequence, but some are unable to produce NO_3^- reductase, while others are unable to produce N_2O reductase (Knowles, 1981, 1982; Firestone, 1982; Lloyd, 1993). In general, NO_3^- reductase and N_2O reductase are the enzymes that are most easily inhibited by O_2 concentrations and consequently, when conditions are only marginally anaerobic, the proportion of N_2O increases. It is thought that only small amounts of NO are produced by denitrification, as the activity of NO reductase is higher than NO_2^- reductase (Lloyd, 1993).

In the unsaturated zone denitrification mostly occurs in the upper 5 to 20 cm of the soil profile (Ryden, 1985; Watson et al., 1992; Luo et al., 1998), principally because it is the region with the highest concentrations of organic C (Brady and Weil, 2002). Thus, the denitrification activity decreases with increasing depth reflecting the absence of a suitable C source (Colbourn et al., 1984; Aulakh et al., 1992; McCarthy and Bremner, 1992; Jarvis and Hatch, 1994; Cannavo et al. 2004). The organic C concentrations arise primarily from the decay of dead vegetation and root exudates (Burt et al., 1999; Buss et al., 2005). Deeper rooting plants likely allow for higher denitrification (Burt et al., 1999). However, the DOC decrease down through the unsaturated zone as it is gradually mineralised to CO_2 (Buss et al., 2005). For this reason, when the denitrification occurs at a depth of more than 50 cm (Jarvis and Hatch, 1994; Ryan et al., 1998; Clough et al., 2000), it is likely a result of DOC leaching from the surface soil (Aulakh et al., 1992; Jarvis and Hatch, 1994; Whitehead, 1995). If the influx of DOC reaches the groundwater table, and if it is sufficient to deplete concentrations of dissolved O_2, it can cause denitrification at the top of the water column (e.g., Starr and Gillham, 1993). However, for denitrification to occur, sufficient DOC must reach the groundwater table and not be mineralised in the unsaturated zone.

Denitrification rates are temporally and spatially extremely variable. Basically, it means that the rate of denitrification varies widely from time to time at the same location, and also from point to point in the soil (Parsons et al., 1991). Spatial variability in the rate of denitrification is naturally large in most soils (Folorunso and Rolston, 1984), and is often increased by the effect of animal grazing, external returns (Luo et al., 1994a, Ruz-Jerez et al., 1994; Luo et al., 1998), varying N fertilisation rates or management practices throughout the year (Hyde at al., 2006). The process of denitrification mostly occurs in anaerobic microsites created by water-filled pores called `hot spots` (Parkin, 1987; Whitehead, 1995; Seitzinger et al., 2006; Stark and Richards, 2008a). These are created by the spatial and temporal changes in soil water levels, soil temperature, O_2 content, availability of organic C and NO_3^-, and by complex interactions between these factors (Smith, 1980; Ryden, 1986; Parkin, 1987; Estavillo et al., 1994; Luo et al., 1999b).

The seasonal pattern of the process reflects the combined effects of changes in soil moisture status affected by rainfall and evaporation rates, and soil temperature (Luo et al., 1994a; Ruz-Jerez et al., 1994). Denitrification tends to increase during early spring with increasing temperature, but decreases as the soil becomes drier. Also in the autumn, there is often an increase in denitrification as the soil becomes wetter and organic-rich (Addiscott, 1996), followed by a decrease as the temperature falls (Whitehead, 1995). Ruz-Jerez et al. (1994) reported the highest losses by denitrification in autumn and winter (April - September), when soil moisture was above field capacity for extended periods due to low evapotranspiration rate. Similarly, Groffman and Tiedje (1989) working with nine soils of different texture and drainage status showed that over 80% of the annual loss of N by denitrification occurred during brief periods (3 to 6 weeks) of high activity, but the loss of N in their experiments was concentrated in spring and fall. Changes in the rate of denitrification with seasonal temperature variations may be masked by variations in the rate of organic C flux. For example, Cannavo et al. (2004) found that freeze-thaw cycles increase the flux of C to the unsaturated zone and can create anaerobic micro-environments in the soil in which denitrification can become established.

Consequently, single point measurements at long time intervals are not sufficient to accurately estimate seasonal or annual losses on a field scale basis (Mosier and Heinemeyer 1985).

2.5.2 Factors affecting biological denitrification

Environmental factors which affect microbiological denitrification have been identified (Firestone, 1982; Tiedje, 1988), and the relative importance of these factors on both the denitrification rate and its variability has been investigated in a number of field studies (e.g. Ryden, 1983; Myrold et al., 1989; Aulakh et al., 1992; Schipper et al., 1993; Avalakki et al., 1995). Apparently, the activity of denitrifiers is directly affected and regulated by proximal factors, such as soil O_2, NO_3^- and readily mineralisable organic C (Smid and Beauchamp, 1976; Sahrawat and Keeney, 1986; Groffman et al. 1987; Tiedje, 1988; Jarvis et al., 1991; Weier et al., 1993a, 1993b; Tate, 1995; de Klein et al., 2001; Dobbie and Smith, 2001; Šimek and Cooper, 2002; Seitzinger et al., 2006; Stark and Richards, 2008b). In the field, proximal factors are sequentially affected by various physical and biological soil factors such as soil moisture content, soil structure, temperature and hydrological conditions (distal factors, Groffman et. al. 1987; Seitzinger et al., 2006) making regulation of *in situ* denitrification very complex. Furthermore, the agricultural managements (e.g. fertilisation intensity and timing, irrigation practices, grazing intensity, tillage type and management intensity, crop and residue type) can have direct and indirect effects on gaseous N emissions as they affect N turnover rates and the release of readily available and mobile forms of N (Stark and Richards, 2008a, 2008b).

Soil oxygen (O_2)

Most denitrification occurs when conditions are anaerobic and consequently when the supply of molecular O_2 is insufficient for the microorganisms decomposing organic matter, at least at some microsites within the soil. In this situation, the denitrifying bacteria utilise O atom in NO_3^- and NO_2^- to produce CO_2 from decomposed organic matter (Whitehead, 1995). Therefore, the O_2 concentration is considered to be the principal regulator of denitrification in the soils (e.g. Smith and Tiedje 1979; Mosier et al. 1986). Numerous examples illustrate how denitrification starts when dissolved O_2 levels reach a certain low threshold (Buss et al., 2005). The process generally occurs in suboxic environments with O_2 concentrations below 0.2 mg O_2 L^{-1}; however, there were a few studies reporting the concentration also below 2 mg L^{-1} (Vogel et al., 1981; Trudell et al., 1986; Starr and Gillham, 1993; Christensen et al., 2000; Böhlke et al., 2002; Puckett and Cowdery, 2002; Gallardo and Tase, 2005). Completely anoxic conditions are not required (Seitzinger et al., 2006). As the presence of O_2 inhibits synthesis of new denitrifying enzymes (Smith and Tiedje, 1979), denitrification rates tend to increase when the O_2 concentration in soil decreases (Parkin and Tiedje, 1984; Tiedje, 1988; Arah et al., 1991; DeSimone and Howes, 1998).

Soil water content

Soil water content is an important factor influencing aeration (Bremner and Shaw, 1958; Knowles, 1981; Grundmann and Rolston, 1987; Myrold, 1988; Ruz-Jerez et al., 1994), because with increasing soil moisture content, air in soil pores is displaced by water. Thus, the influence of soil moisture on the denitrification rate is due to reduction in O_2 concentration which is essential before denitrification starts (Ruz-Jerez et al., 1994). In addition, water in soil pores controls diffusive substrate movement (NO_3^- or soluble C) to the microsites where denitrification occurs (Luo et al., 1999a). Studies have suggested that insufficient diffusion can limit NO_3^- or C availability even when these materials are present at relatively high concentrations in well-aggregated soils (Ryden, 1983; Myrold and Tiedje, 1985). Soil water content can be expressed as a percentage of water holding capacity (WHC), which is a specific ability of a particular type of soil to hold water against the force of gravity. For appreciable denitrification to occur, it is usually necessary for the soil moisture content to be greater than 60% of the WHC (Aulakh et al., 1992) or for soil water tension to be below 2-20kPa. The greatest increase in denitrification normally occurs between 100% and 200% of WHC, as air disappears from the larger soil pores (Knowles, 1981; Ruz-Jerez et al., 1994).

Smith and Arah (1990) and Aulakh et al. (1992) have reported critical values for soil water content, expressed as water-filled pore space (WFPS) of 65% to 90%. The critical value of WFPS for denitrification is generally greater in coarse-textured than in fine-textured soils. For example, reported threshold soil water contents range from 74% to 83% in sandy and sandy loam soils, from 62% to 83% in loam soils, and from 50% to 74% in clay loam soils (Barton et al., 1999). De Klein and van Logtestijn (1996) proposed that in many cases, the critical WFPS for many soils is an equivalent to field capacity or above. The critical air-filled porosity below which denitrification was accelerated was found to be 30% (Jordan, 1989).

In typically aerobic unsaturated zones, a small amount of denitrification may occur, even when the soil water content is low. The process may occur within anaerobic microsites created by water-filled pores (Stark and Richards, 2008b) formed in the pore spaces within clumps of finer-grained particles (aggregates) or in fine-grained sediments. Solutes diffuse in and out via the interaggregate spaces or in lower permeability environments via interconnected macropores (Buss et al., 2005).

In the field, an increasing soil moisture content of the soil as a result of episodic rainfall or irrigation events often restricts soil aeration (Rolston et al., 1982; Ryden, 1983; Sextone et al., 1985; Lowrance 1992; Van Kessel et al., 1993; Barton et al., 1999). The extent to which rainfall or irrigation affect the denitrification rates depends on soil texture, porosity, structure, organic matter, and drainage characteristics (Seitzinger et al., 2006), which also determine the threshold moisture content required before denitrification takes place (Smith and Arah, 1990) and the duration of enhanced denitrification following a rainfall or irrigation event (Barton et al., 1999).

Poorly drained finer textured soils have smaller pores that lead to greater water retention and a greater opportunity for creating anaerobic microsites than free draining coarser textured soils (Sexstone et al., 1985; Bijay-Singh et al., 1989; Groffman and Tiedje 1989; de Klein and van Logtestijn 1994; Barton et al., 1999). Consequently, in finer textured soils, anaerobic microsites are more likely to be present at lower WFPS and appear to be enhanced for longer periods than in coarser soils. Generally, annual denitrification losses are greater in loam soils (up to 110 kg N ha^{-1} yr^{-1}) than sandy or clay textured soils (less than 10 kg N ha^{-1} yr^{-1}; Barton et al., 1999). In soils other than loams, soil texture may limit denitrification because the soil is well aerated (sands; e.g. Groffman and Tiedje, 1991; Barton et al., 1999) or C diffusion is limited (clays; e.g. Myrold and Tiedje, 1985).

In some systems, the scale of interaction between oxic and suboxic environments is small in space (centimetres or less) and time (< 1 day) and therefore nitrification and denitrification are (on average) tightly coupled (Seitzinger et al., 2006). They can occur simultaneously, in separate microsites, on opposite sides of an aerobic-anaerobic interface (Knowles, 1978). However, in some systems oxic and suboxic conditions are separated substantially in space (tens of meters to kilometres) and/or time (weeks to years) and therefore the production of NO_3^- is distal in time and/or space from denitrification (Seitzinger et al., 2006).

Nitrate (NO_3^-)

Nitrate is required as an electron acceptor for denitrification. Nitrate and NO_2^- are supplied principally by the hydrolysis and subsequent nitrification of urea fertilizer (Christianson et al., 1979), or readily decomposable excretal N from the grazing animals (Ruz-Jerez et al., 1994; Humphreys et al., 2009). The threshold value of NO_3^- for higher rates of denitrification in pasture soils has been reported to be in the range from 2 to 5 kg NO_3^--N ha^{-1} in the top 7.5 to 10 cm (Ryden, 1986; Jordan, 1989). In most agricultural soils, fertiliser additions increase soil NO_3^- such that denitrification is not limited by NO_3^- availability (Barton at al, 1999). However, NO_3^- availability could limit denitrification in soils not receiving additional N inputs via fertilisation or fixation (Barton at al, 1999); e.g. in unfertilised grassland soils (Groffman et al., 1993; Tenuta and Beauchamp, 1996). The availability of NO_3^- to denitrifiers depends not only on the rate of NO_3^- production, but also on the transport from the bulk soil solution to the denitrifying microsite, and the rate of NO_3^- consumption in the soil (Barton et al., 1999). Another major factor limiting denitrification can be high plant uptake (Ryden, 1983).

Mode of NO_3^- delivery to the site of denitrification by diffusion and advection occurs periodically or episodically (Seitzinger et al., 2006). In soils not receiving high N inputs, diffusion of NO_3^- from the nitrifying microsite (aerobic) to the denitrifying microsite (anaerobic) can potentially limit denitrification (Myrold and Tiedje, 1985; Murray et al., 1989; Ambus and Christensen, 1993). Low availability and accessibility of NO_3^- in denitrifying microsites is influenced by low water content, which is considered to be the most important factor limiting denitrification in warm, dry summers (Luo et al., 1999a). Not just the water content, but also the water residence time has been recognized as an important factor controlling the proportion of N inputs that are denitrified (Seitzinger et al., 2006). Water residence time is influenced by an interaction between the geology and hydrology of the site (Seitzinger et al., 2006). The response time of denitrification to changing conditions at the landscape or watershed scale is influenced by the degree to which nitrification of NH_4^+ and denitrification are coupled within the system (Ruz-Jerez et al., 1994). For example, in terrestrial soils, changes in the frequency of rainfall events may alter the lag time between nitrification and denitrification and affect the total annual denitrification rate (Seitzinger et al., 2006). On the other hand, there can be a lag time of years between changes in N inputs to terrestrial soils (e.g., fertilizer application) and changes in rates of groundwater denitrification (Bohlke, 2002; Van Drecht et al., 2003). Despite this, Hofstra and Bouwman (2005) found on a basis of analysis of 336 soil denitrification measurements that N input was an important factor explaining denitrification rates in the soils. Denitrification did not show a simple relationship with N input, as many other factors were important in explaining the variability in the rates. Furthermore, significant relationships between N_2O and NO_3^--N, and between N_2O and NH_4^+-N indicated a strong involvement of nitrification in the whole process (Allen et al., 1996).

2.5.3 Chemical denitrification

If NO_3^- is reduced by abiotic reactions, the process is known as chemical denitrification. For example, in acid conditions, NO_2^- forms nitrous acid (HNO_2) and this may then decompose spontaneously:

$$2\ HNO_2 \rightarrow NO + NO_2 + H_2O$$

Normally, the NO, at least, will volatilize. However, while the soil is largely aerobic, the volatilization is restricted. Thus, the NO is converted to NO_2^-, which dissolves in soil water to form HNO_3 (Nelson, 1982). In the sub-surface, these reactions are minor in comparison with biological denitrification (Buss et al., 2005); however, several observations have indicated its potential importance (Whitehead, 1995). Chemo-denitrification likely involves ferrous iron as a chemical reducing agent, and therefore may be significant in particular soils (Smith and Arah, 1990).

2.5.4 Significance of denitrification

Denitrification removes bioavailable N from natural and human-altered systems that would otherwise be available for primary production or microbial assimilation. Therefore, it is considered as a process which significantly influences ecosystems and all their biochemical cycles (Seitzinger et al., 2006). In low N systems, denitrification contributes to N limitation by further decreasing N concentrations and by reducing the N: P ratio of recycled nutrients. In highly N-limited systems, denitrification controls C sequestration by decoupling the N and C cycles (Falkowski, 1997). Due to denitrification a significant amount of N can be lost from the soil-plant system in agricultural and forest soils (Ryden, 1986; Myrold, 1988) with negative economic consequences for crop production (Barton et al., 1999). Alternatively, in systems highly enriched with N anthropogenic sources (e.g. in freshwater and marine aquatic systems), denitrification can have positive effects by reducing the export of N, and thus reducing eutrophication of downstream ecosystems associated with excess N inputs from anthropogenic activities on land (Kim and Burger, 1997, Seitzinger et al., 2006). Thus, the denitrification is one of the main pathways for replenishing atmospheric N previously fixed by biological, atmospheric and industrial processes (Lewis, 1986). If N_2O is the end-product of denitrification, emissions can contribute to ozone depletion and global warming (Wang et al., 1976; Crutzen and Ehhalt, 1977).

2.6 Effect of farm /grassland management on N losses

2.6.1 Grass-clover sward

There is evidence that substantial amounts of NO_3^- can be leached from intensively grazed grass—clover swards, even in the absence of fertilizer N (Walker, 1962). Nitrogen leaching from a fertilized grass sward compared with mixed sward pastures grazed by sheep at the same N inputs, when fertilizer input to grass sward matched biologically fixed N_2 in mixed sward, resulted in no difference in overall NO_3^- losses (Cuttle et al., 1992). This suggests that NO_3^- leaching from grass systems is similar at similar total N inputs regardless of the source of N (Cuttle et al., 1992; Ledgard, 2001; Stopes et al., 2002; Andrews et al., 2007).

On the other hand, a number of studies reported that NO_3^- leaching from unfertilized grass-clover swards is always lower than from fertilized swards grazed by either sheep (Ruz-Jerez et al., 1995; Cuttle et al., 1998) or cattle (Ryden et al., 1984; Owens et al., 1994; Tyson et al., 1997; Hooda et al., 1998). Furthermore, the losses from grass-clover sward in production years 6 to 8 represent only 9 to 13% of the comparable losses from grass sward

(Owens et al., 1994; Tyson et al., 1997; Hooda et al., 1998; Eriksen et al., 2004). Higher leaching losses from grazed fertilized grass swards compared with unfertilized grass-clover systems may be explained by reduction in BNF in grass-clover sward over time and thus, by reduction in DM production during the grazing season. This subsequently leads to lowering the deposition of N via animal excreta on grass-clover sward due to lowering the grazing intensity. For this reason, leaching from the fertilized system is unlikely to be enhanced directly by a higher input in synthetic fertilizer but by its positive effect on grass production leading to increased recycling of N in dung and urine to the sward.

2.6.2 Response to N fertilization

In grassland, a substantial leaching indicates that the total supply of N during the season has exceeded the requirements for grass growth (Whitehead, 1995) and yield potential (Havlin et al., 2005). Several investigations have shown that less than 20 kg NO_3^--N $ha^{-1}y^{-1}$ leached at less than 250 kg N $ha^{-1}y^{-1}$ of fertilizer N (Barraclough et al., 1984; Webster and Dowdell, 1984; Bergstrom, 1987: Garwood and Ryden, 1986; Triboi, 1987). In general, the losses of inorganic and organic N increase with increasing fertilizer input (Watson et al., 1992; Smith et al., 1995; Ledgard et al., 1998; Watson et al., 2000a); however, the scatter is wide and generalized relationships are unlikely to exist due to differences in sites, soils, drainage/aeration status, sward age, past and present management (Jarvis et al., 1995). The response of N leaching to N fertiliser supply is not linear and seems to remain low until N additions reach a threshold level (Barraclough et al., 1992), which is closely linked to yield response (McSwiney and Robertson, 2005). This breakpoint represents an optimum N supply by meeting crop demand and limiting environmental impact (Stark and Richards, 2008b). While the quantity of synthetic fertilizer input represents the major factor controlling N leaching losses from agricultural systems, the magnitude of losses is also influenced by the time and method of its application (Havlin et al., 2005). Nitrogen applied synchronously with high crop N demand by matching the peak of N uptake with a peak of N mineralisation is unlikely to be leached (Havlin et al., 2005).

2.6.3 Response to slurry application

Although N leached from slurry is normally in the form of NO_3^-, the application of large amounts of slurry during autumn may result in some leaching of NH_4^+ and also DON, as has been shown with pig slurry applied to a light sandy soil in the Netherlands (Steenvoorden et al., 1986). Factors that curtail the amount of N leached from slurry applied to grassland include the occurrence of NH_3 volatilization, denitrification, and the fact that the organic N mineralises slowly (Whitehead, 1995). Furthermore, the cumulative effect of annual fertilizer application to the same plots likely increases the effect of slurry application on N leaching in the following years (Eriksen, 2001). Measurements that have been made on NO_3^- leaching following the application of slurry to grassland have usually shown the amounts to be small (Whitehead, 1995), i.e. less than 1% of the slurry N applied (Burford et al., 1976).

In addition, the timing of the slurry application is also an important factor affecting N leaching from slurry (Whitehead, 1995, Chambers et al., 2000). When diluted cow slurry was applied at rates between 150 and 250 kg N ha^{-1} to grassland plots on a shallow calcareous soil over chalk at monthly intervals from September to January, the proportion of N leached increased from 17% for September application to 43% for November application and only 10% or less for slurry applied in December and January (Froment et al., 1992). This may be attributed to low uptake of inorganic N at the end of growing season and low mineralisation rates during the cold months. In order to reduce NO_3^- leaching losses, the improved guidelines on the efficient use of manure N prohibit applications of high available N content manures to soils between October 15th and January 15th (Chambers et al., 2000).

2.6.4 Response to grazing

The major cause of high N leaching losses under grazing is the return of N in excreta to the swards via localized deposition of urine and dung (Eriksen et al., 2004). Excretal urine returns are highly concentrated at rates up to 1000 kg N $ha^{-1}y^{-1}$ (Haynes and Williams 1993) and spatially variable (Jarvis et al., 1995). Concentrations of NO_3^- that develop in the soil of a urine patch greatly exceed the uptake capacity of the grass (Whitehead, 1995) and therefore are likely to be lost from the soil-plant system. Thus, most of the leached NO_3^- from grassland grazed by dairy cows is derived from urine patches (Ryden, 1984; Clough et al., 1996; Cuttle et al., 2001). An increase in grazing intensity of the production systems by increasing stocking densities leads to an increase in the quantities of N leached from the systems (Cuttle et al., 1992, Ruz-Jerez et al., 1995; Tyson et al., 1997; Cuttle et al., 1998; Watson et al., 2000b; Wachendorf et al., 2004; 2006). Long grazing seasons the same way like higher stocking densities lead to greater volumes of urine being deposited per ha. Also the time of the year at which the urine is deposited has a large influence on the extent to which N is leached (Whitehead, 1995). Urine N deposited later in the grazing season on free-draining soils is generally associated with a greater risk of N losses to groundwater (Sherwood et al., 1988; Sherwood and Fanning 1989; Cuttle and Bourne, 1993; Decau et al., 2004; Wachendorf et al., 2006; Jewkes et al., 2007). In contrast, Humphreys et al. (2009) reported that the overall NO_3^- concentrations in groundwater on poorly drained heavy clay-loam soils are not affected by grazing at high stocking densities over a long grazing season. This may be a result of high denitrification potential associated with high C content along with relatively moist conditions of the soils on site. Generally, N derived from urine together with any surplus fertilizer N tends to accumulate in the soil until autumn (Sherwood and Fanning, 1989) and then when the soil reaches the field capacity point, it becomes susceptible to leaching or denitrification.

2.6.5 Response to cultivation of permanent or temporary grassland

Permanent grassland generally refers to grassland that is renovated at intervals of not less than five years, or more typically at intervals of approximately ten years. Temporary grassland generally refers to grass-leys in arable rotation with forage maize or other crops with lifetimes from five or six months to seven or eight years (Humphreys et al., 2009). Due to a big increase in the use of forage maize in the northwest of Europe, large areas under permanent grassland has been cultivated and incorporated into crop rotation areas (Humphreys et al., 2009).

Ploughing of grassland, particularly of long term grassland sward with a build-up of organic N pool, leads to disruption of aggregates and consequently to exposure of soil-bound NH_4^+ compounds and organically-bound N to the atmosphere and thus induces mineralisation. This microbiological process results in a release of nutrients, particularly N, which are otherwise tied up in the SOM (Whitehead, 1995; Jarvis et al., 1995, 1996; Shepherd et al., 2001, Buss et al., 2005; Humphreys et al., 2009). Although some of the N mineralised as a result of ploughing is taken up by subsequent crops, the amount mineralised often exceeds the mount needed by the reseeded grass or subsequent arable crop, and therefore considerable losses via leaching and denitrification may occur (Whitehead, 1995). The extent of the losses is dependent upon the sward age (Cameron and Wild. 1984; Bergstrom, 1987; Roberts et al., 1989; Lloyd 1992; Whitmore et al., 1992; Scholefield et al., 1993; Djurhuus and Olsen 1997; Shepherd et al., 2001). This is due to a build up of soil organic N pool through accumulation (immobilization), which occurs in a soil profile after new sward establishment. A number of studies on the effect of cultivation on N losses have been carried out (Cameron and Wild. 1984; Bergstrom, 1987; Roberts et al., 1989; Whitmore et al., 1992; Lloyd 1992; Scholefield et al., 1993; Djurhuus and Olsen 1997; Shepherd et al., 2001). For example, losses up to 490 kg N ha y^{-1} were recorded during a three year study at Rothamsted, when old permanent grassland was ploughed on a soil that contained 8100 kg N ha^{-1} to a depth of 25 cm at the time of ploughing (Jenkinson, 1986). Similarly, high NO_3^--N concentrations up to 450 mg N L^{-1} were measured in the water draining from the field in the first season following ploughing of old grassland (Whitmore et al., 1992).

The concentration of N in stubble, roots and etc., is likely to increase substantially with sward age as well (Whitehead et al., 1990). In addition to the effect of sward age, the amounts of N in the stubble, roots etc. are influenced by the previous sward management (i.e. fertilizer N or manure application). The amounts of NO_3^- leached after ploughing tend to reflect these differences (Whitehead, 1995). This was observed in a study comparing NO_3^- leaching after grass-leys with different management histories: (i) low N inputs, (ii) moderate N inputs and (iii) excessive inputs of fertilizer N and slurry were ploughed. Losses of NO_3^--N over three years were approximately 120, 250 and 1000 kg ha^{-1} for the above three treatments, respectively (Lloyd,1992).

Overall, losses of N by leaching tend to decrease as a function of time after cultivation and this is in agreement with decreasing residual effect and decreasing soil inorganic N content in soil profile (Eriksen, 2001). The residual effect of ploughing may be as short as one growing season (Shepherd et al., 2001) or may last up to several years (Jenkinson, 1986 Roberts et al., 1989; Whitmore et al., 1992). This is due to variation in the SOM content between the soils, their mineralisation rates and the amount of annual rainfall. Thus, reseeding in late summer/autumn is likely to be more risky and cause greater N losses during the following winter compared with ploughing and reseeding in spring.

A few studies have looked at changes in SON following cultivation. Under continuous arable cultivation, the size of the SON pool is relatively constant at ca. 15 to 20 kg SON ha^{-1} (0 to 23 cm), decreasing with leaching in early winter and increasing markedly during the period of rapid root growth in spring. Under ploughed grassland, the SON pool size tends to be larger at ca. 20-25 kg SON ha^{-1} (0 to 23 cm). Although the changes are larger than under continuous arable farming, they occur at the same times of the year and in the same way (Murphy et al., 2000). In the study at Rosemaund, the SON pools in the soil profile (0-90 cm) after ploughing and reseeding of long term (> 50 years) grassland were even higher (70 to 500 kg SON ha^{-1}). Both the SON and soil inorganic N (SIN) pools were increased as a result of physical disruption of soil aggregates and incorporation of grass residues following cultivation (Bhogal et al., 2000). The topsoil SON concentrations were enhanced over 10 months following cultivation (Bhogal et al., 2000).

Substantial leaching may also occur following ploughing of grass—clover leys that received no fertilizer N (Watson et al., 1993). As grass-clover leys often form the basis of organic farming systems, the extent to which they contribute to overall NO_3^- leaching is limited: (i) the leys in the rotation are normally ploughed only once in 3 or 4 years and; (ii) organic farming systems do not receive synthetic fertilizer N, though they may receive organic manures and slurries. On the other hand, an incorporation of green manure crops by ploughing of ley tends to increase NO_3^- losses (Dalgaard et al., 1998; Di and Cameron 2002). In general, with good management practices, the total amounts of NO_3^- leached from organic systems are unlikely to produce an average concentration in the drainage water of more than 11.3 mg NO_3^--N L^{-1} (Watson et al., 1993), which is the maximum admissible concentration in drinking water (European Council, 1991).

2.7 International drivers and national legislation related to N

Water Framework Directive (2000/60/ EC)

European Union (EU) strengthened and amalgamated existing legislation on water protection by introducing the Water Framework Directive (WFD) in 2000. In Europe the WFD has changed the concept of water quality standards by introducing the concept of water body specific targets, which are now fundamental to WFD. These targets are based on a water body’s natural, unpolluted state, which serves as a reference condition, with the aim to achieve ‘good’ biological and chemical status. Member states are required to protect waters with high quality status, prevent deterioration, and restore degraded waters to good status by 2015 with implementation of programmes of measures (POM) by 2012. This will lead to considerable variation in threshold values for waters within countries and across the EU.

Good ecological status is determined on a range of criteria such as the biodiversity of aquatic flora and fauna, microbial contamination, nutrient concentrations and habitats (Humphreys, 2008d). Thus, the WFD integrates multiple water quality parameters which include measures of hydrological, hydrogeological, hydromorphological and biological properties as well as their interactions (Stark and Richards, 2008b). Member states are committed to control chemical pollution, prevent further deterioration, and enhance the condition of aquatic ecosystems, while simultaneously promoting the sustainable use of water.

The WFD, together with daughter directives and amendments such as the Groundwater Directive (European Parliament and Council, 2006) and the Directive on Environmental Quality Standards in the Field of Water Policy (COM 2006/397) has increased legislative pressure on farmers and communities to reduce N loss from agricultural land and other sources with the objective of preventing eutrophication and other types of ecological deterioration of receiving water bodies.

The Nitrates Directive (91/676/EEC)

With the introduction of the Nitrates Directive in 1991, the EU for the first time addressed the wider implications of N in the environment and further restricted NO_3^- discharge in order to prevent groundwater and surface water contamination from agricultural sources. The Directive requires member states to designate vulnerable zones where NO_3^- leaching into already polluted waters causes additional contamination. Where necessary, member states have to establish action programmes, which promote the application of codes of good agricultural practices. Moreover, the eutrophication status of freshwater, groundwater, estuaries and coastal waters has to be monitored every four years (Stark and Richards, 2008b). To protect against eutrophication, the EU has set a limit of 11.3 mg NO_3^--N L^{-1} for groundwater, irrespective of whether it is to be used for drinking purposes. Regulations implementing the Nitrates Directive were put in place in Ireland in 2006 under Statutory Instrument (SI) 378, 2006, subsequently replaced by SI 610 in 2010. These SI applies to the entire national territory. These regulations set limits on stocking rates on farms in terms of the quantity of N from livestock manure (170 kg N ha^{-1} $year^{-1}$) that can be applied mechanically or directly deposited by grazing livestock on agricultural land.

EU Drinking Water Directive (98/83/EC)

The EU set standards for NO_3^- in potable water at 11.3 mg NO_3^--N L^{-1} (50 mg NO_3^- L^{-1}) and for NO_2^- at 0.15 mg NO_2^--N L^{-1} unless derogation has been specifically sought. Regulations governing the quality of drinking water in Ireland are outlined in the SI No. 278 (2007) which are based on EU regulations.

Freshwater Fish Directive (78/659/EEC)

Nitrite and NH_4^+ are toxic to aquatic animals. The EU guideline concentration of NO_2^- in rivers supporting salmonid fish is 0.01 mg N L^{-1}, while for cyprinids it is 0.03 mg N L^{-1}. The mandatory NH_4^+ concentration in rivers supporting salmonid fish and cyprinids is less than 1 mg N L^{-1}.

Habitats Directive (92/43/EEC) and the Birds Directive (79/409/EEC)

The Habitats Directive and the Birds Directive require member states to protect sensitive habitats and establish action programmes to restore ecosystems from anthropogenic impacts including eutrophication to achieve favourable conservation status. The role of N in aquatic eutrophication has been greatly underestimated in the past (Stark and Richards, 2008b). For this reason, an implementation of new standards and legislation with greater emphasis on water habitats and whole aquatic ecosystems threatened by nutrient contamination and loss of biodiversity has been recommended.

Directive on ambient quality and cleaner air for Europe (2008/50/EC), also known as the CAFE Directive

The CAFE Directive was transposed into Irish legislation by the Air Quality Standards Regulations (S.I.180/2011), which revoked and replaced three earlier statutory instruments (S.I.33 of 1999, S.I. 271 of 2002 and S.I.53 of 2004). These regulations set limit target values for a range of pollutants, including N_2O and other NO_x.

Kyoto Protocol on greenhouse gases (UNFCCC, 1997)

By signing the Kyoto Protocol in 1997, governments of 37 industrialized countries agreed to reduce the emissions of the GHG (i.e. CO_2, methane (CH_4), N_2O, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6)) on average by 5% against the levels from 1990 over a five year period (2008-12). Ireland is committed to limit GHG emissions by 13% in the period 2008 to 2012, and by 25 to 30% in the period 2012 to 2020 compared with 1990 levels. As part of international efforts to stabilize atmospheric GHG concentrations, signatories of the Kyoto protocol are also committed to establish national inventories of the soil organic carbon (SOC) content and its changes in relation to specific land use or climatic effects.

Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (UNICE, 1999)

The Protocol sets emission ceilings for 2010 for four pollutants: sulphur, oxides of N (NO_x), volatile organic compounds (VOCs) and NH_3. These ceilings were negotiated on the basis of scientific assessments of pollution effects and abatement options. Parties whose emissions have a more severe environmental or health impact and whose emissions are relatively cheap to reduce will have to make the biggest cuts. Once the Protocol is fully implemented, Europe's NO_x emissions should be cut by at least by 41%, and its NH_3 emissions by 17% compared to 1990.

The Protocol also sets tight limit values for specific emission sources (e.g. combustion plant, electricity production, dry cleaning, cars and lorries) and requires best available techniques to be used to keep emissions down. Farmers will have to take specific measures to control NH_3 emissions. Guidance documents with the Protocol provide a wide range of techniques and economic instruments for the reduction of emissions in the relevant sectors.

National Emissions Ceiling Directive (NECD, 2001/81/EC)

NECD set upper limits for the national total emissions in 2010 of the key pollutants (i.e. sulphur dioxide (SO_2), NO_x, VOCs and NH_3) responsible for acidification, eutrophication and ground-level ozone pollution. Since particulate matter has been added to the list of pollutants only in the 2006, it will be included in the NECD after 2010. The NECD national emission ceilings to be achieved by Member States by 2010 are between 11 and 1 167 ktonnes yr^{-1} for NO_x and between 7 and 780 ktonnes yr^{-1} for NH_3 emissions. Ireland is committed to reduce NO_x emissions to 65 ktonnes yr^{-1} and NH_3 emissions to 116 ktonnes yr^{-1} by 2010.

Since the pollutants are transboundary (i.e. they are transported in large quantities across Europe), Member States must tackle these pollutants together. The NECD is currently being reviewed to produce new emissions ceilings targets for 2020.

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3. Soil surface N balances* and soil N dynamics in a clay-loam soil under Irish dairy production systems

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Abstract

This study evaluated the effect of a dairy system involving grazing over the winter on a soil surface balance (SSB) and soluble N dynamics in a clay loam soil in comparison with conventional grazing systems. The SSBs were calculated for each paddock within three dairy systems for two years. Inputs included N entering the soil in synthetic fertilizer, slurry, excreta, atmospheric deposition and white clover biological N fixation. Outputs consisted of N leaving the soil in harvested and grazed herbage. Nitrogen surplus was calculated as the difference between N inputs and outputs. Soluble N was assessed in soil extracts at three depths to 0.9 m. The management of the systems resulted in N surplus from 113 to 161 kg N $ha^{-1}y^{-1}$ and N use efficiency of the soil component from 63 to 72% without significant variation between the systems. The system had no effect on soil N dynamics as it was likely buffered by inherent soil properties (heavy texture, high C, pH) and the presence of shallow groundwater. The biochemical anaerobic reduction processes (i.e. denitrification, dissimilatory nitrate reduction to ammonium) likely ensured soil oxidised N consistently low (<20 kg ha^{-1}). Consequently, the system involving grazing over the winter on these soils did not create an additional environmental pressure via N losses to groundwater and N_2O emissions compared with conventional grazing systems. The dynamics of soil inorganic N was mainly controlled by the hydrological factors and soil temperature, which are the most important factors controlling microbial activity, biochemical processes and leaching.

Keywords: soil surface N balance, permanent grassland, dairy production, grazing over winter, soil N dynamics

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[*] Although not presented in the following chapter, the farm gate N balances for ES-100N, ES-0N and LS-0N for 2008 and 2009 year were also calculated (data not written up for publication). Inputs included N entering the farm gate of each system as synthetic fertilizer N, imported silage, concentrates, atmospheric deposition and white clover BNF. Outputs consisted of N leaving the farm gate in milk, calves, exported silage and liveweight change. The farm gate N surplus was calculated as the difference between N inputs and outputs to and from the farm gate of each system. The calculated farm gate surplus was 159 kg N $ha^{-1}y^{-1}$ in ES-100N, 90 kg N $ha^{-1}y^{-1}$ in ES-0N and 87 kg N $ha^{-1}y^{-1}$ in LS-0N system without significant variation between the systems. Similarly, there were no differences in NUEs between the systems. The NUE ranged from 33% in ES-100N, to 40% in ES-0N and 50% in LS-0N system.

3.1 Introduction

Organic dairy production systems generally operate at low stocking densities relative to conventional dairy systems. Low stocking densities offer a potential to extend the grazing season throughout the autumn and winter. While animal excreta are a valuable source of nitrogen (N) and other nutrients for plants (Silva et al., 1999), high quantities of N in urine and dung (typically equivalent to over 200 and 2000 kg N ha^{-1}; Haynes and Williams, 1993, Jarvis et al., 1995; Dai, 2000; ten Berge et al., 2002) deposited in small area patches (Lantinga et al., 1987; Bakker et al., 2004) result in high N concentrations both in time and space (Decau et al., 2004; Hutchings et al., 2007). These greatly exceed plant requirements (Steele, 1982; Ball and Ryden, 1984), mostly during the months, when grass growth and thus N uptake is temperature limited. Furthermore, the hydrolysis of urea increases pH of the soil over several units (Haynes and Williams, 1993; Shand et al., 2002), which has a solubilising effect on the soil organic matter (SOM; Wachendorf et al., 2005). Consequently, there is a potential for substantial N losses following grazing, albeit at low stocking rates, particularly during the winter months when a significant effective rainfall (ER) occurs (Francis, 1995; Hack-ten Broeke and van der Putten, 1997, Jewkes et al., 2007).

The loss of N from farming systems is an important environmental concern since it contributes to air pollution and contamination of waterbodies. Within Europe, this resulted in an implementation of legislation at national and international levels, in particular, the EU Nitrates Directive (European Council, 1991), The Water Framework Directive (European Parliament and Council, 2000), the Directive on National Emission Ceilings (European Parliament and Council, 2001), Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (UNICE, 1999) and Kyoto Protocol on Greenhouse Gases (UNFCCC, 1997). For this reason the quantification of N losses from farming systems through calculation of nutrient balances has become a priority agro-environmental indicator (Aarts et al., 1999; OECD, 2003, Bassanino, et al. 2007; Payraudeau, et al., 2007; Panten, et al., 2009). Several N balances have been developed, which differ mainly in where the system boundary is drawn, which spatial and temporal resolutions can be achieved and which inputs and outputs are taken into consideration (e.g., Simon et al., 2000; Beegle et al., 2002; Gustafson et al., 2003; Hedlund et al., 2003; Grignani et al., 2005, Humphreys et al., 2008a). In a simple nutrient input-output accounting system, farm is regarded as a ‘black box’ and only inputs and outputs at the farm gate are quantified. The calculated N surplus thus reflects the potential loss of reactive N compounds (Oenema et al., 2003) and describes the overall N pressure caused by agricultural activities (Schröder et al. 2004; Bach and Frede, 2005; Nevens et al., 2006). While this approach neglects management practices and internal nutrient fluxes between soil–plant–animal and environment (Trott et al., 2003; Kustermann et al., 2008), N surplus calculated using soil surface balance (SSB) responds to various grassland managements and influences several components (i.e. N emissions and soil fertility; Kustermann et al., 2010). The SSB records all N that is added to the soil and that leaves the soil with harvested products or crop residues and accordingly N surplus or deficit is a measure of the total N loss from the soil (Parris, 1998; OECD, 2001). Calculated SSB has been well correlated to N concentrations in the groundwater (Korsaeth and Eltun, 2000; Buciene et al., 2003; Kutra and Aksomaitiene, 2003; Sieling and Kage 2006; Salo and Turtola; 2006). There are, however, only a few studies that related SSB to inorganic N in the soil profile (Uhlen, 1989; Nyborg et al., 1995). And since soil organic N plays an important role in processes such as N leaching, mineralisation and plant uptake (Ros et al., 2009), it is also essential to include it in the N balances and N cycling studies (Murphy et al., 1999, 2000; Siemens and Kaupenjohann, 2002; Jones et al., 2004).

The main objectives of this study were: (i) to quantify N losses from a soil component of dairy production system involving grazing over the winter compared to conventional dairy production through calculation of SSB; (ii) to evaluate the effect of this grassland N management practice on soil soluble inorganic and organic N content (SIN, SON) down to 0.9 m depth and (iii) to determine management and climatic factors affecting soil soluble N dynamics in a clay loam soil profile.

3.2 Materials and Methods

3.2.1 Site description

The study was conducted at Solohead Research Farm (52 ha) in Ireland (52˚51’N, 08˚21’W) from February 2008 to February 2010. The local climate is humid temperate oceanic. Over the last 10 years the site received on average 1018 mm of annual rainfall and this resulted in a mean annual effective rainfall (ER) of 552 mm. The mean growing season length was approximately 305 days, based on a soil temperature above 5 ºC at 0.05 m depth (Parson 1988). Annual grass production rates measured under high input of fertilizer N (i.e. 250 to 370 kg N ha^{-1}) over the last 10 years period ranged between 13.5 and 14.7 t dry matter (DM) ha^{-1}.

The dominating soils are poorly drained Gleys (90%) and Grey Brown Podzolics (10%) with a clay loam texture and low permeability (Table 3.1). Soil texture exhibits very small heterogeneity down to 0.9 m. Sand and gravel lenses are also present on site which come to the surface in places and allow for fast infiltration. The mean SOM, organic carbon (C) and total N content at 0 to 0.3 m depth was 6.55%, 4.48% and 0.48% respectively with a corresponding C:N ratio of 9.3. At the same depth, soil bulk density (BD) and total porosity was 1.09 g cm^{-3} and 58.7%. The pH values varied from 6.19 to 7.09. Elevation on site ranges from 148.5 to 155.5 m Above Ordnance Datum (AOD). Depth to bedrock (Cappagh White Devonian Sandstone Formation (Archer et al. 1996)) is very uneven ranging from 5 to 10 m. Overlying quaternary till contains a perched watertable (depth of 0 to 2.2 m below ground level (bgl); Fig. 3.1), which is an unconfined poorly productive aquifer. The watertable is closest to the surface during the winter season. Although a number of ditches (4 m bgl) and tile drains (1.8 m bgl with spacing of 25 m) were installed between 1960 and 1995 across the farm to improve the drainage on site by lowering the watertable (Gleeson, T., personal communication), much of the farm remains seasonally wet, waterlogged or flooded due to impeded drainage.

3.2.2 Climatic and edaphic data collection

Soil temperature, volumetric soil moisture at 5 cm depth and rainfall were recorded automatically every half an hour at the meteorological station (Campbell scientific Ltd, Loughborough, U.K.) located in the central part of the research farm. Water filled pore space (WFPS) at 5 cm depth was calculated as the ratio of the volumetric soil moisture content to total pore space as described by Luo et al. (2008). Daily ER and soil moisture deficit (SMD) for the whole experimental period were determined using the model of Schulte et al. (2005) for grassland systems in Ireland based on the poorly drained soil criterion. Input weather data were combined using site specific rainfall and additional meteorological data from Moorepark Research Centre (maximum and minimum air temperature, wind speed and solar radiation), which is 23 km distant from Solohead Research Farm.

3.2.3 Experimental design and descriptions of the farming systems

The treatments corresponded to three grass-clover based dairy production systems involving two different grazing seasons and corresponding annual stocking densities:

ES-100N – Early spring calving with fertilizer N: mean calving date of 17th February, grazing period from February to November, annual stocking density of 2.2 cows ha^{-1} and receiving synthetic fertilizer N input of 100 kg ha^{-1} annually.

ES-0N – Early spring calving without fertilizer N: mean calving date of 17th February, grazing period from February to November, annual stocking density of 1.6 cows ha^{-1} and receiving no synthetic fertilizer N input.

LS-0N – Late spring calving without fertilizer N: mean calving date of 17th April, annual stocking density of 1.7 cows ha^{-1} between calving and 1st September and then 1.3 cows ha^{-1} until closing date at the end of January, and receiving no synthetic fertilizer N input. The stocking rate was reduced by adding an extra 3.7 ha to the area of the system.

The main characteristics of the different systems are presented in Table 3.2. Each farming system consisted of 18 Holstein-Friesian dairy cows calving during a three-month period each spring. Cows were turned out to graze immediately after calving and remained outside both day and night until drying off the following winter. Exceptions were made on occasions when the ground was too wet and cows were retained indoors to avoid damaging the grassland. The length of the grazing season for each system was determined according to a number of days at pasture as described by Humphreys et al. (2009). The cows were milked twice daily.

During 1999, most of the area of the farm (52 ha) was divided into 8 blocks (each an area approximately 6 ha) depending on the soil type and drainage status as described by Humphreys et al. (2008a). Six of these blocks were assigned into this experimental study (34 ha). Each block was divided into four paddocks (each>1 ha), one paddock from each block was assigned to each of the three systems in a randomized complete block design. The paddocks were predominantly used for grazing and to a lesser extent for silage. The sward was dominated by perennial ryegrass *(Lolium perenne L.)* with white clover (*Trifolium repens L.).* The clover content of herbage was 20.8% in ES-100N, 28.0% in ES-0N and 29.4% in LS-0N system. Pasture was allocated to livestock in a rotational grazing system. Each herd was moved to a new paddock whenever they had reached the post-grazing sward height target of approximately 5 cm, as measured twice per day with 50 drops of a Filips rising plate meter. As a result, each paddock was rotationally grazed on up to 12 occasions per grazing season. The rotation length varied between 21 days in spring and summer, and extending to over 42 days in autumn/winter. The entire area of each system was grazed between turn-out and closing for the first silage in late March or early April (Table 3.2). The proportion of area closed for silage was dependent on herbage growth rates and grazing demand within each system and year. The harvesting frequency was from one to two cuts per season; first cut in the May and the second cut in early July. Following harvest for silage the area was used for grazing.

During the housing period, the cows were merged into one group. They were offered silage supplemented with purchased protein concentrates. The slurry collected over the winter period was applied to the soil and evenly distributed between the systems using an umbilical system in late January, late March, April, June, late September and early November.

In the ES-100N system, fertilizer N was applied in split applications to grazing areas in February, March and April as urea (0.46 g N g^{-1}) at application rates of 29 kg N ha^{-1} each time and in May as calcium ammonium nitrate (CAN, 0.275 g N g^{-1}) with an application rate of 34 kg N ha^{-1}. Fertilizer to silage areas was split into two applications with 29 kg N ha^{-1} applied for early grazing in February and 85 kg N ha^{-1} applied in April. No fertilizer N was applied either for grazing or silage after early May; reliance was replaced by biological N fixation (BNF) in association with the white clover in the sward. The white clover content of herbage DM was maintained by broadcasting 5 kg ha^{-1} of clover seed (cultivars Chieftain and Crusader, 1:1) onto silage stubble after the harvest of first-cut silage. The silage area was rotated from year to year and approximately 0.2 of the farm area was over-sown with white clover seed each year.

3.2.4 Soil surface balances (SSBs)

This approach uses the soil surface as the system boundary. The entries were chosen in correspondence with the methodology of the Organisation for Economic Co-operation and Development (Parris 1998, Van Eerdt and Fong, 1998; OECD, 2001). Inputs included N entering the soil component annually through the soil surface as synthetic fertilizer N, slurry, animal excreta, atmospheric deposition and white clover BNF. Outputs consisted of N leaving the soil component annually as harvested and grazed herbage. The soil surface N surplus was calculated as the difference between N inputs and outputs to and from the soil component. An estimate of N input through non-symbiotic N fixation was not included. Based on the N cycle, the surplus consisted of ammonia volatilization, denitrification, leaching and N accumulation into SOM (Van Beek et al., 2003). Soil surface N balances were calculated for each paddock of the dairy systems for each year. Nitrogen inputs and outputs were quantified and expressed as N fluxes on a per-year basis. Nitrogen concentrations used for calculation of related fluxes were obtained by chemical analysis of the samples or set by standards.

Fertilizer, slurry and excreta deposition

The amounts and composition of fertilizer and slurries applied on each paddock were recorded for two consecutive years. The quantities of N excreted during grazing and indoors by each herd were calculated as a difference between cows N intake in feeds and N output in milk and calves, accounting for live weight change (Watson and Atkinson, 1999; Swensson, 2003; Powell et al., 2006). The proportion of this N excreted in each paddock was estimated according to a number of grazing days in a particular paddock assuming that cows spent two hours per day in the yard for milking.

Atmospheric deposition of N

Atmospheric deposition was measured using a rainfall collector *in situ* fortnightly. The rainfall water was analysed for ammonium N (NH_4^+-N), total oxidised N (TON) and nitrite N (NO_2^--N) on a Thermo Konelab analyser (Technical Lab Services, Ajax, Ontario Canada) and total dissolved N (TDN) was measured by chemiluminescence after catalytic combustion at 720°C using a Shimadzu TOC-VCPH analyzer with an ASI-V autosampler. The deposition rates were calculated by multiplying the annual rainfall by its N concentration.

White clover BNF

White clover BNF in stolon, roots and stubble in each paddock was estimated from white clover content in the sward and herbage production using a mechanistic model as described by Humphreys et al. (2008a). White clover content of herbage in each paddock was measured from 30 herbage snips (each 10 cm × 30 cm) randomly taken with an electric hand shears (Accu-shears Gardena®, Ulm, Germany) in April, June, August and November of each year. Snipped samples were bulked for each paddock and white clover was manually separated from the remainder of the herbage. The proportion on a DM basis was estimated by drying both samples in oven with forced-air circulation at 100°C for 16 h.

N removed in grazed and harvested herbage

During the grazing period, pre-grazing herbage DM yields from each paddock were measured by cutting four random strips (each 5 m × 0.55 m wide) using a HRH-536 lawn-mower (Honda®, Georgia, U.S.A.) at a cutting height of 5 cm above ground level prior to grazing. Pre-silage herbage DM yields were measured by cutting three random strips (5 m

× 1.1 m) within each paddock using an Agria auto-scythe (Etesia U.K. Ltd., Warwick, U.K.) prior silage harvesting. On each occasion, the cut herbage was bulked, weighed and DM determined by drying a 100 g sub-sample as described above. A second 100 g sub-sample was stored at -20°C, freeze-dried and milled through a 0.2 cm sieve prior analysing for N content using a LECO 528 auto-analyser (LECO Corporation, St. Joseph, MI, USA). Annual herbage DM production was calculated as a sum of pre-grazing and pre-harvesting herbage DM yields. It is well known that the machine processing and drying of grass in the field can lead to significant dry matter loss at harvest (Stilmant et al., 2004) due to crumbling of dry leaf parts (especially for legumes and herbs), respiration loss and incomplete machinery collection. The herbage removal by grazing is also associated with unavoidable post grazing residues depending on a grazing management (Carnevalli et al., 2006). For these reasons, the herbage removed from the paddocks was estimated to be 90% of the annual herbage production (Watson and Atkinson, 1999).

3.2.5 Soil soluble N dynamics

Soil soluble N was assessed in soil extracts. Soil samples were taken from three paddocks within each system to a depth of 0.9 m bgl. Sampling was carried out in October, November 2008, February, May, August, September, December 2009 and February 2010. At each sampling, fifteen cores per paddock were taken randomly using a Geonor MCL3 hydraulic auger (Geonor A/S, Olso, Norway). Each core was subdivided into three depths (m): 0 to 0.3, 0.3 to 0.6 and 0.6 to 0.9 m and samples were bulked to one composite sample at each depth within each paddock. Immediately after sampling, samples were crumbled, mixed, and plant material and stones were removed. The samples were subjected to extraction within an hour and extracts were obtained by shaking subsamples of field–moist soil with 2M KCl continuously for three hours at a solution ratio of 2:1 (400ml:200g, ratio v/w; Bremner 1965). Following shaking, the soil suspension was left to stand for five minutes before filtering (Whatman no.2 filtered paper, d = 12.5 cm, 0.45 µm). Prior to chemical analyses, the KCl extracts were diluted 1 in 10. Total soluble N (TSN), TON and NH_4^+-N in the samples were analysed as described above. Soluble organic N was calculated as the difference between TSN and soluble inorganic N (SIN = TON + NH_4^+-N). Gravimetric soil moisture content was determined by drying subsamples in an oven at

105^{o}C for 24 hours. All soil N results were expressed on an area basis using BD data for the soil at each depth. Soil BD was measured using the cylinder core method (Blake and Hartge, 1986). Four replicate samples at each depth were taken at six random locations across the farm. A steel cylinder (d = 4.6 cm; L = 5 cm) was hammered into the soil sufficiently to fill the inner cylinder without any soil compression at required depth. Soil cores obtained by empting the cylinders were examined for signs of shattering or compression. On return to the laboratory, any stones > 0.02 m were weighted and volume was determined by water displacement in the graduated cylinder. The BD was calculated after drying the samples at 105°C for 75 hours.

3.2.6 Statistical analyses

Statistical analyses were performed using the SAS software, version 9.01 (SAS Institute Inc., Cary, North California, USA). Normality distribution of residuals was tested with PROC UNIVARIATE. Transformation of variables was not required in any case. The experimental unit of the SSBs was a single paddock. The N fluxes and N surplus were analysed for differences between the systems by two-way analysis of variance (PROC MIXED). The model included fixed effects of the system and year and their interaction. Soil N results were analysed using a three way analysis of variance using PROC MIXED. The time factor (i.e. sampling date) was entered as a repeated measure with a compound symmetry (CS) covariance structure. All the other factors (system and sampling depth and all the interactions) were entered as fixed effects. Post hoc treatment comparisons were made according to Tukey and Bonferroni.

In order to find an indicator that affects soil N content and dynamics, single and multiple stepwise linear regression analyses with all measured N species and climatic factors averaged for a week/month were performed using the PROG REG procedure. The relationships between soil N species and SSB fluxes were also described using linear regressions (PROG REG). All found relationships between the variables were diagnosed for linearity, constant variance, outliers, normality and co-linearity.

3.3 Results

3.3.1 Climatic and edaphic data

The annual rainfall in 2008 and 2009 was exceptionally high, 1405 and 1403 mm, respectively and exceeded a ten years mean by 24% (Fig. 3.2a). Uncharacteristically wet weather conditions in 2008 and 2009 were also evident from WFPS records at 5 cm depth indicating complete soil saturation over 14 months. Higher SMD values during the summer (16.3 to 26.9 mm day^{-1}) reflected drier soil conditions; however SMD did not exceed a value of 40 mm day^{-1}(Fig. 3.2c). Mean estimated SMD in 2008/09 was 4 mm day^{-1} and in 2009/10 was 6 mm day^{-1}. The monthly mean soil temperature ranged from winter lows of 3.0 °C to summer highs of 15.9 °C (Fig. 3.2d). There was very little variation between the years (9.8°C in 2008 and 10.4°C in 2009). Rainfall exceeded evapotranspiration over seven months from July until January (Fig. 3.2b).

3.3.2 Soil surface balances (SSBs)

Soil surface balances for the systems are presented in Table 3.3. In ES-0N and LS-0N systems, white clover BNF was the most dominant N input into soil component, averaged 35% and 41% of the total N inputs, respectively. Slurry applied on the soil surface was the second most important source of N in the soil component of these systems accounting for 34% and 32% of the total inputs, respectively. Although, the cows spend on average 37 days in 2008 and 35 days in 2009 in the paddocks without significant variation between the systems ($P>0.05$), the amount of N excreted during grazing was estimated to be greater in ES-0N than in LS-0N system ($P<0.05$), and represented 30 and 25% of the total N inputs, respectively. In contrast, the nutrient management of ES-100N was based on an application of synthetic fertilizer. In spite of this, N fertilizer accounted only for 25% of the total N input. The application of fertilizer reduced white clover content in the swards from 31% in ES-0N and LS-0N to 21% in ES-100N ($P<0.05$) and consequently decreased the amount of BNF in ES-100N to 66 kg N ha^{-1}y^{-1} ($P<0.05$; 17% of total N input into the soil component). Moreover, there was an interaction between the effect of the system and the year on BNF ($P<0.05$) since the overall clover content on the farm was higher in 2009 than in 2008

($P<0.05$). The amount of N excreted by grazing animals was higher in ES-100N compared with ES-0N and LS-0N systems ($P<0.05$). Nitrogen supplied to the soil component of this system through slurry application amounted to 109 kg N $ha^{-1}y^{-1}$ (27% of total N input) and was not different in comparison with the other systems. Atmospheric N deposition was low (6.5 kg N ha^{-1} y^{-1}) and assumed to be consistent across the site. The total N inputs into the soil components of ES-0N and LS-0N were lower ($P<0.05$), comprising only 80 to 81% of that into ES-100N system.

Nitrogen uptake by herbage varied widely between the paddocks, however there was no difference in N uptake and thus in the herbage production between the systems (from 225 to 267 kg N $ha^{-1}y^{-1}$). The N output from the soil component of the systems consisted of herbage proteins removed by grazing or harvesting for silage. The N content of herbage for grazing and harvesting was similar in all dairy production systems. However, the N content of herbage for silage decreased from 24.2 g kg^{-1} to 18.7 g kg^{-1} ($P<0.05$) and the N content of herbage for grazing increased from 27.7 g kg^{-1} to 30.5 g kg^{-1} ($P = 0.05$) in the second year of the study. The mean annual export of N from the soil component of the systems ranged from 202 to 241 kg N $ha^{-1}y^{-1}$ without significant differences between the systems and years of the study. In ES-100N, N in grazed and harvested herbage accounted for 82% and 18% of N removed, respectively. The proportion of N in grazed herbage was lower in ES-0N system ($P<0.05$) accounting for 79% of the total N removed in herbage. The amount of N removed by grazing from LS-0N was even lower ($P<0.05$) contributing to the total N output only by 63%. Due to efficient recycling of N within the grazing systems, the proportion of total N input to the soil component that was removed as N in harvested or grazed herbage ranged within 63% and 72%, without significant variation between the systems. Similarly, there were no differences in N surpluses at the soil surface level between the systems and the years. The surpluses ranged from 113 kg N $ha^{-1}y^{-1}$ in LS-0N to 161 kg N $ha^{-1}y^{-1}$ in ES-100N. Linear regression revealed a positive correlation between total N input and N uptake by the herbage ($R^2 = 0.30$, $P<0.05$; Fig. 3.3a) and also between total N input and N surplus ($R^2 = 0.83$, $P<0.0001$; Fig. 3.3b).

3.3.3 Soil soluble N dynamics

3.3.3.1 Soluble organic N

The SON levels decreased ($P<0.0001$) with the sampling depth and exhibited a high intra-annual variability (from $P<0.05$ to $P<0.0001$) down to 0.9 m depth (Table 3.4). The variation at 0 to 0.3 m showed a seasonal pattern with a minimum occurring during the winter and maximum in the late summer (September 2009, Fig. 3.4a). Soil SON down to 0.6 m depth and C:N ratio at 0.3 to 0.6 m were affected by an interaction between the system and sampling date ($P<0.05$; Table 3.4). There was no difference in the SON content between the systems at 0.6 to 0.9 m depth. The C:N ratio of organic matter ranged from 1.9 to 33.6, and was not affected by the sampling depth. Soluble organic N pool was greater than SIN comprising 69, 66 and 65% of TSN at 0 to 0.3, 0.3 to 0.6 and 0.6 to 0.9 m depth, respectively.

3.3.3.2 Soluble inorganic N

Similar to SON, NH_4^+-N was not influenced by the effect of the system ($P>0.05$). However, it differed between sampling dates (from $P<0.05$ to $P<0.0001$) and decreased with the sampling depth ($P<0.0001$; Table 3.4). The intra-annual variation did not follow a clear seasonal pattern (Fig. 3.4b). The topsoil content ranged from 0.01 to 59.6 kg ha^{-1} with a peak in December 2009. Ammonium represented the second most important fraction of TSN (19.8 to 29.4%), and subsequently TON made up on average only 8.2% of TSN pool to 0.9 m depth (Table 3.4).

The content of TON in the soil profile was also not affected by the system ($P>0.05$). Its content also differed between sampling dates ($P<0.0001$), but it increased with the sampling depth ($P<0.0001$; Table 3.4) and showed an opposite distribution to NH_4^+-N. Moreover, the levels at each sampling depth exhibited a clear seasonal pattern with an increase during spring and summer months (February to August), and a decrease during the main drainage season (August to February; Fig. 3.4c).

3.3.4 Factors affecting soil soluble N dynamics

Total N input positively influenced TSN ($R^2 = 0.43$, $P<0.05$; Fig. 3.3c) and SON ($R^2 = 0.32$, $P<0.05$; Fig. 3.3d), however it had no effect on SIN, NH_4^+-N and TON in the soil profile. The levels of TSN ($R^2 = 0.36$, $P<0.05$; Fig. 3.3e) and SON ($R^2 = 0.27$, $P<0.05$; Fig. 3.3f) were also positively controlled by N surplus. Also in this case, N surplus did not affect the levels of SIN, NH_4^+-N and TON.

The content of TSN ($R^2 = 0.55$, $P<0.0001$), SON ($R^2 = 0.38$, $P<0.0001$), SIN ($R^2 = 0.65$. $P<0.0001$) and NH_4^+-N ($R^2 = 0.72$, $P<0.00001$) was positively correlated to gravimetric soil moisture content at the corresponding soil depth (Fig. 3.5). In contrary, TON content was negatively related to hydrological variables such as rainfall ($R^2 = 0.18$, $P<0.001$), effective rainfall ($R^2 = 0.35$, $P<0.0001$), gravimetric soil moisture content ($R^2 = 0.12$, $P<0.05$) and WFPS ($R^2 = 0.28$, $P<0.0001$), and was positively related to soil temperature ($R^2 = 0.47$, $P<0.0001$) and soil moisture deficit at 5 cm depth ($R^2 = 0.27$, $P<0.0001$; Table 3.5).

3.4 Discussion

3.4.1 Climatic and edaphic data

The years of the study had an exceptionally high rainfall compared with previous years (Fig. 3.2a), which resulted in lower herbage production. Higher annual ER and longer drainage seasons (Fig. 3.2b) led to a greater potential for N leaching. High soil moisture conditions caused long periods of anoxic conditions and considerable reduction potential of the soils. This likely promoted reduction biochemical processes such dissimilatory NO_3^- reduction to NH_4^+ (DNRA) and denitrification (Necpalova et al., 2012).

3.4.2 Soil surface balances (SSBs)

In order to assess and improve N utilisation and to evaluate the potential impact of grazing over the winter on the environment compared with conventional practices, SSBs were calculated for each paddock within three dairy production systems. The variability (standard deviation: mean) of the inputs and outputs to and from the soil component within each system (depending on the SSB component considered) was generally very high (Table 3.3). The large variation in some of the N inputs or outputs signifies that some processes may lead to carry-over of N between the years (e.g. BNF; Ledgard et al., 1999) or may be related to the divergences in grassland management (e.g. timing and number of silage cuts). Despite this, some components of the SSB were closely related to the intensity of the farming systems (e.g. the amount of N excreted).

A deposition of organic N on grassland farms represents an alternative implemented indicator of environmental pressure and sustainability. The European Commission has set a threshold value for organic N from animal manures at 170 kg $ha^{-1}y^{-1}$ (European Council 1991; SI 610, 2010). The survey carried out in Ireland indicated that approximately 45% of the grazed dairy grasslands exceed the limit to be applied (Coulter et al. 2002). Also, in the present study the amount of organic manures deposited on the soil surface exceeded a threshold value in all studied systems (from 58 kg N ha^{-1} in ES-100N to 15 kg N ha^{-1} in LS-0N system). The quantities of organic N applied in slurries were equal between the systems and the total number of grazing days per paddock did not vary either. Consequently, the differences between systems in the amounts of N excreted during grazing were a result of stocking rate. Since the ES-100N was stocked at 2.2 cows ha^{-1}, grazing resulted in a 25% increase in N excreted compared with ES-0N stocked at 1.6 cows ha^{-1}. Reduced stocking density in LS-0N between September and January also resulted in a small, but significant difference in excreted N between ES-0N and LS-0N.

The BNF was quantitatively the most important N input to the soil component of ES-0N and LS-0N systems. Therefore, the estimate of BNF rate was crucial as it had a strong impact on SSBs of these systems. The model used in the present study was based on a white clover herbage production taking into account synthetic fertilizer input, if any, and also the proportion of N fixed in non-harvested organs. Reported annual BNF rates in grasslands across Europe and New Zealand are highly variable (kg N ha^{-1}): 38 on organic farms in Austria (Pötsch, 2000), 68 and 83 on organic dairy farms in Germany (Scheringer and Isselstein, 2001; Kustermann et al., 2010), 87 on organic dairy farms in Denmark (Halberg et al., 1995), 75 on organic prototype farm Frydenhaug in Norway (Steinshamn et al., 2004), 10 to 270 on dairy farms in New Zealand (Ledgard et al., 1999, Ledgard, 2001) and up to 373 in non-fertilised grass-clover swards at Wageningen in the Netherlands

(Elgersma et al., 2000). Accordingly, the rates estimated in the present study are comparable with the previously published range. The application of synthetic fertilizer at a rate of 100 kg ha^{-1} in ES-100N reduced the amount of N fixed through BNF by 46%. This reduction was attributed to the decrease in white clover content by 32% in comparison with the systems not receiving synthetic fertilizer, which is in agreement with previous studies (e.g. Ledgard et al., 1999, Elgersma et al., 2000; Ledgard, 2001). For the calculations of the SSBs, we assumed atmospheric N deposition of 6.5 kg N ha^{-1} yr^{-1} based on two year measurements at Solohead Research Farm. However, this value might underestimate N deposition, since only wet N deposition was determined.

Although the total N inputs into soil components of ES-0N and LS-0N comprised 80 to 81% of that into the ES-100N system, all the systems showed similar rates of herbage uptake and thus herbage production. This suggests that BNF replaced an equivalent quantity of synthetic fertilizer (Andrews et al., 2007) and this resulted in a similar potential of the systems for utilization by grazing or harvesting. The systems had different stocking densities and thus different grass and silage requirements. And although the number of grazing days in the paddocks did not differ between the systems, the proportion of the herbage grazed and cut for silage differed considerably. This suggests that the grazing requirements were fully supported by the herbage production within each system; however, the bulk silage requirements for the winter herd were not supported equally. The more detailed analyses of the feeding requirements and the herbage production within each system denote that the ES-100N and ES-0N systems were not self contained in the respect of silage production and the developed silage deficit was covered by the additional silage production in system LS-0N.

The SSBs revealed that the land components of the systems generated N surplus in both years, ranging from 113 N ha^{-1}y^{-1} in LS-0N to 161 N ha^{-1}y^{-1} in ES-100N, without significant variation between the systems and years of the study. This suggests that grazing over the winter in LS-0N did not create an extra environmental pressure via N losses on an annual basis in comparison with early spring calving systems (ES-100N and ES-0N). Surpluses of N were clearly linked to N inputs as reported elsewhere (Oenema et al., 1998; Jarvis, 1999). For this reason, N surplus was not only a consequence of N fertilisation (synthetic fertilizer, slurry) and grazing pressure (excreta) but also BNF.

A large number of budgeting studies have been carried out in different agroecosystems (e.g. Schroder et al., 2003; Nielsen and Kristensen, 2005; Nevens et al., 2006; Bassnino et al., 2007; Gustafson et al., 2007; D`Haene et al., 2007; Fangueiro et al., 2008), but it is often difficult to compare them due to small, but significant differences in the approaches (Leip et al., 2011). The surpluses estimated in the present study are in accordance with results reported for SSBs on dairy farms in Netherlands (-50 to 500 kg N ha^{-1} y^{-1}; Van Beek et al., 2003) and Norway (64 kg ha^{-1} y^{-1}; Steinshamn et al., 2004). Low N surpluses are generally indicating high N use efficiencies (NUEs) and *vice versa* (Leip et al., 2009). In the current study, the NUEs at the soil surface level were comparable with a NUE for the SSB of the experimental farm De Marke in the Netherlands (67%; Oenema et al. 2003) and Frydenhaug in Norway (89%; Steinshamn et al., 2004). In addition, the NUEs of the soil components of the studied systems indicated that there is still considerable potential for nutrient management improvements. This is also evident from a weak linear correlation between N uptake and N inputs (R^2 = 0.30) suggesting that N inputs may be decreased without a decrease in the herbage production (Simon et al., 2000; Ondersteijn et al., 2003).

The losses during grazing, harvesting and storage were considered to be 10% of the herbage production, which is consistent with the results of others (Kjus, 1990, Rotz and Muck, 1994; Watson and Atkinson, 1999; Carnevalli et al., 2006). Nevertheless, the herbage that is lost either during harvesting or is refused by grazing animals on the pasture do not necessarily escape from the soil component and re-enters the productive cycle through mineralisation of plant residues in the soil (Steinshamn et al., 2004; del Prado et al., 2006). Detailed measurements of N losses escaped from the soil component of the paddocks used in the present study in 2008 and 2009 through N leaching and direct nitrous oxide (N_2O) emissions were already reported (Li et al., 2011; Necpalova et al., 2012). Losses of N by leaching were estimated by multiplying the mean N concentrations in groundwater with the volume of ER and averaged 20.2 kg ha^{-1}y^{-1} without significant variation between the systems or the years of the study (Necpalova et al., 2012). The N_2O fluxes from a fertilised, ES-0N and LS-0N system measured using the static chamber technique were also not significantly different and amounted to 6.4 kg N ha^{-1} y^{-1} (Li et al., 2011). This implies that the land component of the studied dairy production systems created similar pressure on the environment in the terms of N leaching to groundwater and

N_2O emissions from the soil surface. The unaccounted N ranged from 86 kg N ha^{-1} y^{-1} in LS-0N to 134 kg N ha^{-1} y^{-1} in ES-100N and on the fundamental basis of the N cycle was partially lost through denitrification as dinitrogen gas, volatilised as ammonia or was accumulated to the soil organic pools.

3.4.3 Soil soluble N dynamics

There was a hypothesis that SON and SIN would temporarily increase during the winter months since grazing over the winter leads to a substantial uneven deposition of highly concentrated excreta on the soil surface (Bakker et al., 2004; Decau et al., 2004; Hutchings et al., 2007) while grass growth and thus N uptake is temperature limited and considerable ER occurs (Jewkes et al., 2007). A significant two way interaction between the system and sampling date on SON and C:N ratio indicated that the extent of the effect of the system on soluble organic matter changed over time. But from more detailed analyses and SON time course it is clear that the effect of time and seasonal changes are noticeably more important than the effect of the system. Soil SIN was not affected by the production system at any sampling depth. Consequently, the soil N dynamics under all systems exhibited a similar trend over time, despite the differences in the time of supply (grazing season) and the form (i.e. synthetic fertilizer, BNF) of N inputs. This suggests that grazing over the winter that characterized the LS-0N dairy production system did not affect the size of soil soluble N pools and their dynamics. The lack of response or not detecting the increase in the current study could be attributed to the fact that the variation in size of SON and SIN pools has been buffered by the biochemical processes related to inherent soil properties on site (heavy texture, high soil pH, high soil organic C content; Table 3.1), continuous anaerobic conditions during the study period (i.e. wet years 2008 and 2009) and to the presence of shallow groundwater (0 to 2.2 m bgl; Fig. 3.1) in the soil profile (Grignani and Zavattaro, 2000). The high natural attenuation and denitrification capacity of these soils and the absence of significant responses of SIN and water quality to grassland managements on this site has been already reported (Humphreys et al., 2008b, Necpalova et al., 2012).

The TON content in the soil profile was very low. This could be partially attributed to immobilization by plants or microbes to sustain herbage production or to reduction biochemical processes leading to exhaustion of TON via DNRA (Hill 1996, Stepniewski and Stepniewska 2009) or denitrification (Jacobs and Gilliam 1985; Lowrance 1992). From its very clear seasonal pattern, it is apparent that TON pool was also influenced by leaching to groundwater. Its content considerably increased at each soil depth during spring and summer months, likely as a consequence of a stimulating effect of higher temperatures and rainfall on SOM mineralisation (Cavazza et al., 1986; Grignani and Acutis, 1994), and started to decrease at the beginning of the drainage season until it got completely washed out at the end of the year. The NH_4^+-N pool represented up to 29% of the TSN in the soil profile, which may be also a result of reduction anaerobic processes (i.e. DNRA). The intra-annual variation in NH_4^+-N content was difficult to interpret as it did not have a predictable pattern. Greater content of SON compared with SIN was likely a feature of the grassland age (Murphy et al. 2000) and high clay content (Velthof et al. 2010). Although SSBs suggested that a proportion of unaccounted N could be accumulated into organic N pools, there was no clear evidence of an annual increase in SON pool over the study period. However, the periods of net immobilisation (from February to September) and net mineralisation (from September to February) were observed. In addition, low C:N ratio of the soils on site (Table 3.1) denotes that soils are N rich and C limited. In general, these soils are characterised by very low N immobilization and greater NH_4^+-N pool derived from deaminisation of organic C sources (Tate, 1995; Bengtsson et al., 2003).

3.4.4 Factors affecting soil soluble N dynamics

In order to determine management and climatic factors affecting soil N in the soil profile, the influence of management variables (i.e. annual N input, N output, N uptake and N surplus) and climatic variables (i.e. rainfall, ER, SMD, soil temperature, WFPS, gravimetric soil moisture content) on a monthly and weekly basis was investigated using a single and multiple linear regression approach. A positive correlation between N surplus and TSN, and SON content suggested that every kilogram of N surplus increased TSN by 0.06 kg ha^{-1} and SON by 0.05 kg ha^{-1}. Similar relationships were found between N input and TSN, and SON. The SIN was not sensitive to N input and N surplus, which is in contrast to the findings of Jarvis (1999), and Grignani and Zavattaro (2000). Furthermore, there was no explanatory relationship found between SIN content and N uptake as it has been reported in other studies (Brandi-Dohrn et al., 1997, Grignani and Zavattaro, 2000). This indicates that

SIN content in clay loam soils results from a great number of interacting factors such as biochemical (i.e. nitrification, denitrification, DNRA) and physical processes (leaching) and simple relationships are not sufficient to explain the size of this pool in the soil profile.

The size of SON and NH_4^+-N pools seemed to be positively driven by gravimetric soil moisture content at corresponding soil depth, which explained 38% and 71% of the variation in SON and NH_4^+-N content, respectively. Soil moisture directly regulates diffusity and O_2 exchange between the soil and the atmosphere (Davidson and Schimel 1995) and thus has a considerable control over O_2-dependent biochemical processes such as decomposition, deaminisation, ammonification and nitrification (Davidson 1991; Havlin et al., 2005). In contrary, TON content was negatively related to a number of hydrological variables and positively related to the soil temperature and SMD at 5 cm depth. The temporal variation in soil temperature triggers the dynamics and activity of microbial biomass (Bengtsson et al., 2003; Havlin et al., 2005), but also indirectly affects the evapotranspiration rates and aerobic conditions of the topsoil. For these reasons, these relationships imply that the size and dynamic of TON depends on biochemical processes, likely nitrification, but also that TON is a highly susceptible pool for leaching when significant water movement occurs.

3.5 Conclusions

In order to assess and improve N utilisation, and to evaluate the potential impact of grazing over the winter on the environment compared with other practices, SSBs were calculated for each paddock within three dairy production systems. Since BNF replaced an equivalent quantity of synthetic fertilizer, there was no difference in herbage production and potential for utilization by grazing or harvesting between the systems. The management of the systems resulted in a similar N surplus (113 to 161 kg N ha^{-1} y^{-1}) and NUE of the soil component (63 to 72%) leading to similar environmental pressure via N losses on an annual basis.

The correlation between the grassland management and soil N dynamics in the clay loam soil profile was difficult due to high natural buffering capacity of the soils associated with high soil organic C, high soil pH, anaerobic conditions and the presence of a shallow groundwater table; i.e. grazing over the winter period on a clay loam soil had no effect on the soil N dynamics. Anaerobic reduction processes such as denitrification and DNRA likely ensured consistently low soil TON content. Consequently, the performance of grazing over the winter on these soils did not create additional environment pressure via N losses to groundwater and N_2O emissions compared with conventional grazing systems.

The management factors such N input and N surplus influenced the dynamics of SON pool, while SIN dynamics was mainly affected by the hydrological factors and soil temperature, which are the most important factors controlling microbial activity, biochemical processes and leaching.

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Table 3.1 Soil properties at Solohead Research Farm at three different depths. All values are means of at least three determinations with standard deviations in parentheses.

Depth	Sand	Silt	Clay	Bulk density	Particle density	Total porosity	CEC	pH	Total N	Total organic C	Total inorganic C	Organic matter†	C:N ratio
M	%	%	%	g cm^{-3}	G cm^{-3}	%	Meq/100gDM		%	%	%	%	
0.0-0.3	36.7 (6.4)	35.0 (3.5)	28.3 (3.1)	1.09 (0.16)	2.52 (0.15)	58.7 (6.5)	25.4 (2.3)	6.60 (0.2)	0.48 (0.05)	4.48 (0.52)	0.09 (0.03)	6.55 (0.84)	9.34 (0.27)
0.3-0.6	36.0 (4.4)	36.0 (2.0)	28.0 (2.7)	1.43 (0.26)	2.59 (0.15)	44.5 (10.2)		7.00 (0.2)	0.22 (0.05)	2.02 (0.41)	0.08 (0.08)	2.74 (0.53)	9.09 (0.28)
0.6-0.9	36.0 (6.1)	35.7 (3.2)	28.3 (2.9)	1.70 (0.20)	2.67 (0.20)	37.1 (6.8)		7.65 (0.2)	0.06 (0.02)	0.49 (0.16)	0.54 (0.29)	1.63 (0.84)	7.88 (0.69)

† calculated from loss on ignition results (%) using the Ball's equation: OM = (0.476*loss on ignition) - 1.87 (Ball, 1964)

Table 3.2 Details of the experimental systems at Solohead Research Farm in 2008 and 2009. ES-100N - early spring calving with Fertiliser N. ES-0N - early spring calving without Fertiliser N. LS-0N - late spring calving without Fertiliser N.

	2008			2009		
	ES-100N	ES-0N	LS-0N	ES-100N	ES-0N	LS-0N
Mean first grazing date	21st Feb	19th Feb	16th Apr	20th Feb	22nd Feb	15th April
Mean last grazing date	12th Nov	12th Nov	14th Jan	18th Nov	18th Nov	26th Jan
Mean days grazing cow^{-1}	220	234	231	218	234	235
Total area (ha)	8.5	11.3	10.5/14.2†	8.5	11.3	10.5/14.2†
Proportion of area harvested for silage						
1st cut (Apr – May)	0.5	0.3	0.5	0.4	0.2	0.5
2nd cut (Jun – Jul)	0.0	0.4	0.2	0.1	0.3	0.5
Stocking rates on grazing areas (cows ha^{-1})						
Feb-Mar	2.1	1.6		2.1	1.6	
Apr-May	4.2	2.3	3.4	3.4	2.0	3.2
Jun-Jul	2.1	2.8	2.3	2.4	2.4	3.3
Aug-Sep	2.1	1.6	1.7	2.1	1.6	1.7
Oct-Nov	2.1	1.6	1.3	2.1	1.6	1.3
Dec-Jan			1.3			1.3
Total stocking rate	2.1	1.6	1.5	2.1	1.6	1.5

† From September to January, an extra area 3.7 ha was included to LS-0N system, which was used for grazing heifers/calves during the rest of year. This area was not included in the analyses.

Table 3.3 Soil surface N balances (kg ha^{-1} yr^{-1}) for the three dairy production systems: ES-100N - early spring calving with N-fertiliser, ES-0N - early spring calving without N-fertiliser, LS-0N - late spring calving without N-fertiliser. Superscripts indicate which means are significantly different from one another on the basis of Tukey test.

	2008-2009			P value		
N flow (kg ha^{-1})	ES-100N (SD)	ES-0N (SD)	LS-0N (SD)	System	Year	System x year
N input (kg ha^{-1}):						
N in synthetic fertilizer	100	0.0	0.0			
BNF	66 (31.8)^{b}	112 (41.4)^{a}	134 (56.5)^{a}	<0.05	NS	<0.05
N in excreta during grazing	119 (32.0)^{a}	95 (14.1)^{ab}	82 (42.9)^{b}	<0.05	NS	NS
N in slurry	109 (85.9)	109 (54.6)	103 (54.7)	NS	NS	NS
Atmospheric deposition	6.5	6.5	6.5			
total N input	401 (99.1)	323 (71.4)	325 (90.3)	<0.05	NS	NS
N output (kg ha^{-1})						
N in grazed grass	219 (69.0)^{a}	178 (42.5)^{ab}	147 (40.7)^{b}	<0.05	NS	NS
N in harvested grass	48 (54.1)	47 (44.9)	89 (43.2)	NS	NS	NS
N uptake by herbage	267 (48.4)	225 (35.5)	236 (54.8)	NS	NS	NS
N removed in herbage†	240 (43.6)	202 (31.9)	212 (49.3)	NS	NS	NS
N surplus (kg ha^{-1})	161 (95.9)	121 (71.7)	113 (101.4)	NS	NS	NS
N use efficiency (%)	63 (16.7)	65 (17.9)	72 (31.1)	NS	NS	NS

† The herbage removed from the paddocks was estimated to be 90% of the annual herbage production (Watson and Atkinson, 1999).

Table 3.4 Mean soil soluble N content (kg ha$^{-1;}$ n = 24) under three dairy production systems at three different depths from October 2008 to February 2010. ES-100N - early spring calving with N-fertiliser, ES-0N - early spring calving without N-fertiliser, LS-0N - late spring calving without N-fertiliser. Superscripts indicate which means are significantly different from one another on the basis of Tukey test.

N content	ES-100N	ES-0N	LS-0N	P value		
(kg ha^{-1})	(SE)	(SE)	(SE)	System	Sampling date	System x Time
0-0.3 m						
Soluble organic N	66.5 (6.47)	60.7 (7.69)	53.9 (6.77)	NS	<0.0001	0.05
C:N ratio	5.4 (1.37)	5.5 (1.08)	4.9 (1.23)	NS	<0.0001	NS
Ammonium N	26.2 (3.14)	26.0 (2.81)	25.4 (2.95)	NS	<0.0001	NS
Total oxidised N	1.8 (0.50)	1.6 (0.44)	2.0 (0.49)	NS	<0.0001	NS
Total inorganic N	28.0 (3.20)	27.7 (2.89)	27.4 (2.91)	NS	<0.0001	NS
0.3-0.6 m						
Soluble organic N	30.9 (2.75)	36.2 (3.86)	32.9 (4.03)	NS	<0.05	<0.05
C:N ratio	4.9 (0.63)	7.4 (1.17)^{a}	4.9 (0.50)^{b}	<0.05	<0.0001	<0.05
Ammonium N	13.3 (1.19)	13.2 (0.82)	12.9 (1.42)	NS	<0.05	NS
Total oxidised N	3.8 (0.72)	4.2 (0.70)	4.0 (0.65)	NS	<0.0001	NS
Total inorganic N	17.0 (1.25)	17.4 (0.89)	16.9 (1.47)	NS	<0.05	NS
0.6-0.9 m						
Soluble organic N	28.8 (5.26)	25.2 (3.74)	21.3 (3.31)	NS	<0.05	NS
C:N ratio	6.5 (1.50)	7.3 (1.52)	7.5 (1.77)	NS	<0.05	NS
Ammonium N	7.5 (1.17)	8.2 (1.61)	7.1 (0.96)	NS	<0.0001	NS
Total oxidised N	5.1 (1.00)	5.7 (1.10)	6.2 (0.88)	NS	<0.0001	NS
Total inorganic N	12.6 (1.48)	13.9 (1.71)	13.2 (1.14)	NS	<0.0001	NS

Table 3.5 Results of single and multiple regression analyses with total oxidised N and soil inorganic N in all samples (n = 72) as dependent variable (mg kg^{-1}) and environmental factors as independent variable.

Dependent variable (mg kg^{-1})	Environmental factor (x, z)	Unit	Relationship	Model R^2	P value
Total oxidised N (y)	gravimetric soil moisture content (x)	g kg^{-1}	Y = -0.004x + 1.772	0.115	<0.05
	soil temperature (x)	°C	Y = 0.119x - 0.303	0.468	<0.0001
	rainfall (x)	Mm	Y = -0.179x + 1.622	0.182	<0.001
	effective rainfall (x)	Mm	Y = -0.209x +1.521	0.353	<0.0001
	soil moisture deficit (x)	Mm	Y = 0.054x + 0.697	0.270	<0.0001
	WFPS (x)	%	Y = -0.027x + 3.722	0.279	<0.0001
Soil inorganic N (y)	gravimetric soil moisture content (x) and temperature (z)		Y = 0.042x + 0.160z - 6.535	0.699	<0.0001

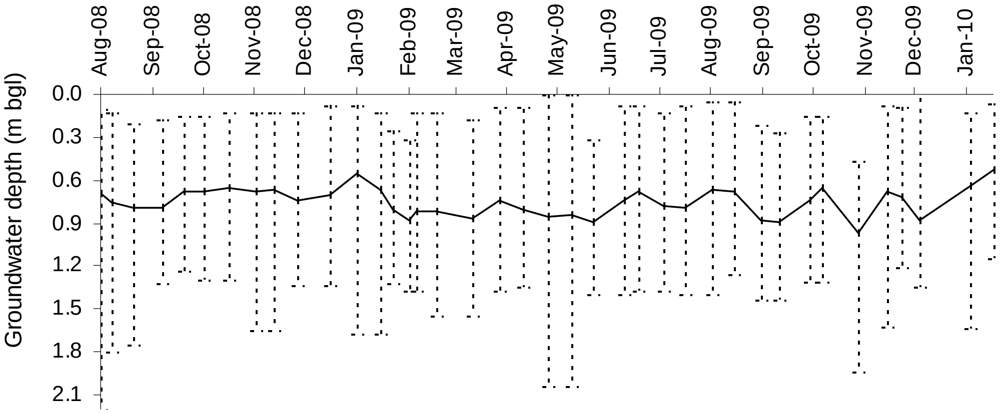


Fig. 3.1 Temporal variation of ground watertable depth from August 2008 to February 2010. Vertical bars represent the maximum and minimum below ground level (bgl) and solid line represents mean groundwater depth (n = 66)

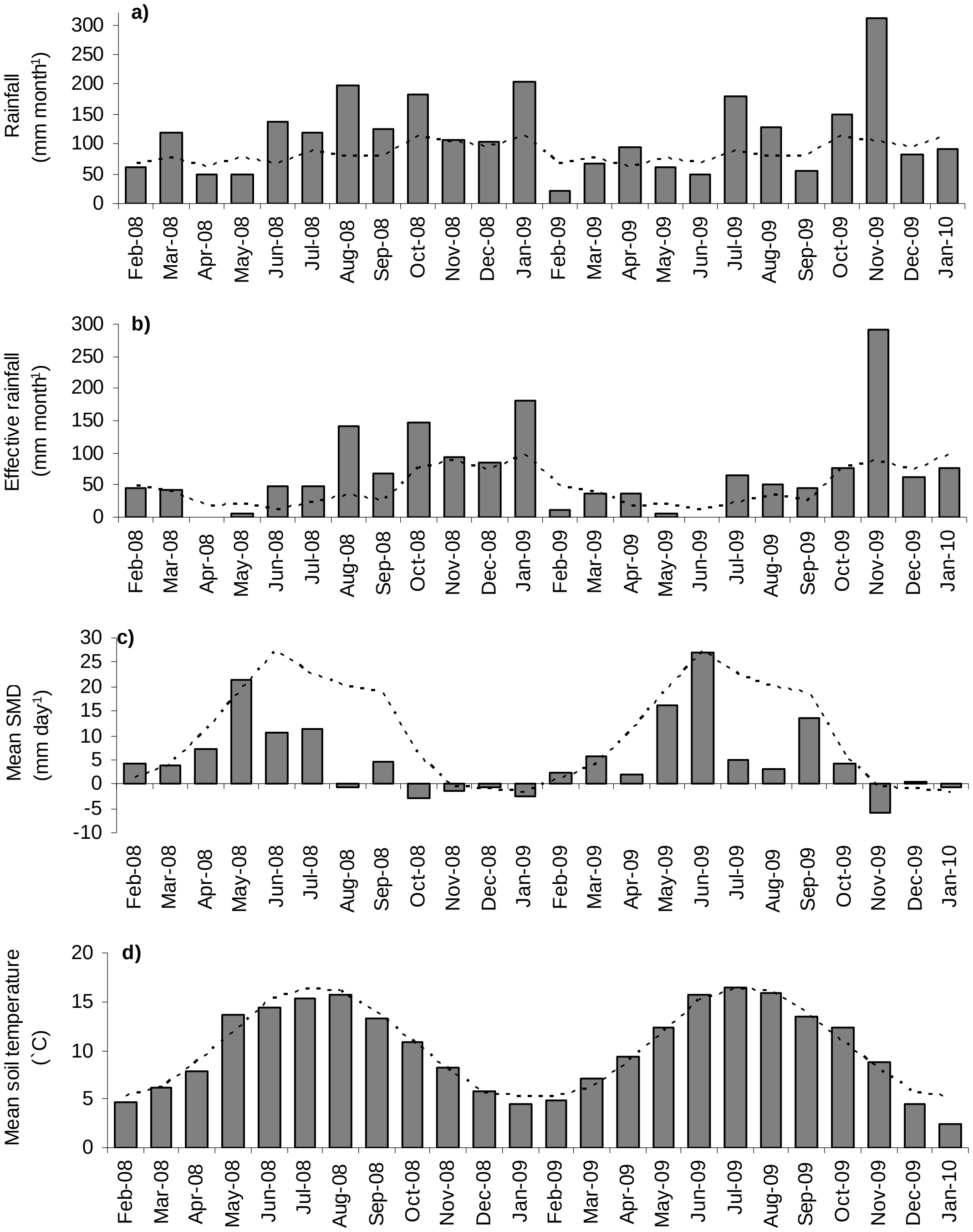
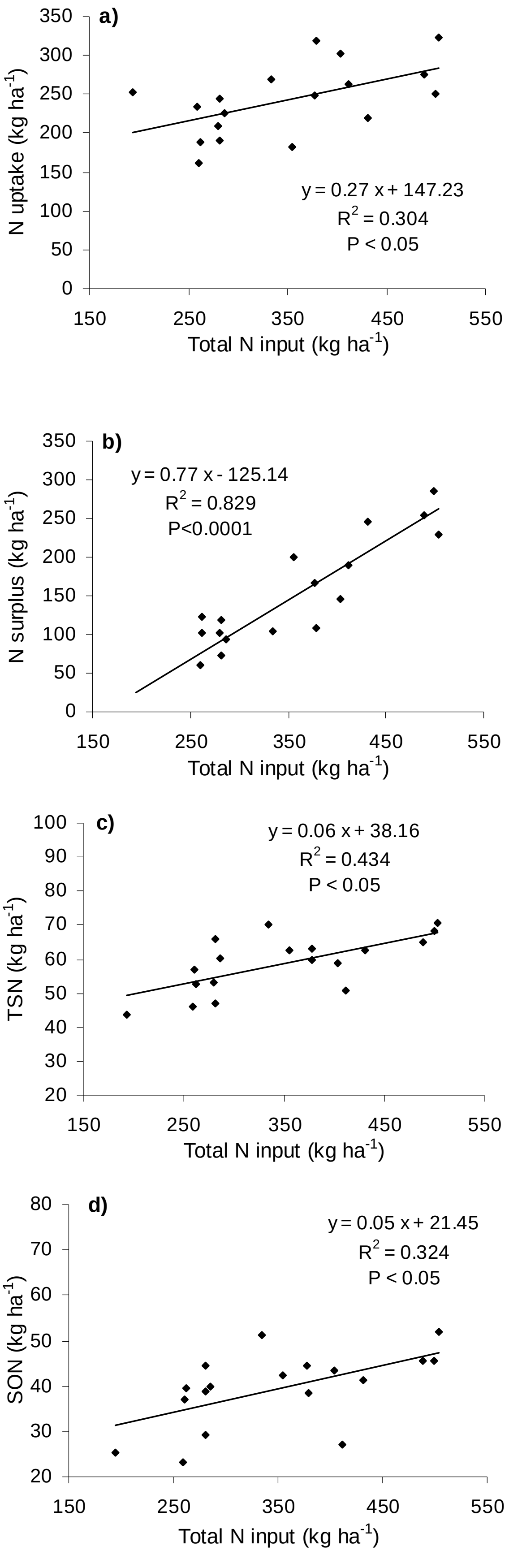


Fig. 3.2 Meteorological data at Solohead Research Farm from February 2008 to February 2010: a) monthly rainfall (mm month^{-1}), b) monthly effective rainfall (mm month^{-1}), c) monthly mean soil moisture deficit (SMD, mm d^{-1}) and d) monthly mean soil temperature (°C) at 0.05 m depth. The dashed line represents a ten year mean.


a)
N uptake (kg ha^{-1})
0
50
100
150
200
250
300
350
Total N input (kg ha^{-1})
150
250
350
450
550
y = 0.27 x + 147.23
R^2 = 0.304
P < 0.05
b)
N surplus (kg ha^{-1})
0
50
100
150
200
250
300
350
Total N input (kg ha^{-1})
150
250
350
450
550
y = 0.77 x - 125.14
R^2 = 0.829
P<0.0001
c)
TSN (kg ha^{-1})
20
30
40
50
60
70
80
90
100
Total N input (kg ha^{-1})
150
250
350
450
550
y = 0.06 x + 38.16
R^2 = 0.434
P < 0.05
d)
SON (kg ha^{-1})
20
30
40
50
60
70
80
Total N input (kg ha^{-1})
150
250
350
450
550
y = 0.05 x + 21.45
R^2 = 0.324
P < 0.05

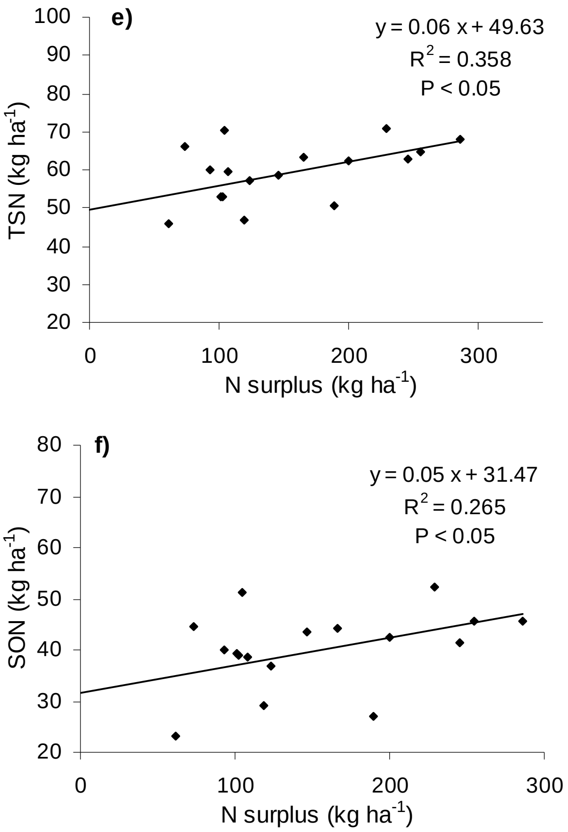


Fig. 3.3 Relationships between total N input (kg ha^{-1}) and a) herbage N uptake (kg ha^{-1}), b) N surplus (kg ha^{-1}), c) total soil soluble N content (TSN, kg ha^{-1}), d) soil soluble organic N content (SON, kg ha^{-1}), and between N surplus and e) TSN (kg ha^{-1}), f) SON (kg ha^{-1}) in the soil profile at 0 to 0.9 m depth.

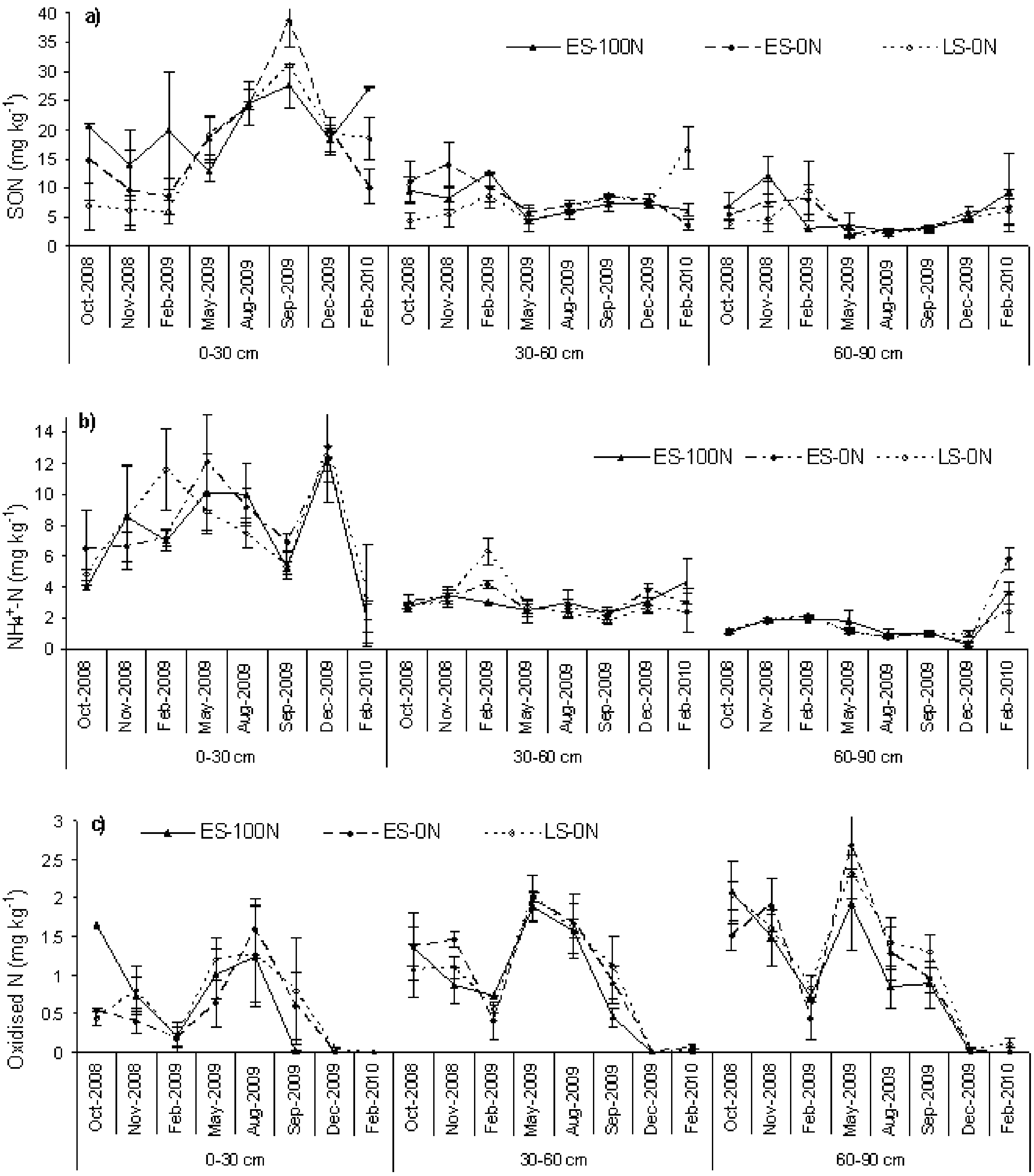


Fig. 3.4 Seasonal dynamics of soil soluble N (mg kg^{-1}): soluble organic N (SON); ammonium N (NH_4^+-N) and oxidised N under three dairy production systems at three different depths: a) at 0 to 30 cm, b) at 30 to 60 cm and c) at 60 to 90 cm. ES-100N - early spring calving with N-fertiliser, ES-0N - early spring calving without N-fertiliser, LS-0N - late spring calving without N-fertiliser. Vertical bars represent standard error of the means.

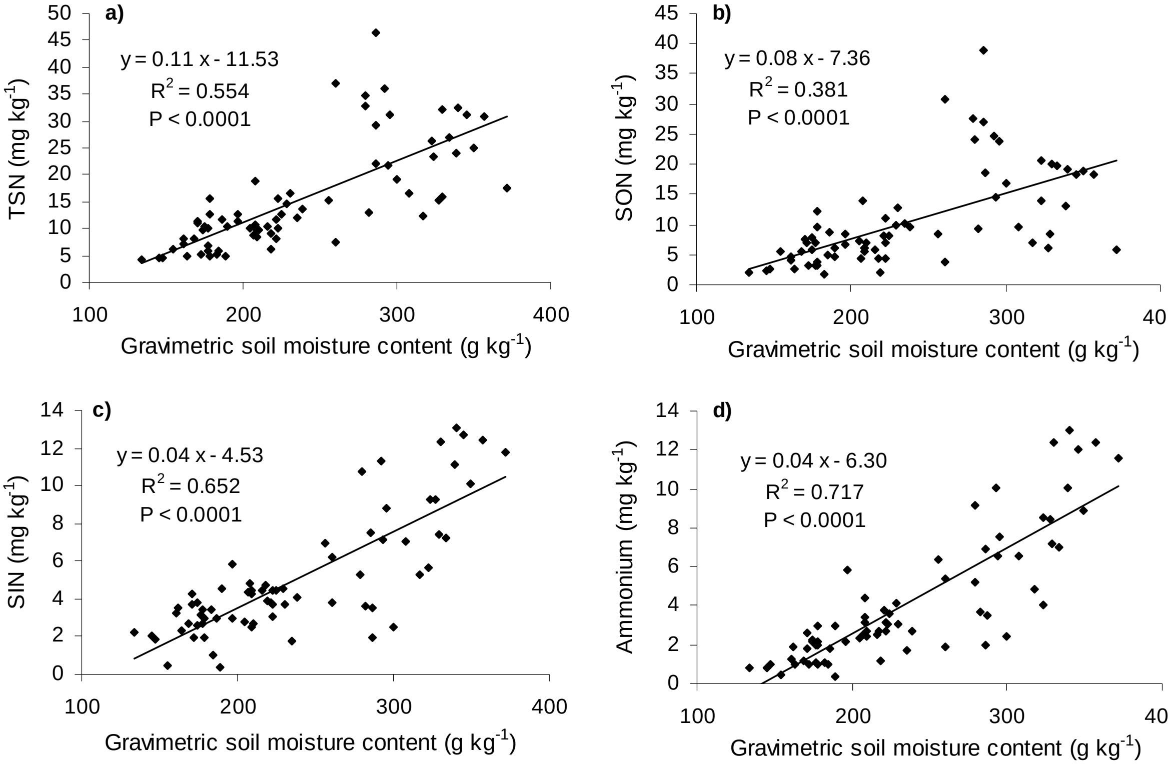


Fig. 3.5 Relationships between gravimetric soil moisture content (g kg^{-1}) and a) total soluble N content (TSN, mg kg^{-1}), b) soluble organic N content (SON, mg kg^{-1}), c) soil inorganic N content (SIN, mg kg^{-1}) and d) ammonium N content (mg kg^{-1}) in the soil profile at 0 to 0.9 m depth.

4. N leaching to groundwater from dairy production involving grazing over the winter on a clay-loam soil

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Abstract

This study investigated concentrations of various N species in shallow groundwater (< 2.2 m below ground level) and N losses from dairy production involving grazing over the winter period on a clay loam soil with a high natural attenuation and denitrification capacity in southern Ireland (52˚51'N, 08˚21'W) over a two year period. A dense network of shallow groundwater piezometers was installed to determine groundwater flow direction and N spatial and temporal variation. Estimated vertical travel times through the unsaturated zone (<0.5 yr, time lag) allowed the correlation of management with groundwater N within a short space of time. There was a two way interaction of the system and sampling date ($P < 0.05$) on concentrations of DON, oxidised N and NO_3^--N. In contrast, concentrations of NH_4^+-N and NO_2^--N were unaffected by the dairy system. Grazing over the winter had no effect on N losses to groundwater. Mean concentrations of DON, NH_4^+-N, NO_2^--N and NO_3^--N were 2.16, 0.35, 0.01 and 0.37 mg L^{-1}, respectively. Soil attenuation process such as DNRA resulted in increased NH_4^+-N levels. For this reason, DON and NH_4^+-N represented the highest proportion of N losses from the site. Some of the spatial and temporal variation of N concentrations was explained by correlations with selected chemical and hydro-topographical parameters (NO_3^--N/Cl^- ratio, distance of the sampling point from the closest receptor, watertable depth, depth of sampling piezometer, DOC concentration). A high explanatory power of NO_3^--N/Cl^- ratio and the distance of the sampling point from the closest receptor indicated the influence of point sources and groundwater-surface water interactions.

Keywords: extended grazing, permanent grassland, N leaching, shallow groundwater, time lag, DNRA

4.1 Introduction

The European Union Water Framework Directive (EU WFD; European Parliament and Council, 2000) attempts to achieve at least ‘good ecological status’ for all waterbodies by 2015 with implementation of programmes of measures (POM) by 2012. The main POM currently in place to achieve the goals of the WFD in Ireland is the Nitrates Directive (European Council, 1991), enacted in 2006 under Statutory Instrument (SI) 378, 2006, subsequently replaced by SI 610 in 2010. For nitrate (NO_3^-), the WFD utilises a maximum admissible concentration (MAC) of 50 mg L^{-1} for groundwater set under the Groundwater Directive (GWD; Parliament and Council, 2006). In the context of the WFD, groundwater is defined as a saturated zone in fractured bedrock or in significant bodies of sand and gravel. Shallow groundwater (< 30 m below ground level (bgl)), which generally forms a perched watertable in glacial till subsoils is not considered part of this groundwater definition. Such shallow groundwater is important where there is a direct interaction between such shallow groundwater bodies and a surface waterbody (Fenton et al., 2009a). Heterogeneities in soil and subsoil anisotropies, hydrological properties and topography make transport pathways highly variable, and there is generally a time lag or delay between losses at the surface and nutrient changes in groundwater (Fenton et al., 2011). Estimation of such a time lag is important when correlating surface management with shallow groundwater quality.

Organic systems of production generally operate at low stocking densities relative to conventional systems. Low stocking densities offer the potential to extend the grazing season throughout the autumn and winter. Grass-clover swards are considered to have poor spring growth, however relatively high growth rates can be expected during late summer and autumn. Such a system requires a calving date in late April or May, rather than the typical mean calving date in late February or March for conventional spring-calving dairy system in Ireland. From a sustainability perspective, grazing during the winter, albeit at low stocking rates, carries considerable risk of nitrogen (N) losses to groundwater (Jewkes et al., 2007), despite the fact that the grass growth can take up a considerable quantity of N during the mild winter conditions experienced in Ireland (Humphreys et al., 2009).

Previous research in temperate grassland indicated that deposition of urine in the late autumn and winter leads to increased N leaching (Cuttle and Bourne, 1993; Williams and Haynes, 1994; Stout et al., 1997; Di and Cameron, 2002; Decau et al., 2004). The hydrolysis of urea following the deposition of urine also increases the pH of the soil over several units and can reach values of up to 9 (Haynes and Williams, 1993; Shand et al., 2002). This has a solubilising effect on soil organic matter and leads to higher dissolved organic N (DON) leaching losses (Wachendorf et al., 2005). Consequently there is a potential for substantial mineral and organic N leaching losses to groundwater if significant effective rainfall (ER) occurs after grazing (Francis, 1995; Hack-ten Broeke et al., 1996), which is likely during the winter in Ireland. However, there is currently little data available on the environmental impact of grazing by dairy cows at relatively low stocking density over the winter on N leaching and groundwater quality. The current study investigated the relationship between losses from grazing and N concentrations in shallow groundwater on glaciated till soils with poor drainage conditions and an inherent high natural attenuation and denitrification capacity.

The primary objective of the current study was to install a high density monitoring network on a dairy farm to investigate the effect of a system of dairy production involving grazing over the winter on a clay loam soil on concentrations of various N species in shallow groundwater and N losses over a two year period. The secondary objective was to identify spatial and temporal patterns in N concentrations and to elucidate groundwater flow direction. To study the level of dilution and proximity to source of contamination on site, chloride anion (Cl^-) and NO_3^--N/Cl^- ratios were also investigated.

4.2 Materials and Methods

4.2.1 Site description

The study was conducted at Solohead Research Farm (52 ha) in Ireland (52˚51’N, 08˚21’W) from February 2008 to February 2010. The local climate is humid temperate oceanic with a long potential growing season from February to mid December. During the last 10 years the site received on average 1017.5 mm of annual rainfall, and this resulted in mean annual ER of 551.8 mm. Mean growing season length was approximately 305 days, based on a soil temperature above 5 °C (Parson, 1988) at 0.05 m depth. Annual grass production rates measured under high input of fertilizer N (i.e. 250 to 370 kg N ha^{-1}) over the last 10 years period ranged between 13.5 and 14.7 t dry matter (DM) ha^{-1}.

The dominating soils are poorly drained Gleys (90%) and Grey Brown Podzolics (10%) with a clay loam texture and low permeability (Table 4.1). Soil texture exhibits very small heterogeneity down to 0.9 m. Sand and gravel lenses are also present which come to the surface in places and allow for fast infiltration (Fig. 4.1). The mean soil organic carbon and total N content at 0 to 0.3 m depth is 4.48% and 0.48%, respectively with a corresponding soil bulk density of 1.09 g cm^{-3}. Elevation on site ranges from 148.5 to 155.5 m Above Ordnance Datum (AOD). Potential point sources of pollution on the farm are indicated in Fig. 4.2a. The depth to bedrock (Cappagh White Devonian Sandstone Formation (Archer et al., 1996)) on site is very uneven ranging from 5 to 10 m. The sandstone aquifer is a low permeability confined aquifer with saturated hydraulic conductivity (k_s) of 0.001 to 0.02 m day^{-1}, low dissolved oxygen (1 to 4 mg L^{-1}) and electrical conductivity of less than 150 millivoltmeter (mV) (Jahangir et al., 2012). The overlying quaternary till contains a perched watertable (depth of 0 to 2.2 m bgl; elevation of 147.3 to155.2 m AOD, Fig. 4.3), which is an unconfined and poorly productive aquifer. The watertable is shallowest during the winter season. Although a number of ditches (4 m bgl) and tile drains (1.8 m bgl with spacing of 25 m) were installed between 1960 and 1995 across the farm to improve the drainage on site by lowering the watertable (Gleeson, T., personal communication). Nevertheless much of the farm remains seasonally wet, waterlogged or flooded due to impeded drainage.

4.2.2 Weather data collection

Weather data (soil temperature, volumetric soil moisture at 0.05 m depth and rainfall) was recorded every 30 min using the Solohead Meteorological station (Campbell scientific Ltd, Loughborough, U.K). Daily weather data (rainfall, maximum and minimum air temperature, wind speed and solar radiation) were inputted into the grassland hybrid model of Schulte et al. (2005) to estimate daily ER and soil moisture deficit (SMD) based on poorly drained soil criterion. Water filled pore space (%) at 0.05 m depth was calculated as the ratio of the volumetric soil moisture content to total pore space (total porosity) as described by Luo et al. (2008).

4.2.3 Experimental design and descriptions of the dairy systems

The treatments (Fig. 4.2b) corresponded to three grass-clover based dairy production systems (each > 8.5 ha) involving two different grazing seasons and corresponding annual stocking densities:

ES-100N – Early spring calving with fertilizer N: mean calving date of 17th February, grazing period from February to November, annual stocking density of 2.2 cows ha^{-1} and receiving annual fertilizer N input of 100 kg ha^{-1}.
ES-0N – Early spring calving without fertilizer N: mean calving date of 17th February, grazing period from February to November, annual stocking density of 1.6 cows ha^{-1} and received no fertilizing N input.
LS-0N – Late spring calving without fertilizer N: mean calving date of 17th April, annual stocking density of 1.7 cows ha^{-1} between calving and 1st September and then 1.3 cows ha^{-1} until closing date at the end of January, and receiving no fertilizer N input.

The main characteristics of the different systems are presented in Table 4.2. Each farming system consisted of 18 Holstein-Friesian dairy cows that calved down during a three-month period each spring. Cows were returned outside to graze immediately after the calving date and remained outside until drying off the following winter, except when the ground was too wet and cows were occasionally retained indoors to avoid damaging the grassland. The length of the grazing season for each system was determined according to a number of days at pasture as described by Humphreys et al. (2009).
During 1999, most of the area of the farm (52 ha) was divided into 8 blocks (each an area approximately 6 ha) depending on soil type and drainage status as described by Humphreys et al. (2008a). Six of these blocks were assigned into this experimental study (34 ha). Each block was divided into four paddocks (each > 1 ha), one paddock from each block was assigned to each of the three systems in a randomized complete block design. The paddocks

were predominantly used for grazing and to a lesser extent for silage. The pasture was dominated by 76% perennial ryegrass (*Lolium perenne L.*) with 24% white clover (*Trifolium repens L.*) and was allocated to livestock in a rotational grazing system. Thus, each paddock was rationally grazed on up to 12 occasions per grazing season. The rotation length varied between 21 days in spring and summer, and extending to 42 days or more in autumn/winter. During the main grazing season, the cows were outside by day and night, and were milked twice daily. The entire area of each system was grazed between turn-out and closing for first silage in late March or early April (Table 4.2). Following harvest for silage, the area was again used for grazing.

The slurry collected over the winter period was applied to the soil and evenly distributed between the three systems using an umbilical system in late January, late March, April, June, late September and early November.

In the ES-100N system, fertilizer N was applied in split applications to grazing areas in February, March and April as urea (0.46 g N g^{-1}) at application rates of 29 kg N ha^{-1} each time and in May as calcium ammonium nitrate (CAN, 0.275 g N g^{-1}) with an application rate of 34 kg N ha^{-1}. Fertilizer to silage areas was split into two applications with 29 kg N ha^{-1} applied for early grazing in February and 85 kg N ha^{-1} applied in April. No fertilizer N was applied for either for grazing or silage after early May; reliance was replaced by biological N fixation in association with white clover to supply N in the soil for the remainder of the growing season. The white clover content of herbage DM was maintained by spreading 5 kg ha^{-1} of clover seed (cultivars Chieftain and Crusader, 1:1) onto silage stubble after the harvest of first-cut silage. The silage area was rotated from year to year and approximately 0.2 of the farm area was over-sown with white clover seed each year.

4.2.4 Groundwater sampling and analyses

In July 2008, twelve piezometers constructed from polyvinyl chloride pipes, were installed in each paddock; 288 piezometers in total. The slotted screen opening interval on the lower 0.2 m of the casing was covered by a filter sock. The annulus (< 0.03 m) between casing and the piezometer wall was grouted with sand and bentonite on the soil surface to prevent water channelling down the outside of the casing. In each paddock 10 piezometers were used for water quality assessment and two were used to measure watertable depth. Samples were taken fortnightly, after purging the piezometers, during the main winter drainage period and following periods of high rainfall during other times of the year. Sampling was conducted 31 times between 20th August 2008 and 2nd February 2010 (19 and 12 times during drainage seasons 2008/2009 and 2009/2010 respectively). On each occasion a 50 ml sample was taken from each piezometer and bulked into two composite samples per paddock. All samples were filtered (Whatman no.2 filter paper, d = 0.125 m, 0.45 µm) within an hour after sampling and then analysed for ammonium N (NH_4^+-N), total oxidised N and nitrite N (NO_2^--N) on a Thermo Konelab analyser (Technical Lab Services, Ajax, Ontario Canada). Total dissolved N (TDN) and dissolved organic carbon (DOC) were measured by chemiluminescence after catalytic combustion at 720°C using a Shimadzu TOC-VCPH analyzer with an ASI-V autosampler. Dissolved organic N (DON) was calculated as the difference between TDN and dissolved inorganic N (DIN = total oxidised N + NH_4^+-N). Nitrate N (NO_3^--N) was calculated as the difference between total oxidised N and NO_2^--N. If the result was negative, the proportion of DON or NO_3^--N was assumed to be negligible, i.e. not significantly different from zero. Chloride and dissolved reactive phosphorus were determined calorimetrically using Aquakem 600 Discrete Analyser.

Both NO_3^--N and Cl^- are negative ions and do not absorb to the soil matrix. While NO_3^--N concentrations are reduced by biochemical processes, Cl^- is biologically inactive and serves as a conservative tracer for NO_3^--N. Because they are transported similarly (Davis et al., 2007), the NO_3^--N/Cl^- ratio is generally used to study the flow pathways or point sources (Obenhuber and Lowrance, 1991; Fenton 2009b). In this study, Cl^- and NO_3^--N /Cl^- ratio were used to identify the level of dilution and proximity to source of contamination on site.

Nitrogen losses of all N species (kg ha^{-1}) for each system were estimated by multiplying the mean N concentrations (mg L^{-1}) recorded on the sampling date with the volume of ER (mm) between two sampling occasions with an assumption that the N concentrations recorded in the groundwater were representative of concentrations in the ER reaching the piezometer screen. Due to high soil organic carbon, it was assumed that the unsaturated zone had a high denitrification capacity (Humphreys et al., 2008b). Therefore N concentrations or loads found in shallow groundwater on site do not represent losses from the agricultural system, for example from LS-0N, but instead represent transformed losses from LS-0N buffered by biochemical processes during migration through the unsaturated zone.

4.2.5 Watertable depth and vertical travel time

Shallow watertable levels were measured fortnightly using an electric-level indicator with an acoustic signal (DIP-50 Geosense, Suffolk, U.K.) as a part of regular groundwater sampling regime. All piezometers on site (n = 380) were surveyed to convert watertable depths to m AOD, and a groundwater flow map was constructed using a proportion of these piezometers in January 2010. Mean nutrient contour maps were constructed in the same way.

Vertical travel times (Tt (yr)) were calculated to estimate the residence time of solute/nutrients in the unsaturated zone, or in other words, how long leached nutrients migrate to the watertable. The time lag was calculated for twelve paddocks across the farm using the methodology of Fenton et al. (2011). The variables needed were: depth of unsaturated zone (mean depth to watertable in a particular paddock for the duration of the study), ER (m) for a particular period (February 2009 to February 2010) and effective porosity. Total porosity was measured in four replicate soil samples taken at three depth sections (0 to 0.3, 0.3 to 0.6 and 0.6 to 0.9 m) at twelve locations around the farm as described by Hao et al. (2007). The effective porosity was determined as 70% of total porosity values, which coincided with values taken for this site by Fenton et al. (2009a).

4.2.6 Statistical analyses

Statistical analyses were performed using the SAS software, version 9.01 (SAS Institute Inc., Cary, North California, USA). Normality distribution of residuals was tested with PROC UNIVARIATE. All the N concentration variables were transformed using a natural log ($y = \log(x + 1)$) and were analysed using a two way analysis of variance (PROC MIXED). The time factor such as the sampling date was entered as a repeated measure with a compound symmetry (CS) covariance structure and the other factors (system and system × sampling date interaction) were entered as fixed effects. The chloride concentrations and C:N ratios were analysed using the same model without previous transformations.

Without taking the biochemical processes in the soil into account it was attempted to correlate other parameters with N species in the shallow groundwater. Correlations between chemical and hydro-topographical variables (elevation of groundwater sampling screen opening interval, depth of sampling piezometer, distance of the sampling point from the closest receptor, watertable depth, NO_3^--N/Cl^- ratio and DOC) averaged for a sampling point and concentration of N species in the groundwater were determined by Pearson's correlation analyses (PROG CORR). In order to find indicators that affect N concentrations in the groundwater single and multiple stepwise linear regression analyses with all measured N species and other factors were performed using a PROG REG procedure. This procedure allowed a classification of the importance of the studied factors based on their significance in explaining the variance of measured variables. All relationships found were diagnosed for linearity, constant variance, outliers, normality and co-linearity. The annual N losses were subjected to two way analyses of variance (PROC MIXED) with a repeated measure covariance structure investigating the effect of the system, year and their interaction. Post hoc treatment comparisons were made according to Tukey and Bonferroni.

4.3 Results

4.3.1 Weather data

The annual rainfall in 2008 and 2009 was exceptionally high, 1405 and 1403 mm, respectively and exceeded ten years mean by 24% (Fig. 4.4a). In 2008, the highest monthly rainfall occurred in August (199 mm) and October (183 mm) and the lowest was recorded from February to May (from 48 to 118 mm $month^{-1}$). In contrast in 2009, the highest monthly rainfall occurred in November (310 mm) and January (205 mm) and the lowest was recorded from February to June (from 22 to 95 mm $month^{-1}$). Uncharacteristically wet weather conditions in 2008 and 2009 were also evident from water filled pore space records at 0.05 m depth indicating complete soil saturation during 14 months. Higher SMD values during the summer (16 to 27 mm day^{-1}) reflected drier soil conditions; however SMD did not exceed value of 40 mm day^{-1}. Mean estimated SMD in 2008/09 was 4 mm day^{-1} and in 2009/10 was 6 mm day^{-1} (Fig. 4.4d). The daily mean soil temperature at 0.05 m depth is shown in Fig. 4.4e. The monthly mean ranged from winter lows of 3.0°C to summer highs of 15.9°C. There was very little variation between the years (9.8°C in 2008 and 10.4°C in 2009). Rainfall typically exceeded evapotranspiration during seven months from July until January. Over the first groundwater sampling period (August 2008 to February 2009), site received 923 mm of rainfall, of which ER was 728 mm. Effective rainfall occurred on 108 days within this period, giving a mean recharge of 6.7 mm d^{-1}. Although the amount of rainfall was higher for the second groundwater sampling period (February 2009 to February 2010), the ER of 750 mm was only a slightly different from the previous sampling period. Effective drainage occurred during 115 days which resulted in recharge of 6.5 mm d^{-1} (Fig. 4.4c).

4.3.2 Vertical travel time, watertable depth and groundwater flow

The estimated vertical travel time through the unsaturated zone to shallow groundwater ranged between 0.21 and 0.57 years at different locations around the farm (Fig. 4.1). The watertable depth below the surface was relatively shallow (Fig. 4.3) and its seasonal variation could impose seasonal saturation of the topsoil. The mean watertable depth for the first and second sampling period was 0.69 (SD = 0.29) and 0.78 m bgl (SD = 0.29), respectively. The shallowest mean watertable depth was recorded in February 2010 with minimal and maximal contour of 147.8 and 154.7 m OAD, respectively. The deepest mean watertable was recorded in November 2009 with minimal and maximal contour of 147.3 and 154.7 m OAD, respectively.

The groundwater flow map (Fig. 4.2a) created in January 2010 shows groundwater flow direction mirroring surface topography. The watertable depth was intercepted by two deep narrow open drains constructed along the northern and western edge of the paddocks. Except for these possible receptors, there is also the larger river Pope bordering the farm on the south-east and east. The central area and north-west are up-gradient and hydrologically connected through shallow flow lines to down-gradient areas around the river in south-east. The minimal contour of 148.08 m AOD was located in the north-east of the farm, near the river. The maximal contour (155.17 m AOD) was observed on the top of the mound in the centre of the farm. The hydraulic gradient of the watertable between these two points is relatively high (3.5%) and is a reflection of a land slope. Groundwater head contours show groundwater flow direction towards the river, however there are some partial flows diverting from the main flow towards the drains in the north.

4.3.3 Effect of dairy production systems on N concentrations in groundwater

Mean concentrations of N species recorded in shallow groundwater under each of the dairy systems are presented in Table 4.3. There was a significant two way interaction (form $P<0.0001$ to $P<0.05$) between system and sampling date on concentrations of TDN, DON, oxidised N and NO_3^--N (Table 4.3, Fig. 4.5). In contrast, concentrations of NH_4^+-N and NO_2^--N were unaffected by the dairy system, however, the effect of the sampling date was highly significant ($P < 0.0001$). The mean C:N ratio of the dissolved organic matter was quite low (12.0. or 13.3) and also influenced by two way interaction ($P < 0.05$) between the dairy system and sampling date.

4.3.4 Spatial and temporal pattern of nutrient concentrations in groundwater

The temporal variation of N concentrations in shallow groundwater is presented in Fig. 4.5; their spatial variation around the farm is illustrated using groundwater nutrient contour maps (Fig. 4.6). Although, there was a considerable within year variation observed for all concentrations of N species in groundwater (Table 4.3, Fig. 4.5), the concentrations were independent of weather variables. There were no relationships found between the concentrations and amount of rainfall, ER, SMD or soil temperature on a daily, weekly or monthly basis. While there was no clear seasonal pattern observed for concentrations of DON, DIN concentrations, particularly NO_3^--N exhibited sharp increases and declines during both winter seasons. This pattern was not observed for Cl^- concentrations (Fig. 4.5).

Some of the spatial and temporal variation of N concentrations was explained by the relationships with the chemical and hydro-topographical variables (Table 4.4). The coefficient of multiple determination (model R^2) represents the proportion of variation explained by all independent variables. However, for each combination of independent and dependent variables, the partial correlation coefficient (partial R^2) measured the strength of the correlation between two variables when the effects of other variables were held constant.

4.3.4.1 DON

Dissolved organic N concentrations ranged from 0 to 50.28 mg L^{-1}, with a mean of 2.16 mg L^{-1}. The model developed as a result of multiple linear regression analysis between DON mean concentrations and some chemical and hydro-topographical variables explained 47.9% of the variation ($P < 0.001$; Table 4.4). The concentrations were positively influenced by NO_3-N/Cl^- ratio ($R^2 = 0.213$, $P = 0.012$) and by the distance of the sampling point from the closest receptor ($R^2 = 0.266$, $P = 0.001$). Elevated concentrations of DON were observed around the farm yard migrating down gradient (August 2008 to May 2009) and in the south-west corner of the farm (August 2008 to March 2009; Fig. 4.6a).

4.3.4.2 Ammonium N

The concentrations of NH_4^+-N were lower compared with DON, within the range of 0 to 14.11 mg L^{-1}, with a mean value of 0.35 mg L^{-1}. Multiple linear regression analysis between mean concentrations and some selected variables explained 88.7% of the variation ($P < 0.0001$; Table 4.4). The model indicated that the NH_4^+-N concentrations were positively correlated to NO_3-N/Cl^- ratio ($R^2 = 0.639$, $P < 0.0001$), watertable depth ($R^2 = 0.179$, $P < 0.0001$), distance of the sampling point from the closest receptor ($R^2 = 0.039$, $P = 0.015$) and elevation of the sampling screen ($R^2 = 0.031$, $P = 0.018$). Increased NH_4^+-N concentrations were detected in the western part of the farm along an old drain (September 2009 to February 2010), around the farm yard (March to September 2009) and in the south-west corner of the farm (September to December 2008; Fig. 4.6b).

4.3.4.3 Nitrate N

Nitrate concentrations ranged from 0 to 4.24 mg L^{-1} with a mean of 0.37 mg L^{-1}. However, increased concentrations were recorded on the top of the mound in the central part of the farm migrating down gradient (September 2008 - December 2008, November 2009 - February 2010); in the south-west corner of the farm (September 2008 - February 2009) and on the northern farm boundary (all year round; Fig. 4.6c). From all the selected factors the concentrations of NO_3^--N were positively correlated only to the depth of sampling piezometer ($R^2 = 0.210$, $P = 0.013$; Table 4.4).

4.3.4.4 Nitrite N

The levels of NO_2^--N were very low, lower than 0.52 mg L^{-1}. Despite this, the developed model explained the variation very well ($R^2 = 0.826$, $P < 0.0001$; Table 4.4). The most important controlling factor influencing NO_2^--N levels was NO_3-N/Cl^- ratio ($R^2 = 0.592$, $P<0.0001$), DOC concentration ($R^2 = 0.110$, P =.0.045), water table depth ($R^2 = 0.072$, $P = 0.090$) and the distance of the sampling point from the closest receptor ($R^2 = 0.051$, $P = 0.014$). All the factors were affecting the concentrations positively.

4.3.4.5 Cl^- anion and Nitrate/Cl^- ratio

Exceptionally high variation was observed for Cl^- concentrations ranging from 2.77 to 199.02 mg L^{-1}, giving a mean of 17.45 mg L^{-1}. The distribution of Cl^- concentration in shallow groundwater was positively related to watertable depth ($R^2 = 0.291$, $P = 0.003$) and to the distance of the sampling point from the closest receptor $R^2 = 0.159$, $P = 0.011$). Elevated concentrations of Cl^- were observed around the farm yard migrating down gradient (August 2008 - December 2008; March 2009 - November 2009); in the south-west corner of the farm (August 2008 - November 2009) and on the northern farm boundary (August 2008 - January 2009, September 2009 - January 2010; Fig. 4.2c).

Nitrate/Cl^- ratio, a proxy for point source proximity, occurred within the range of 0 to 0.59 with peaks recorded in the western part of the farm along the old drain (November 2009-February 2010) and in the south-west corner of the farm (September 2008-January 2009; Fig. 4.6d).

4.3.4.6 Dissolved reactive phosphorus

Concentrations of dissolved reactive phosphorus were negligible in comparison with other N species concentrations

4.3.5 Annual losses of N to groundwater (after buffering effect of soil)

Annual losses of all N species from the dairy production systems to groundwater buffered by biochemical processes are presented in Table 4.5. The dairy system had no effect on the losses, except for DON. The DON losses from ES-100N were higher by 14 and 27% in 2008/09 and 2009/10, respectively, compared with losses from systems receiving no fertilizer ($P < 0.05$). Dissolved organic N represented 61% and 84% of overall losses in the 2008/09 and 2009/10 periods, respectively. Nitrate N comprised only a small proportion (between 7.9 and 20.2%) of the N losses to groundwater.

Although, cumulative ER caused similar recharge during both sampling periods (728 to 750 mm), the seasonal differences in concentrations led to differential losses over time (Fig. 4.7). The recharge to groundwater occurred more gradually and uniformly during 2008/09; the seasonal pattern of N leaching was similar in all dairy systems and highly depended on the amount of ER. The discrepancy in N leaching between the systems was observed during 2009/10, when losses from ES-100N were higher between March and October compared with systems receiving no fertilizer. However, from October 2009 onwards N leaching from all the systems followed the same seasonal pattern; losses quickly rose due to increased ER and N concentrations followed by decline from November to January as a result of decreased N concentrations, while ER was still high (Fig. 4.7). Dissolved inorganic N losses were significantly lower ($P < 0.05$) in 2008/09 compared with 2009/10. Despite this, the overall N losses between 2008/09 and 2009/10 were not significantly different (Table 4.5).

4.4 Discussion

4.4.1 Weather data

The years of the study had exceptionally high rainfall compared with previous years. This resulted in a higher soil moisture content, higher annual ER and longer drainage seasons (between 108 and 115 days) in both years. High soil moisture conditions led to long periods of anoxic conditions of the soils with considerable redox potential. This promoted reduction biochemical processes such dissimilatory NO_3^- reduction to NH_4^+ (DNRA) and denitrification while mineralisation rates were reduced. The watertable fluctuations across the site were consistent with recharge and also seem to be consistent across the site. Therefore biochemical processes in the soil rather than dilution during vertical migration in the unsaturated zone and mixing in shallow groundwater controlled N concentrations in groundwater.

4.4.2 Vertical travel time, watertable depth and groundwater flow

Depth to the watertable on site was low (therefore unsaturated zone was thin) and, despite fluctuations, remained close to the surface throughout the study. Vertical travel time to groundwater, within or just longer than a single drainage season, calculated in this study agreed with those found by Fenton et al. (2009a). Such time lag allow management and groundwater concentrations (which take a certain time to migrate vertically to groundwater and thereby affect nutrient concentrations) to be compared in an accurate way. The travel times can be justified by the high ER during the study period and the sites high effective porosity values ranging from 19% to 49%.

4.4.3 Effect of dairy production systems on N concentrations in groundwater

In the present study, the concentrations of all N species in shallow groundwater exhibited a large variation within the dairy systems (Table 4.4). A significant two way interaction of the system and sampling date on N concentration of TDN, DON, oxidised N and NO_3^--N indicated that the extent of the main dairy system effect on water quality changed over time. This could be a result of a timing of single successive grazing occasions. However from the statistical analyses it is clear that the effect of the sampling date was notably more important than the dairy system (Table 4.4). Hence, the winter grazing in the LS-0N system did not have a greater deleterious impact on groundwater quality than the earlier calving dairy systems.

4.4.4 Spatial and temporal pattern of nutrient concentrations in groundwater

Despite the fact that the paddocks within the systems had been under almost uniform management, the nutrient contour maps indicated a considerable spatial variation in the concentration of N species in shallow groundwater. Chloride is often used as a conservative tracer to investigate anthropogenic sources in groundwater. The natural background concentration of Cl^- in Ireland is ~ 18 mg L^{-1} (Fenton et al., 2009b) and therefore concentrations below this are generally not from manure or sewage sources. The principal point sources of N contamination indicated by increased NO_3^--N /Cl^- ratio were located in the western part of the farm along the old drain, in the south-west corner of the farm, in the area around the farm yard and on the northern farm boundary (Fig. 4.6d). Some of them are still present (farm yard) and the others have been removed some time ago – i. e. dirty water irrigators (western part of the farm along an old drain), however still affecting the concentrations in groundwater. Horizontal movement on site is slow and therefore the legacy from such sources may remain for some time. Apart from these sources, the recent water quality on the farm is also being influenced by the diffuse sources of contamination such as fertilization and grazing management.

The characterization of spatial and temporal variation in the concentrations provides insights into the control of the distribution of N species and their losses. A considerable temporal variation in N concentrations in shallow groundwater independent of weather variables indicated that the shallow groundwater chemistry is rather controlled by soil parameters (e.g. physical structure, heavy texture and high soil organic matter content) than by ER. However, the weather variables such as rainfall, ER and SMD control the vertical travel time to the watertable. Considering, that this study took place under humid oceanic climatic conditions with exceptionally high rainfall and ER, the vertical travel time of solutes from the soil surface to shallow groundwater (<2.2 m) was short.

On the basis of available data it was not possible to investigate the correlations between soil parameters responsible for the control over groundwater chemistry and N concentrations in groundwater in the present study. However, some hydro-topographical and chemical factors have been analysed in order to explain the variation of N species in shallow groundwater. A high explanatory power of selected variables indicated heterogeneity in hydro-topographical properties between the sampling locations and thus heterogeneity in N transport pathways which affect the spatial distribution of N in the shallow groundwater. However the present models are applicable only to shallow groundwater at Solohead Research Farm.

4.4.4.1 DON

Dissolved organic nitrogen concentrations on site were high (mean of 2.16 mg L^{-1}) and dominant to the other N species, which comprised only a small proportion of TDN in the shallow groundwater. In general, N in groundwater occurs almost exclusively as NO_3^--N as ammonification and nitrification occur in the unsaturated zone and NO_3^--N is mobile in soils to be transported to groundwater in high quantities (Bouwman et al., 2005, Kroeger et al., 2006). There has been very limited attention paid to DON leaching from agricultural systems (Van Kessel et al., 2009) in the past and thus very little is known on the role of DON in the N cycle in agricultural soils (Murphy et al., 2000). It originates from applied manures, dung and urine deposited via grazing animals, plant litter leachates, microbial and root exudates, and hydrolysis of insoluble soil organic matter (Haynes, 2005) and can be subsequently transported in a dissolved or colloidal form (Green et al., 2008). It usually consists of high molecular weight complex humic substances (polyphenol-bound N), which are resistant to microbial attack and unavailable for plant uptake (Stepanauskas et al., 2002; Marschner and Kalbitz, 2003; Neff et al., 2003; Jones et al., 2004; Dijkstra et al., 2007); consequently it turns over slowly and contributes to N leaching to groundwater. In general, DON concentrations beneath the managed grasslands vary between 0.025 mg L^{-1} and 10 mg L^{-1} (Watson et al., 2000; Siemens and Kaupenjohann, 2002; Jones et al., 2004; Vinther et al., 2006, Van Kessel et al., 2009). High DON leaching on this site indicates high DON production, which may be attributed to the presence of legumes in the swards (Oelmann et al., 2007), application of organic manures (Murphy et al., 2000) or slow decomposition processes associated with high soil moisture content (Trasar- Cepeda et al., 2000; Aitkenhead- Peterson et al., 2002). A positive correlation with NO_3^--N/Cl^- ratio also indicates point source influence. Elevated concentrations around the farmyard are likely to be a result of runoff from the yard, milking shed, and slurry and dirty water collection and storage. Horizontal migration of DON with groundwater flow towards lower groundwater elevation is being caused by the differences in hydraulic gradients. In addition, a positive relationship between DON concentrations and the distance of the sampling point from the closest receptor reveals that the River Pope and local drains interact with the groundwater, cause a dilution when the watertable is very shallow and consequently reduce the concentrations of DON at the groundwater-surface water interface.

4.4.4.2 Ammonium N

Ammonium concentrations were also high and comprised more than 45% of DIN. In general, it is directly applied to soils in manures, fertilizers or via urine (after urea hydrolysis in the litter zone) and leached down the profile to be nitrified at depth (Mian et al., 2009). The ion is positively charged and therefore can be bound to negative exchange sites of soil organic matter or clay particles (Feigenbaum et al., 1994; Stark and Richards, 2008). It is highly soluble and mobile when aminization and ammonification are inhibited by low temperatures, or at very high concentrations such as beneath urine patches (Mian et al., 2009). However, elevated DON and NH_4^+-N concentrations in conjunction with low NO_3^- concentrations across the farm and inherent properties of the soils on site are more indicative of DNRA (Kartal et al., 2007, Francis et al., 2007). This biochemical process is mainly mediated by bacteria that are obligate and facultative anaerobes with fermentative metabolism (Koike and Sorenson, 1988). Consequently the process takes place in highly anaerobic soils with high soil organic carbon content (Buresh and Patrick, 1978, Sorenson, 1978), in the same conditions as denitrification (Tiedje et al., 1981; Hill, 1996). The multiple linear regression model in the present study showed that the concentrations of NH_4^+-N were also increased by point sources (western part of the farm along the old drain, around the farm yard and in the south-west corner of the farm) and diluted by the river in the same way as DON. Furthermore, since watertable depth explained a lot of variation in NH_4^+-N, it is assumed that the increased thickness of unsaturated zone allows for a greater time for biochemical transformation (i.e. aminization, ammonification, DNRA) to take place (National Research Council, 1993) and consequently results in higher concentrations in groundwater.

4.4.4.3 Nitrate N

The NO_3^--N concentrations were consistently low, well below the maximum allowable concentration (MAC) of 11.3 mg NO_3^--N L^{-1} for groundwater throughout the study period. Substantial and inconsistent peaks in NO_3^--N relative to Cl^- concentrations provided evidence of substantial biochemical processes taking place in the unsaturated zone. Decreases in concentration could be partially attributed to immobilization by plants (Peterjohn and Correll, 1984; Haycock and Pinay, 1993) or microbes to sustain primary production. However, considering the anaerobic nature of the soils and high soil organic carbon content down to 0.9 m in the soil profile (Table 4.1), low NO_3^--N concentrations in this study are more likely attributed to soil biochemical processes such DNRA (Hill, 1996) or denitrification (Jacobs and Gilliam, 1985; Lowrance, 1992). The presence of these biochemical processes on site may have contributed to the absence of significant water quality responses. Humphreys et al. (2008b) reported a lack of effect of management practices at the surface on water quality at Solohead Research Farm in 2001 and 2002. Mean NO_3^--N concentrations were < 3.0 mg L^{-1}, not exceeding MAC limit during the experimental period and N losses to shallow groundwater were low and largely independent of N inputs, N surpluses, deposition of excreta-N at the soil surface and residual inorganic N in the soil at the start of the drainage season (Humphreys et al., 2008b). Elevated concentrations of NO_3^--N in the present study, recorded on the top of the mound in the central area of the farm relate to the presence of a gravel lens (Fig. 4.2a). The permeability of the gravel lens allows greater leaching at this location and the buffering capacity of the soil is absent as elsewhere on the farm. In addition, the occurrence of highly permeable gravel and the deep watertable increase residence time in presumably aerobic unsaturated zone. This might enhance nitrification rather than denitrification or DNRA at this location. In addition, a positive correlation to the depth of sampling piezometer (depth of screen opening of 0.2 m) points to vertical stratification of NO_3^--N concentrations in groundwater.

4.4.5 Annual losses of N to groundwater (after buffering effect of soil)

The effects of the dairy systems on N losses through leaching were based on their effects on N concentrations in the groundwater. Higher DON losses from ES-100, due to higher DON concentrations compared with the systems receiving no fertilizer could be explained by higher stocking density of grazing animals in this system and thus by higher deposition of excreta over the treatment area. There was no evidence of higher annual N losses to groundwater from the system involving grazing over winter compared with earlier spring calving dairy production systems during both experimental years. Lack of a difference is likely due to buffering capacity of the soils on site.

Since ER caused similar recharge in 2008/09 and 2009/10, the volume of rainfall draining through the root zone each year was not responsible for the differences in N losses between the years. Consequently year to year variation in the DIN and DON losses was likely led by the differences in the pattern and intensity of the rainfall or differences in N concentrations. As the performance of dairy systems did not change, increased DIN concentrations (NO_3^--N and NH_4^+-N) in 2009/10 were likely caused by enhanced mineralisation.

The N leaching from all systems in the 2009/10 followed a typical pattern described in previous leaching studies. An initial increase in losses was followed by a decrease after a peak concentration had been reached at the end of the drainage season, because essentially all N had been washed out of the soil by that time (Steele et al., 1984; Heng et al., 1991; Oenema et al., 1998; Scholefield et al., 1993; Silva et al., 1999; Decau et al., 2003).

High DON losses from grazed grasslands have been previously reported (Dick et al., 2000), and it has been postulated that they may be an important component of N flux to groundwater (Murphy et al., 2000). Reported losses were highly variable and ranged from 0.3 kg DON $ha^{-1}yr^{-1}$ in a grass clover system (Saarijarvi et al., 2004) to a maximum of 127 kg DON $ha^{-1}yr^{-1}$ in a pasture following the application of urine (Wachendorf et al., 2005; Van Kessel et al., 2009). Thus, the annual DON losses reported here were within the range of values previously published for grazed grasslands. The majority of NO_3^--N losses to groundwater were attenuated by soil organic carbon rich and anaerobic soils (discussed above). High losses of NH_4^+-N were also indicative of biochemical processes (i.e. DNRA) while migrating throughout unsaturated zone. The loads of DON measured in deep multi level wells (up to 30 m bgl) on site (Jahangir et al., 2012) in 2009/10 were considerably lower (1 kg N ha^{-1} yr^{-1}) in comparison with DON losses measured in the present study. On the other hand, the loads of NO_3^--N were noticeably higher (4.5 kg N ha^{-1} yr^{-1}). This indicates that DON and NH_4^+-N undergo further mineralisation and nitrification while moving throughout subsoil sediments and bedrock formations. Although, the loads of DON and NH_4^+-N are quite high, the horizontal movement to the receptor on site (the River Pope) is very slow (Fenton et al., 2009a) and therefore they are unlikely to deteriorate the surface water quality, unless the sources are close to the local drains connected directly to the river.

4.5 Conclusions

In this study we evaluated the impact of dairy production systems on a clay loam soil on N concentrations and N losses to groundwater over a two year period. A dense network of shallow groundwater piezometers was installed to determine groundwater flow direction, and N spatial and temporal variation. Vertical travel time of approximately one drainage season due to a shallow watertable and high ER allowed correlations between nutrient losses and shallow groundwater nutrient concentrations within a small time lag period. However, the high natural attenuation and denitrification capacity of the soil due to high C and anaerobic conditions ensured low concentrations of nutrients making correlations difficult; i.e. grazing over the winter period had no effect on groundwater quality on this site. The results indicate that any losses from the dairy production systems were instantaneously reduced by denitrification and DNRA, which consequently resulted in increased NH_4^+-N levels. For this reason, DON and NH_4^+-N represented the highest proportion of N losses, presently migrating slowly towards receptors on site. Some of the spatial and temporal variation of N concentrations was explained by correlations with selected chemical and hydro-topographical parameters. Strong correlations to NO_3^--N/Cl^- ratio and the distance of the sampling point from the closest receptor indicated presence of point sources of contamination and groundwater-surface water interactions on site.

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Table 4.1 Soil properties at Solohead Research Farm at three different depths. All values are means of at least three determinations with standard deviations in parentheses.

Depth	Sand	Silt	Clay	Bulk density	Particle density	Total porosity	CEC	pH	Total N	Total organic C	Total inorganic C	Organic matter†	C:N ratio
m	%	%	%	g cm^{-3}	g cm^{-3}	%	Meq/100gDM		%	%	%	%	
0.0-0.3	36.7 (6.4)	35.0 (3.5)	28.3 (3.1)	1.09 (0.16)	2.52 (0.15)	58.7 (6.5)	25.4 (2.3)	6.60 (0.2)	0.48 (0.05)	4.48 (0.52)	0.09 (0.03)	6.55 (0.84)	9.34 (0.27)
0.3-0.6	36.0 (4.4)	36.0 (2.0)	28.0 (2.7)	1.43 (0.26)	2.59 (0.15)	44.5 (10.2)		7.00 (0.2)	0.22 (0.05)	2.02 (0.41)	0.08 (0.08)	2.74 (0.53)	9.09 (0.28)
0.6-0.9	36.0 (6.1)	35.7 (3.2)	28.3 (2.9)	1.70 (0.20)	2.67 (0.20)	37.1 (6.8)		7.65 (0.2)	0.06 (0.02)	0.49 (0.16)	0.54 (0.29)	1.63 (0.84)	7.88 (0.69)

† calculated from loss on ignition results (%) using the Ball's equation: OM = (0.476*loss on ignition) - 1.87 (Ball, 1964)

Table 4.2 Details of the experimental systems at Solohead Research Farm in 2008 and 2009. Each system was stocked with 18 Holstein-Friesian dairy cows. ES-100N - early spring calving with Fertiliser N. ES-0N - early spring calving without Fertiliser N. LS-0N - late spring calving without Fertiliser N.

	2008			2009		
	ES-100N	ES-0N	LS-0N	ES-100N	ES-0N	LS-0N
Mean first grazing date	14th Feb	14th Feb	14th Apr	13th Feb	13th Feb	15th April
Mean last grazing date	12th Nov	12th Nov	14th Jan	18th Nov	18th Nov	26th Jan
Mean days grazing cow^{-1}	220	234	231	218	234	235
Total area (ha)	8.5	11.3	14.2	8.5	11.3	14.2
Proportion of area harvested for silage						
1st cut (Apr – May)	0.5	0.3	0.5	0.4	0.2	0.5
2nd cut (Jun – Jul)	0.0	0.4	0.2	0.1	0.3	0.5
Stocking rates on grazing areas (cows ha-1)						
Feb-Mar	2.1	1.6		2.1	1.6	
Apr-May	4.2	2.3	3.4	3.4	2.0	3.2
Jun-Jul	2.1	2.8	2.3	2.4	2.4	3.3
Aug-Sep	2.1	1.6	1.7	2.1	1.6	1.7
Oct-Nov	2.1	1.6	1.3	2.1	1.6	1.3
Dec-Jan			1.3			1.3
Total stocking rate	2.1	1.6	1.5	2.1	1.6	1.5

Table 4.3 Mean concentrations of N species and Cl^- in groundwater (mg L^{-1}) under three dairy production systems with standard deviations in the brackets. ES-100N - early spring calving with fertiliser N, ES-0N - early spring calving without fertiliser N, LS-0N - late spring calving without fertiliser N. P value<0.05 is significant.

	August 2008 - February 2010			P value		
mg L^{-1}	ES-100N (SD)	ES-0N (SD)	LS-0N (SD)	System	Date	System x date
Total N	3.13 (5.10)	2.79 (2.65)	2.90 (4.50)	0.079	0.0001	0.003
Dissolved organic N	2.35 (3.35)	2.06 (1.89)	2.09 (1.94)	0.077	<0.0001	<0.0001
Ammonium N	0.37 (0.95)	0.35 (1.03)	0.34 (0.80)	0.431	<0.0001	0.470
Total oxidised N	0.33 (0.37)	0.42 (0.53)	0.38 (0.49)	0.440	<0.001	0.006
Nitrite N	0.01 (0.02)	0.01 (0.04)	0.01 (0.03)	0.552	<0.0001	0.245
Nitrate N	0.33 (0.37)	0.41 (0.52)	0.37 (0.48)	0.443	<0.0001	0.004
C:N ratio	13.26 (8.61)	12.01(6.14)	12.05 (9.29)	0.441	<0.0001	0.012
Cl^-	18.50 (13.40)	15.97 (8.12)	17.84 (9.43)	0.221	<0.0001	0.024

Table 4.4 Results of single and multiple regression analyses between N and Cl^- concentrations in groundwater as dependent variable and some chemical and hydro-topographical factors as independent variables.

Dependent variable (mg L^{-1})	Chemical or hydro-topographical factor (a,b,c…)	Unit	Partial R^2	Partial P value	Relationship	Model R^2	Model P value
Total N (y)	NO_3-N/Cl^- ratio (a) distance from the receptor (b)	- m	0.258 0.278	0.0049 0.0005	y = 70.251a + 0.010b + 0.836	0.536	<0.0001
Dissolved organic N (y)	NO_3-N/Cl^- ratio (a) distance from the receptor (b)	m	0.213 0.267	0.0119 0.0012	y = 36.709a + 0.006b + 1.018	0.479	0.0002
Ammonium N (y)	NO_3-N/Cl^- ratio (a) watertable depth (c) distance from the receptor(b) elevation of the screen (d)	- m bgl m m AOD	0.639 0.179 0.039 0.031	<0.0001 <0.0001 0.0150 0.0176	y = 22.881a + 0.528c + 0.001b - 0.040d + 5.528	0.887	<0.0001
Oxidised N (y)	depth of sampling piezometer (e)	m			y = 0.247e + 0.016	0.214	0.0115
Nitrite N (y)	NO_3-N/Cl^- ratio (a) dissolved organic C (f) watertable depth (c) distance from the receptor (b)	- mg L^{-1} m bgl m	0.592 0.110 0.072 0.051	<0.0001 0.0045 0.0090 0.0138	y = 0.514a + 0.0003f + 0.012c + 0.00003b - 0.016	0.826	<0.0001
Nitrate N (y)	depth of sampling piezometer (e)	m			y = 0.238e + 0.020	0.210	0.0125
C^{l-} (y)	watertable depth (c) distance from the receptor (b)	m bgl m	0.291 0.159	0.0025 0.0111	y = 14.331c + 0.036b + 4.818	0.449	0.0004

Table 4.5 Mean annual losses of N species from three dairy production systems to groundwater (kg ha-1 yr-1) with standard deviations in the brackets. ES-100N - early spring calving with Fertiliser N, ES-0N - early spring calving without Fertiliser N, LS-0N - late spring calving without Fertiliser N.

	August 2008 - February 2009			February 2009 - February 2010			P values		
	ES-100N (SD)	ES-0N (SD)	LS-0N (SD)	ES-100N (SD)	ES-0N (SD)	LS-0N (SD)	System	Year	System x Year
Total N	22.9 (7.89)	21.4 (4.65)	20.0 (4.80)	19.2 (13.08)	18.4 (11.66)	19.3 (8.95)	0.271	0.202	0.797
Dissolved organic N	19.1 (5.39)	17.2 (2.76)	16.5 (3.44)	14.1 (11.04)	10.6 (4.48)	11.7 (4.72)	0.042	<0.0001	0.809
Ammonium N	1.9 (2.76)	1.4 (0.37)	1.3 (0.34)	2.6 (2.18)	3.2 (4.51)	3.0 (2.56)	0.796	0.011	0.597
Oxidised N	1.9 (0.64)	2.9 (2.70)	2.3 (1.57)	2.8 (1.16)	3.8 (2.45)	3.6 (2.45)	0.476	0.003	0.870
Nitrite N	0.03 (0.03)	0.04 (0.04)	0.04 (0.05)	0.06 (0.05)	0.11 (0.12)	0.09 (0.10)	0.915	0.001	0.636
Nitrate N	1.8 (0.62)	2.8 (2.7)	2.2 (1.52)	2.8 (1.14)	3.7 (2.40)	3.5 (2.44)	0.465	0.004	0.865

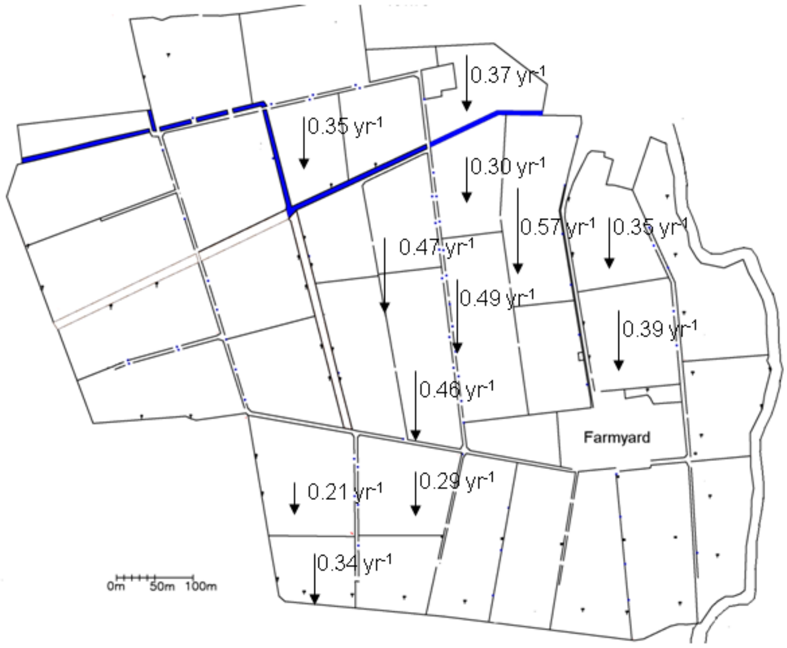
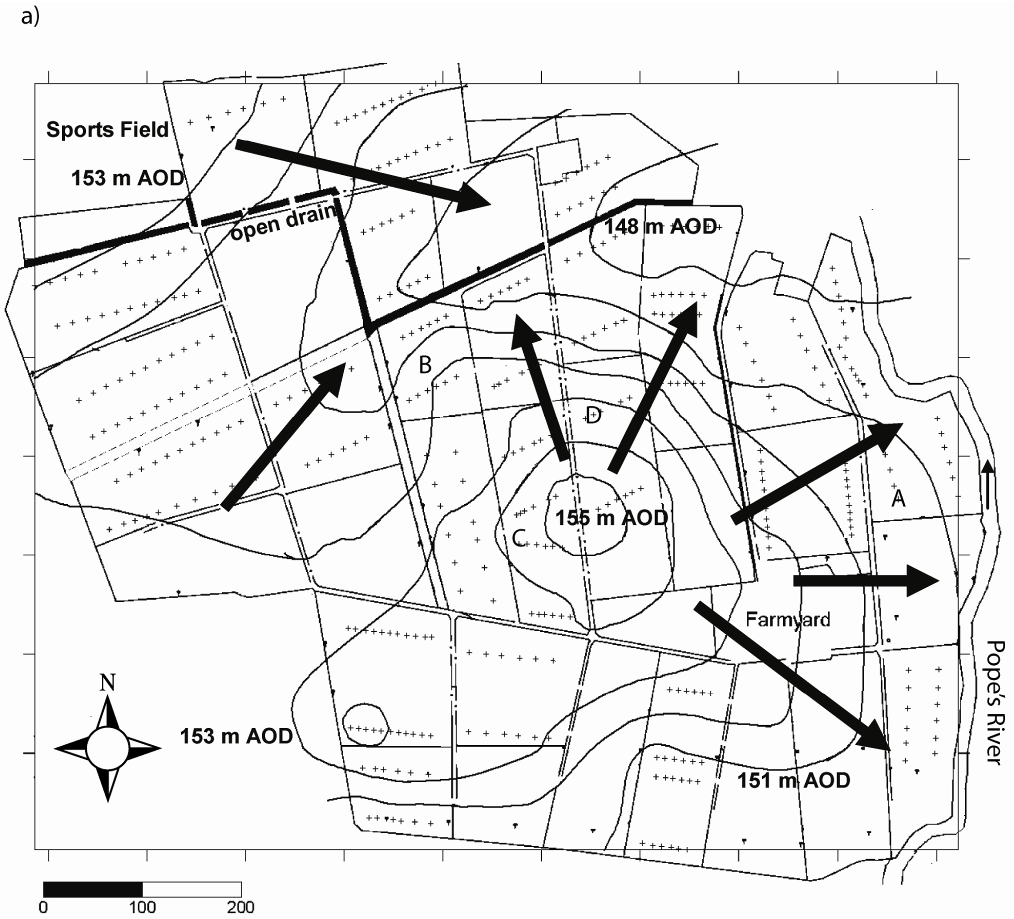
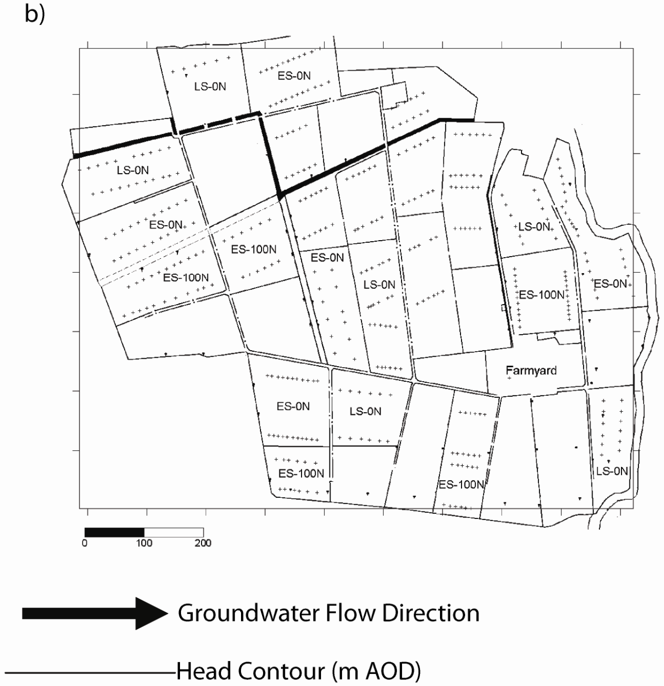


Fig. 4.1 Vertical travel time (yr) to shallow groundwater in several paddocks taking effective rainfall of 0.75 m.



A Slurry Tank - possible point source
B Old drain discharging to surface water - deep and interacts with groundwater
C Historical dirty water application site - possible point source
D Gravel lenses with increased infiltration capacity



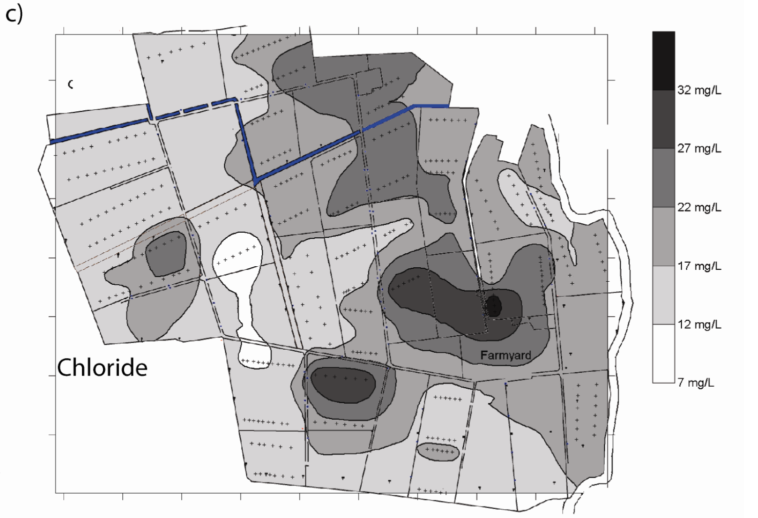


Fig. 4.2 a) Groundwater flow map at Solohead Research Farm. Groundwater head contours are based on watertable data from 380 wells installed in this area. Each well is indicated by a dot on the map; b) designated experimental treatments; c) chloride spatial distribution over experimental period.

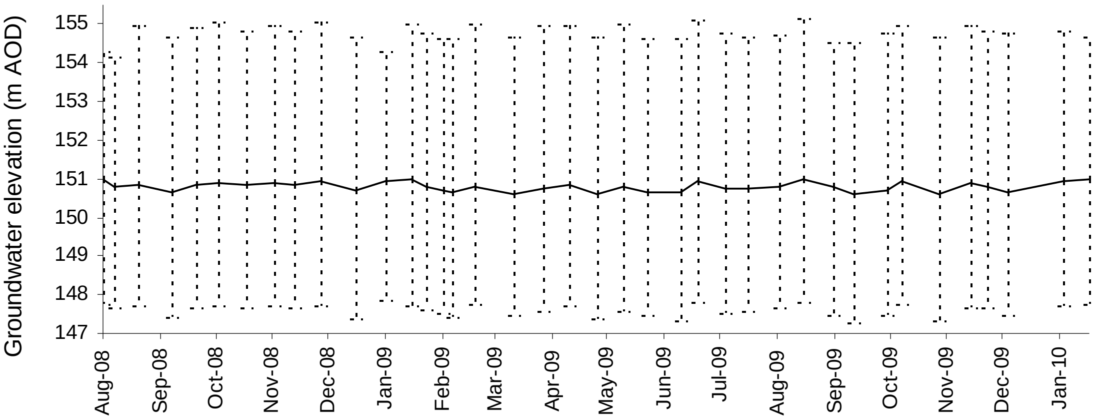


Fig. 4.3 Mean groundwater level (m AOD). Vertical bars represent the maximum and minimum level.

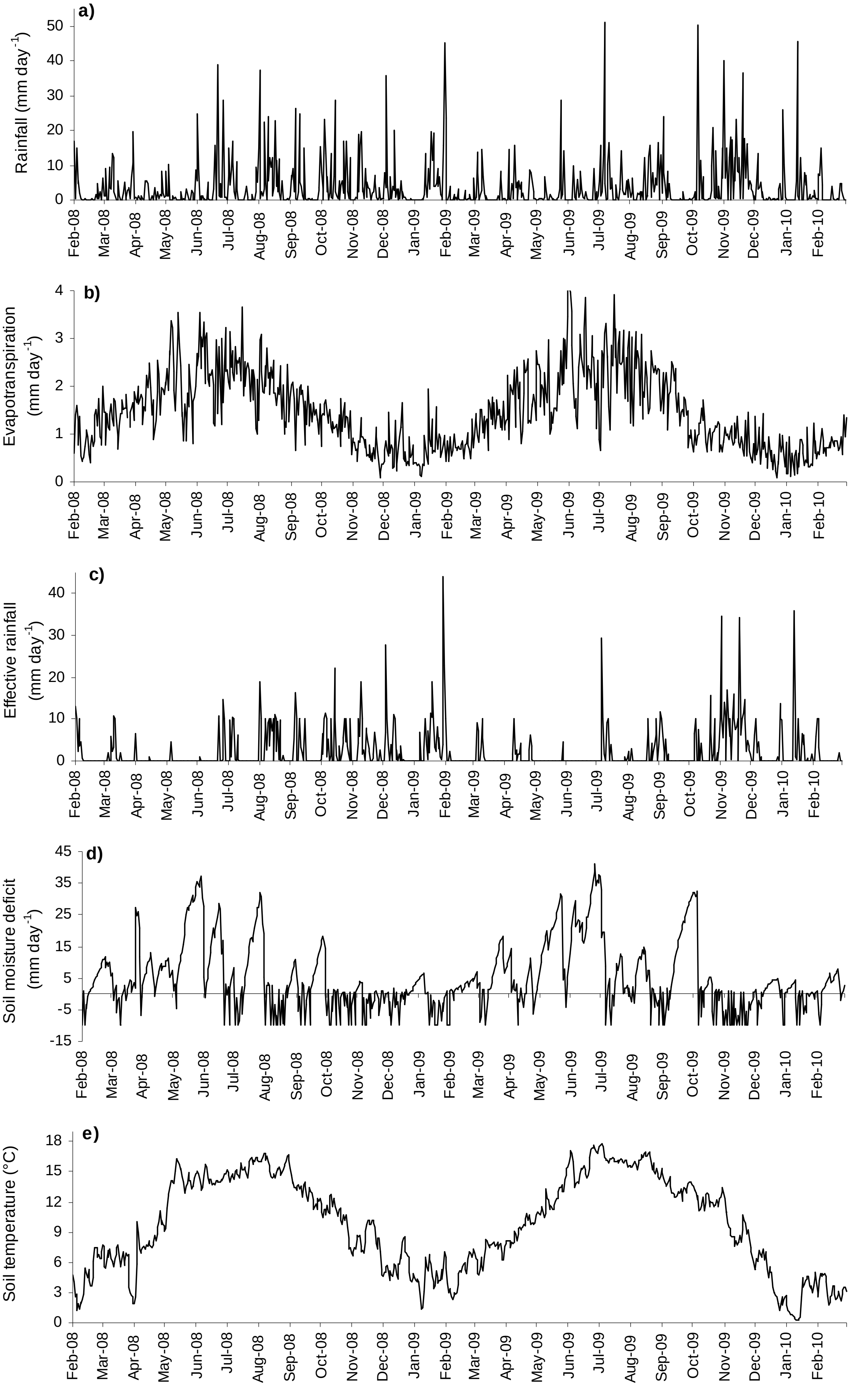
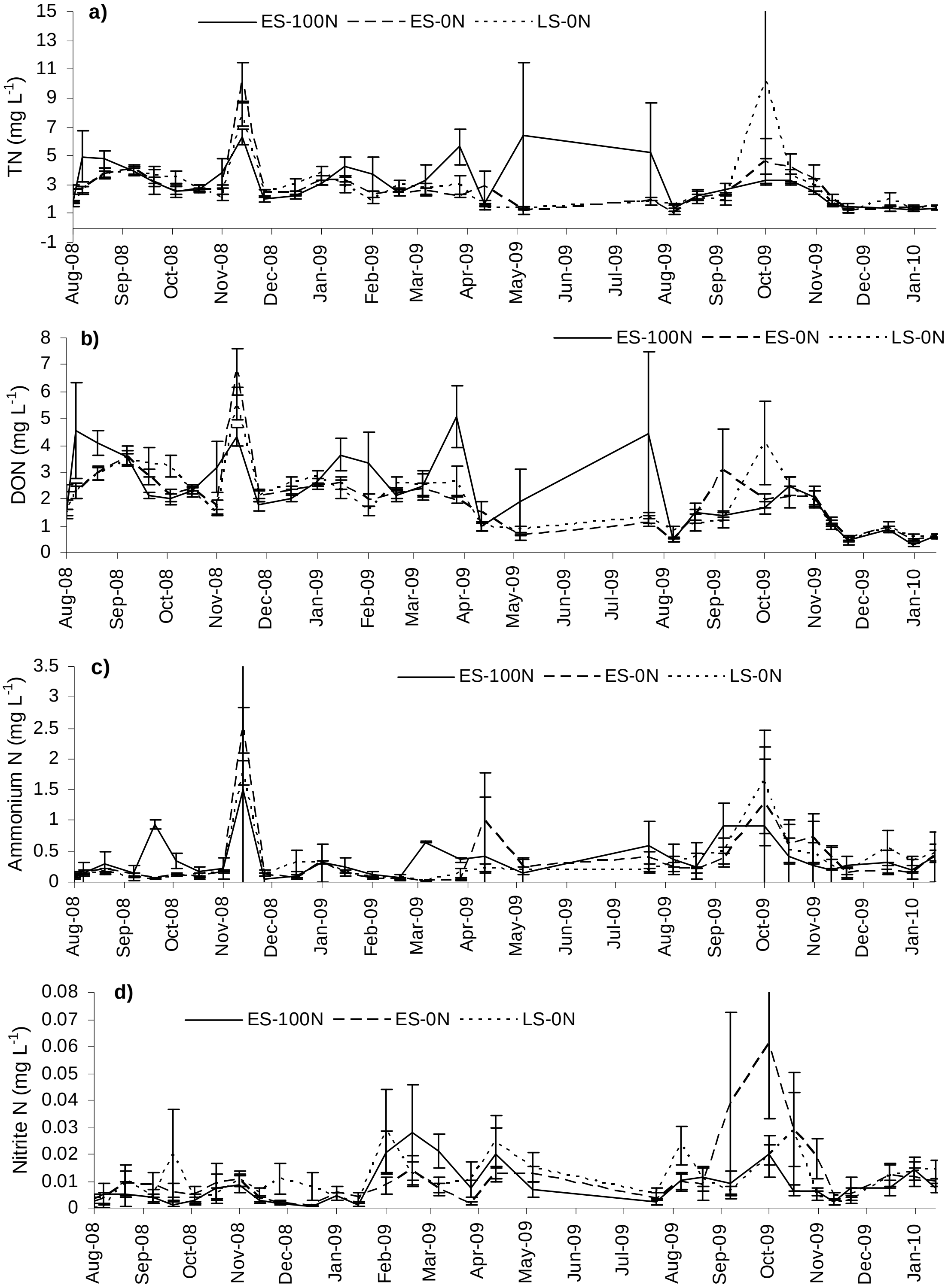

a)
Rainfall (mm day^{-1})
0
10
20
30
40
50
b)
Evapotranspiration (mm day^{-1})
0
1
2
3
4
c)
Effective rainfall (mm day^{-1})
0
10
20
30
40
d)
Soil moisture deficit (mm day^{-1})
-15
-5
5
15
25
35
45
e)
Soil temperature (°C)
0
3
6
9
12
15
18
Feb-08
Mar-08
Apr-08
May-08
Jun-08
Jul-08
Aug-08
Sep-08
Oct-08
Nov-08
Dec-08
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10
Feb-10

Fig. 4. 4 Meteorological data at Solohead Research Farm from February 2008 to February 2010: a) daily rainfall (mm d^{-1}), b) daily evapotranspiration (mm d^{-1}), c) effective rainfall (mm d^{-1}), d) soil moisture deficit (mm d^{-1}) and e) daily mean of soil temperature at 0.05 m depth (°C).


a)
ES-100N
ES-0N
LS-0N
TN (mg L-1)
-1
1
3
5
7
9
11
13
15
b)
DON (mg L-1)
0
1
2
3
4
5
6
7
8
c)
Ammonium N (mg L-1)
0
0.5
1
1.5
2
2.5
3
3.5
d)
Nitrite N (mg L-1)
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
Aug-08
Sep-08
Oct-08
Nov-08
Dec-08
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10

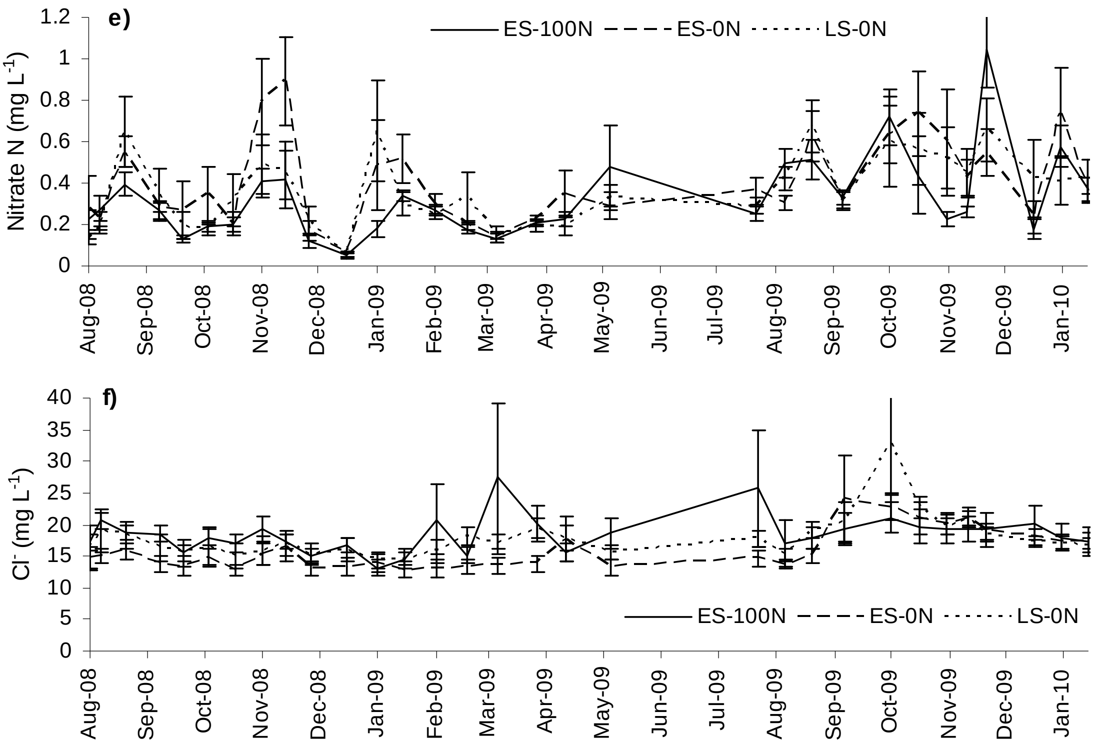
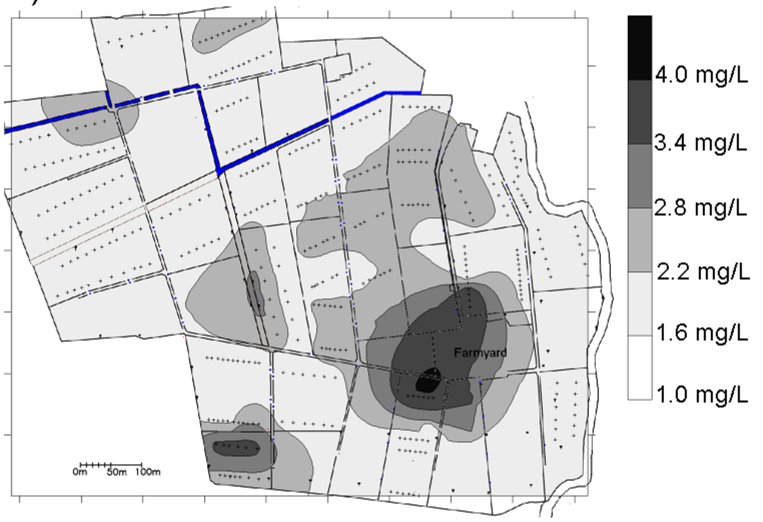
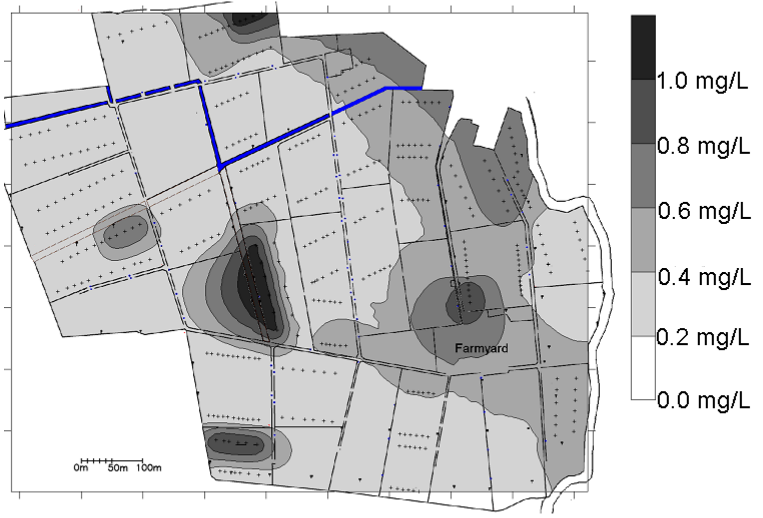


Fig. 4.5 Temporal variation of concentrations (mg L^{-1}) of a) total N (TN), b) dissolved organic N (DON), c) ammonium N, d) nitrite N, e) nitrate N and f) chloride in groundwater under three dairy systems: ES-100N - early spring calving with Fertiliser N, ES-0N - early spring calving without Fertiliser N, LS-0N - late spring calving without Fertiliser N. Error bars are SE.

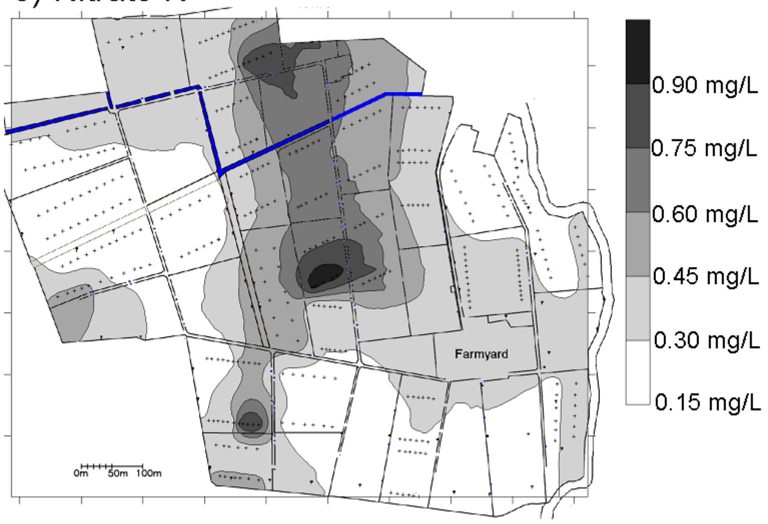
a) DON

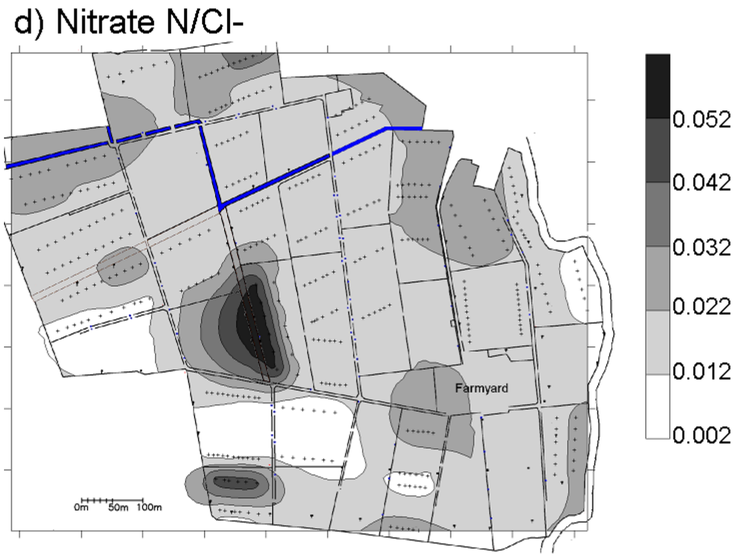


b) Ammonium N



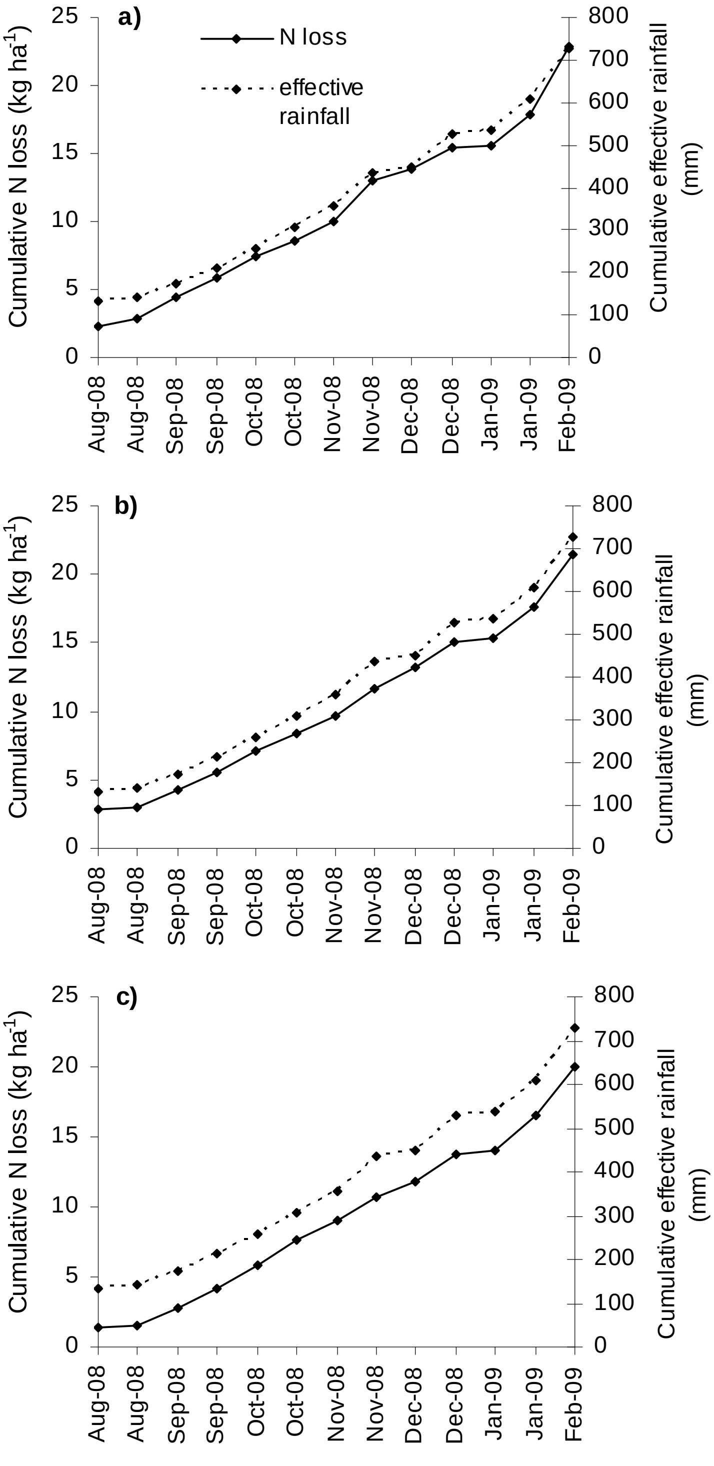
c) Nitrate N





d) Nitrate N/Cl-

Fig. 4.6 Spatial distribution across the farm (mg L^{-1}) a) mean dissolved organic N (DON) b) ammonium N c) nitrate N and d) associated nitrate/Cl^- ratio in shallow groundwater over the study period


a)
b)
c)
N loss
effective rainfall
Cumulative N loss (kg ha^{-1})
Cumulative effective rainfall (mm)
0
5
10
15
20
25
0
100
200
300
400
500
600
700
800
Aug-08
Aug-08
Sep-08
Sep-08
Oct-08
Oct-08
Nov-08
Nov-08
Dec-08
Dec-08
Jan-09
Jan-09
Feb-09

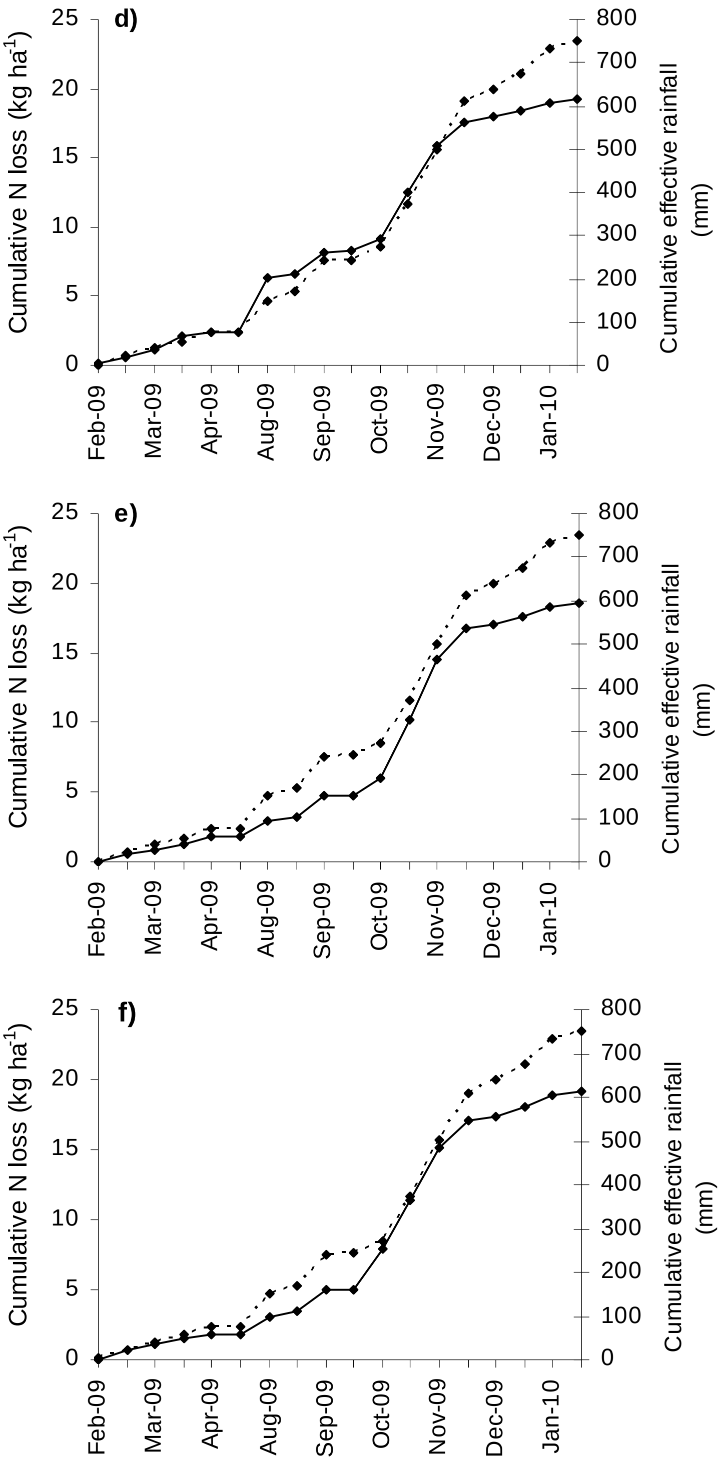


Fig. 4.7 Cumulative N losses (kg ha^{-1}) from three dairy production systems to groundwater in relation to cumulative effective rainfall (mm) in 2008/09: a) early spring calving with Fertiliser N, b) early spring calving without Fertiliser N, c) late spring calving without Fertiliser N and in 2009/10: d) early spring calving with Fertiliser N e) early spring calving without Fertiliser N, f) late spring calving without Fertiliser.

5. Effect of ploughing and reseeding of permanent grassland on soil N, N leaching and nitrous oxide emissions from a clay-loam soil

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Submitted to *Nutrient Cycling in Agroecosystems.*

Conference papers and other publications:

Necpalova, M., Keogh, B., Fitzgerald, E. and Humphreys J. (2009) Effect of cultivation of clover based grassland on N losses to groundwater on a clay-loam soil. Research reports 2009, Teagasc, Moorepark dairy production research centre, Fermoy, Co. Cork, pp. 81.

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Abstract

This study evaluated the effect of grassland renovation on soil total N (TN), soluble N, N leaching to groundwater and nitrous oxide (N_2O) emissions from a clay loam soil on a dairy farm. The experimental area was divided into eight blocks with four paddocks per block (≥1ha). In June, one paddock in each block was renovated by ploughing and reseeding. A dense network of piezometers was installed to determine N concentrations in shallow groundwater. Soil TN along with soluble N assessed in KCl extracts was determined at three sampling depths to 0.9 m. The N_2O fluxes were measured using the static chamber technique. Renovation decreased topsoil TN and soluble organic N ($P<0.05$) resulting in an average loss of 3.1 t and 13.4 kg N ha^{-1} in the 1.7 years following ploughing, respectively. Soil soluble inorganic N was unaffected. In contrast, renovation increased oxidised N in the groundwater ($P<0.0001$) for 1.2 years; dissolved organic N and ammonium remained unaffected. Renovation also increased N_2O fluxes ($P<0.0001$) for 1.3 years, although the peaks developed in response to commencement of grazing. The residual effect decreased as a function of time. The overall losses following renovation were high (>3 t N ha^{-1}), however, the proportion lost via N leaching and N_2O emissions was low (27.11 kg N ha^{-1}y^{-1}) and represented only 5.3% of the inputs into soil. Long periods of anoxic conditions, high soil carbon and considerable reduction potential of the soils likely promoted reduction biochemical processes such as dissimilatory nitrate reduction to ammonium and complete denitrification.

Keywords: permanent grassland, renovation, soil nitrogen, nitrogen leaching, shallow groundwater, N_2O emissions

5.1 Introduction

Permanent grasslands (PGs) are important sources of feed for intensively managed dairy and beef farming systems in North West Europe (Velthof et al. 2010). The proportion of the agricultural land under grassland ranges between 35 and 95% depending on the country (Smit et al., 2008). In Ireland, grassland production occupies about 90% of agricultural land (4 million ha; Richards et al. 2009). It has been often observed in practice that yields and quality of PG decrease during ageing, because of sward deterioration (i.e. compaction, poor drainage, sward composition, weed invasion, soil acidification or erosion) following extreme weather conditions and/or bad management (Velthof and Oenema 2001). For this reason, the managed grasslands are occasionally renovated (ploughed up and reseeded) in order to maintain or increase the sward productivity (Velthof et al. 2010), reduce weeds and maintain clover content (Humphreys and Lawless 2008). The grassland ecosystem accumulates organic nitrogen (N) in the soil (from 20 to 350 kg N ha^{-1} y^{-1}; Hassink 1994; Cute and Scholefield 1995; Velthof and Oenema 2001; Watson et al. 2007), soil microbial biomass and plant phytomass (herbage, roots and their exudates; Davies et al. 2001; Eriksen and Jensen 2001; Vinten et al. 2002). These become a part of dead soil organic matter (SOM) during ageing of grassland (Velthof et al. 2010). Ploughing of grassland leads to physical disruption of aggregates, increased soil aeration and consequently exposure of stable and adsorbed SOM within micro- and macro- aggregates to rapid microbial respiration, which releases inorganic N and provides substrates for nitrifying and denitrifying microorganisms (Six et al. 2004; Buss et al. 2005; Humphreys et al. 2009; Velthof et al. 2010). In addition, the disruption also decreases soil moisture, increases maximum soil temperature and thus accelerates mineralisation process (Lal 2004). For these reasons ploughing of grassland, particularly of long term grassland with a substantial organic N pool may temporarily increase soil inorganic N content. In the case of immediately reseeded grassland (RG), there is a period of several weeks with no or only a small crop uptake of N following ploughing. Thus, the amount mineralised may exceed the amount needed by the succeeding reseeded grass and leads to considerable losses from the soil system via a number of pathways including N leaching and/or nitrous oxide (N_2O)

emissions via nitrification and denitrification, particularly when high soil inorganic N contents coincide with high moisture conditions.

Increasing concentrations of N in the waterbodies and N_2O in the atmosphere have become an international environmental concern. Implementation of the European Union Water Framework Directive (WFD; European Parliament and Council 2000) is aiming to constrain N fluxes to the groundwaters and surface waters with an attempt to achieve at least ‘good ecological status’ for all waterbodies by 2015. By signing the Kyoto Protocol in 1997, governments of 37 industrialised countries agreed to reduce the emissions of the greenhouse gases (GHG) on average by 5% against the levels from 1990 over a five year period (2008-12). Ireland is committed to limit GHG emissions by 13% in the period 2008 to 2012, and by 25 to 30% in the period 2012 to 2020 compared with 1990 levels. To ensure compliance with the WFD and Kyoto protocol it is essential to identify major sources and practices that lead to pollution. Although considerable emissions via leaching and N_2O production following grassland renovation have been already reported (Davies et al. 2001; Mori and Hojito 2007; Velthof et al. 2010), a complete study investigating the fate of N by measuring soil N, N leaching and N_2O emissions following renovation of long term PG under humid conditions is lacking. And furthermore, there has not been an emission factor set up for N_2O emissions following ploughing of PG (IPCC 2011) so they are not yet accounted for in many national inventories of GHG emissions.

Hence, this study was set up to quantify environmental consequences and to explore the fate of N in grass-clover PG on a clay-loam soil being ploughed and reseeded on a dairy farm in southern Ireland with an emphasis on (i) total N (TN) content and soluble N dynamics in the soil profile down to 0.9 m depth, (ii) N leaching to shallow groundwater (<2.2 m below ground level; bgl) and on (iii) N_2O emissions. In order to find out if soil soluble N content at 0.3 to 0.9 m depth is an equivalent indicator of N leaching from clay loam soils to shallow groundwater, the contents were compared with N concentrations in groundwater during the study period.

5.2 Materials and Methods

5.2.1 Site description

The study was conducted at Solohead Research Farm (52 ha) in Ireland (52˚51'N, 08˚21'W) from February 2008 to February 2010. The local climate is humid temperate oceanic. Over the last 10 years the site received on average 1018 mm of annual rainfall and this resulted in mean annual effective rainfall (ER) of 552 mm. The mean growing season length was approximately 305 days, based on a soil temperature above 5 ºC at 0.05 m depth (Parson 1988). Annual grass production rates measured under high input of fertilizer N (i.e. 250 to 370 kg N ha^{-1}) ranged between 13.5 and 14.7 t dry matter (DM) ha^{-1}.

The dominating soils are poorly drained Gleys (90%) and Grey Brown Podzolics (10%) with a clay loam texture and low permeability (Table 5.1). Soil texture exhibits very small heterogeneity down to 0.9 m. Sand and gravel lenses are also present onsite which come to the surface in places and allow for fast infiltration. The mean SOM, organic carbon (C) and TN content of topsoil (0 to 0.3 m depth) was 6.55%, 4.48% and 0.48%, respectively with a corresponding C:N ratio of 9.3. At the same depth, soil bulk density (BD) and total porosity was 1.09 g cm^{-3} and 58.7%. The pH values varied from 6.2 to 7.1. Elevation on site ranges from 148.5 to 155.5 m Above Ordnance Datum (AOD). Depth to bedrock (Cappagh White Devonian Sandstone Formation (Archer et al. 1996)) is very uneven ranging from 5 to 10 m. Overlying quaternary till contains a perched watertable (depth of 0 to 2.2 m bgl; Fig. 5.1), which is an unconfined and poorly productive aquifer. The watertable is shallowest during the winter season. Although a number of ditches (4 m bgl) and tile drains (1.8 m bgl with spacing of 25 m) were installed between 1960 and 1995 across the farm to improve the drainage on site by lowering the watertable (Gleeson, T., personal communication), much of the farm remains seasonally wet, waterlogged or flooded due to impeded drainage.

5.2.2 Climate and edaphic data collection

Soil temperature, volumetric soil moisture at 0.05 m depth and rainfall were recorded automatically every half an hour at the meteorological station (Campbell scientific Ltd, Loughborough, U.K.) located in the central part of the research farm. Daily ER and soil moisture deficit (SMD) for the whole experimental period were determined using a model of Schulte et al. (2005) for grassland systems in Ireland based on a poorly drained soil criterion. Input weather data were combined using site specific rainfall and data from Moorepark Research Centre (maximum and minimum air temperature, wind speed and solar radiation), which is 23 km distant from Solohead Research Farm.

5.2.3. Experimental design and treatments

The farm has been under PG used primarily for grazing by dairy cows and to a lesser extent for silage production for more than 50 years. Prior to this study all the paddocks were ploughed and renovated between 1985 and 1995. The area of the farm (52 ha) was divided into 8 blocks (each of area approximately 6 ha) depending on soil type and drainage status as described by Humphreys et al. (2008a). Each block was divided into four paddocks (>1 ha). In June 2008, one paddock in each block was grazed or cut off to a height of 0.05 m from the surface, inversion ploughed to a depth of approximately 0.2 m, sown with a seed mixture containing perennial grass (*Lolium perenne L.*) and white clover (*Trifolium repens L.*) at a rate of 12 kg ha^{-1} and assigned to RG treatment in a randomized block design. The remaining uncultivated paddocks were assigned to the PG treatment. During 2008 and 2009, grassland received synthetic fertilizer N from 0 to 100 kg N ha^{-1} applied in split applications in February, March and April. The annual input through biological N fixation (BNF) by white clover (24% of pasture) ranged from 66 to 134 kg N ha^{-1}y^{-1} (Necpalova et al. 2012a). Pasture was allocated to livestock (1.59 to 2.1 LU ha^{-1}) in a rotational grazing system.

5.2.4 Soil sampling, KCl extraction and analyses

Soil sampling was carried out in October, November 2008, February, May, August, September, December 2009 and February 2010. At each sampling, fifteen cores per paddock were taken randomly using a Geonor MCL3 hydraulic auger (Geonor A/S, Olso, Norway) to a depth of 0.9 m bgl. Each core was subdivided into three depths (m): 0 to 0.3, 0.3 to 0.6 and 0.6 to 0.9 m and samples were bulked to one composite sample at each depth within each paddock. Immediately after sampling, samples were crumbled, mixed and plant material and stones were removed to get a representative sample. Soil soluble N was assessed in soil extracts. The samples were subjected to extraction within an hour and extracts ware obtained by shaking subsamples of field–moist soil with 2M KCl continuously for three hours at a solution ratio of 2:1 (400ml:200g, ratio v/w; Bremner 1965). Following shaking, the soil suspension was left to stand for five min before filtering (Whatman no.2 filtered paper, d = 0.125 m, 0.45 µm). Prior to chemical analyses, the KCl extracts were diluted 1 in 10. Total soluble N (TSN) was measured by chemiluminescence after catalytic combustion at 720°C using a Shimadzu TOC-VCPH analyzer with an ASI-V autosampler. Total oxidised N (TON) and ammonium (NH_4^+-N) was analysed on a Thermo Konelab analyser (Technical Lab Services, Ajax, Ontario Canada). Soluble organic N (SON) was calculated as the difference between TSN and soluble inorganic N (SIN = TON + NH_4^+-N). All soil soluble N results were expressed on DM basis at each depth using gravimetric soil moisture content, which was determined by drying subsamples in an oven at 105°C for 24 hours. Soil subsamples from October 2008, February and December 2009 were bulked to a composite sample per block, oven dried at 40°C, crushed, sieved (2 mm) and analysed for TN by dry combustion at 1300°C using a LECO CN-2000 elemental analyzer. Soil BD was measured using the cylinder core method (Blake and Hartge 1986).

5.2.5 Groundwater sampling and analyses

In July 2008, twelve piezometers constructed from polyvinyl chloride pipes, were installed in each paddock, 240 piezometers in total. The slotted screen opening interval on the lower 0.2 m of the casing was covered by a filter sock. The annulus (<0.03 m) between casing and the piezometer wall was grouted with sand and bentonite on the soil surface to prevent water channelling down the outside of the casing. In each paddock ten piezometers were used for water quality assessment and two were used for watertable levels measurements. Samples were taken fortnightly after purging the piezometers during the main winter drainage period and after periods of high rainfall during other times of the year. Sampling was conducted 31 times between 20th August 2008 and 2nd February 2010 (19 and 12 times during drainage seasons 2008/09 and 2009/10 respectively). A 50 ml sample was then taken from each piezometer and bulked into two composite samples per paddock. All samples were filtered (Whatman no.2) within an hour after sampling and then analysed for total dissolved N (TDN), NH_4^+-N and TON as described above. Nitrite N (NO_2^--N) was also analysed on a Thermo Konelab analyser. Nitrate N (NO_3^--N) was calculated as the difference between TON and NO_2^--N. Dissolved organic N was calculated as the difference between TDN and DIN (NO_3^--N + NO_2^--N + NH_4^+-N). If the result was negative, the proportion of DON or NO_3^--N was assumed to be negligible, i.e. not significantly different from zero.

Nitrogen losses of all N species for each grassland treatment were estimated by multiplying the mean N concentrations recorded on the sampling date with the volume of ER between two sampling occasions with an assumption that the N concentrations recorded in the groundwater were representative of concentrations in the ER reaching the piezometer screen. Due to high soil organic C (4.48%) it was assumed that the unsaturated zone had a high attenuation and denitrification capacity (Humphreys et al. 2008b, Necpalova et al., 2012b). Therefore the N concentrations or loads found in shallow groundwater on site represent transformed losses following ploughing buffered by biochemical processes during migration through the unsaturated zone.

5.2.6 N_2O flux measurements and analyses

The N_2O fluxes were measured using the static chamber technique (Mosier 1989) in four paddocks per treatment. These paddocks did not receive N fertilizer input during the whole study period. The measurements were carried out fortnightly; on 22 occasions between January to December 2009. The flux measurements were conducted around the same time each sampling day between 11.00 and 15.00 h to minimize diurnal variation. On each sampling day, ten iron chambers per paddock with a volume of 1.45 dm^3 (d = 11.5 cm, h = 14.5 cm) were driven into the soil to a depth of 0.01 m randomly across each paddock. Headspace gas samples were taken after 20 minutes of closure period and transferred to a 7 ml pre-evacuated septum-sealed screw-capped glass vials (Perbio Science, UK) using 25 ml polypropylene syringe. At the same time two background gas samples were taken from each paddock.

Gas samples were analyzed using a gas chromatograph (GC, Varian GC 450; The Netherlands) fitted with a packed column (Porapak® Q 80-100 MESH, 3 m x 1/8 in) using an electron capture detector at 300°C. This system was attached to Combi-Pal automatic sampler (CTC analytics, Zwingen, Switzerland) which extracted the sample from the sampling vial and injected it into the GC. Gases with known N_2O concentrations were used as reference points for the chromatography system. The analysis time of each sample was approximately 4 minutes. It was assumed that the changes of the N_2O concentration in the headspace over time are linear, as shown by Velthof and Oenema (1995) and Ball et al. (1999). Thus, the hourly N_2O fluxes (µg N_2O m^{-2} h^{-1}) for each chamber, giving a direct estimation of the N_2O flux between the soil and the atmosphere (Flechard at al. 2007), were estimated from the slope of the linear increase between background level and headspace concentration in the chamber after closure period. Hourly N_2O fluxes (µg N_2O m^{-1} h^{-1}) for PG and RG were estimated using an arithmetic mean of the fluxes from the individual chambers (Barton et al. 2008). Annual emission rates (kg N_2O-N ha^{-1} y^{-1}) were estimated by integrating hourly rates with time (Flechard at al. 2007; Rafique et al. 2011).

5.2.7 Statistical analyses

Statistical analyses were performed using the SAS software, version 9.01 (SAS Institute Inc., Cary, North California, USA). Normality distribution of residuals was tested with PROC UNIVARIATE.

All groundwater N concentration variables were transformed using a natural log ($y = \log(x + 1)$) and were analysed using a two way analysis of variance (PROC MIXED). The time factor such as sampling date was entered as a repeated measure with a compound symmetry covariance structure and the other factors (e.g. renovation and renovation × sampling date interaction) were entered as fixed effects. The TN, soil soluble N and hourly N_2O fluxes were analysed using the same model without previous transformations. The annual N losses to groundwater were also subjected to two way analyses of variance (PROC GLM) with a repeated measure covariance structure investigating the effect of the renovation, year and their interaction. Post hoc treatment comparisons were made according to Tukey and Bonferroni.

5.3 Results

5.3.1 Climate and edaphic data

The annual rainfall in 2008 and 2009 was exceptionally high, 1405 and 1403 mm, respectively and exceeded the ten year mean by 24% (Fig. 5.2a). Higher SMD values during the summer (16 to 26 mm day^{-1}) reflected drier soil conditions; however SMD did not exceed a value of 40 mm day^{-1}. Mean estimated SMD from August 2008 to February 2009 was 4 mm day^{-1} and from February 2009 to February 2010 was 6 mm day^{-1} (Fig. 5.2d). The monthly mean soil temperature ranged from winter lows of 3.0°C to summer highs of 15.9°C (Fig. 5.2e) with very little variation between the years (9.8°C in 2008 and 10.4°C in 2009). During this study rainfall exceeded evapotranspiration over seven months from July until January (Fig. 5.2c). Over the first groundwater sampling period 2008/09, site received 923 mm of rainfall, of which ER was 728 mm. Effective rainfall occurred on 108 days within this period, giving a mean recharge of 6.7 mm d^{-1}. Although the amount of rainfall was higher for the second groundwater sampling period 2009/10, the ER of 750 mm was only slightly different from the previous sampling period. Effective drainage occurred over 115 days which resulted in recharge of 6.5 mm d^{-1} (Fig. 5.2c).

5.3.2 Soil total N content

Soil TN decreased ($P<0.0001$) with a sampling depth and did not exhibit variability between the sampling dates. Renovation decreased TN at 0 to 0.3 m depth ($P<0.05$; Fig. 5.3), resulting in means of 4.76 ± 0.48 and 4.12 ± 0.54 g N kg^{-1} under PG and RG, respectively. The mean difference between PG and RG represented a loss of 0.66 g N kg^{-1} or, in other words, a 14% reduction of topsoil TN compared with PG. Renovation had no effect on BD, so when expressed on an area basis using BD for PG and RG (Table 5.1), ploughing caused a loss of 3.06 t N ha^{-1}. There was still difference in TN content between the treatments ($P<0.05$) on the last sampling occasion (1.7 years following renovation; Fig. 5.3). Renovation had no effect on TN in the deeper layers (at 0.3 to 0.6 and 0.6 to 0.9 m). The C:N ratio of SOM at 0 to 0.9 m ranged from 7.5 to 9.8, giving a mean of 8.8 and was not affected by grassland renovation or sampling date during the study period.

5.3.3 Soil soluble N pools

5.3.3.1 Soluble organic N

Soil SON decreased ($P<0.0001$) with a sampling depth and exhibited high intra-annual variability ($P<0.0001$) at each sampling depth (Fig. 5.4a). The intra-annual variation at 0 to 0.3 m showed a seasonal pattern with a minimum occurring during the winter and maximum in the late summer (September 2009). Renovation of PG decreased SON at 0 to 0.3 m depth ($P<0.05$) resulting in means of 18.6 ± 9.94 and 15.1 ± 8.54 mg kg^{-1} under PG and RG, respectively. The greatest difference occurred in September 2009 (15 months following ploughing) when the content dropped down from 32.2 mg kg^{-1} in PG to 23.5 mg kg^{-1} in RG samples (Fig. 5.4a). When expressed on an area basis using soil BD for PG and RG (Table 5.1), the mean difference over the 1.7 year period was 13.4 kg ha^{-1} with a maximum of 33.6 kg ha^{-1} in September 2009. There was no difference in SON between the treatments on the last sampling occasion (1.7 years following renovation; Fig. 5.4a). Renovation had no effect on SON in the deeper layers. The C:N ratio of soluble organic matter at 0 to 0.9 m ranged from 1.9 to 45.8 giving a mean of 6.0, and though was not affected by renovation, it was influenced by sampling date ($P<0.0001$). Soluble organic N pool was greater than SIN comprising 66, 66 and 68% of TSN at 0 to 0.3, 0.3 to 0.6 and 0.6 to 0.9 m depth, respectively.

5.3.3.2 Soluble inorganic N

Similar to SON, NH_4^+-N differed between sampling dates ($P<0.001$) and decreased with sampling depth ($P<0.0001$), but was not affected by renovation at any sampling depth (Fig. 5.4b). The intra-annual variation did not follow a seasonal pattern (Fig. 5.4b). The topsoil content ranged from 2.5 to 13.0 mg kg^{-1} with a peak in December 2009. Ammonium represented the second most important fraction of TSN (20.1 to 30.3%) and subsequently TON made up on average only 7.6% of TSN pool.

Similar to NH_4^+-N, TON was also not affected by renovation of PG (Fig. 5.4c). The TON content in the soil profile also differed temporarily ($P<0.0001$), but its content increased with sampling depth ($P<0.0001$) and showed the opposite distribution to NH_4^+-N. The levels at each sampling depth exhibited a clear seasonal pattern with an increase during summer months (February to August) and decrease during the main drainage season (August to February; Fig. 5.4c).

5.3.4 N concentrations in groundwater

5.3.4.1 Dissolved organic N

The DON and its associated C:N ratio exhibited high temporal variation ($P<0.0001$), but not clear seasonal pattern (Fig. 5.5b). The concentrations under PG ranged from 0.01 to 30.91 mg L^{-1} and under RG from 0 to 19.75 mg L^{-1}, with means of 2.18 and 2.01, respectively. Although, DON levels in groundwater were affected by interaction between renovation and sampling date ($P<0.05$), the C:N ratio of organic matter remained unchanged within the range of 2.0 and 55.5 (Table 5.2). There was no relationship found between DON in the groundwater and soil SON concentrations in the soil extracts.

5.3.4.2 Dissolved inorganic N

The concentrations of NH_4^+-N were within the range of 0 and 14.11 mg L^{-1} and were not affected by grassland renovation (Table 5.2). The NH_4^+-N in groundwater was elevated during winter and decreased during summer months (Fig. 5.5c). The concentrations were positively correlated to soil NH_4^+-N at 0.3 to 0.6 m ($y = 20.96x - 20.27$; $R^2 = 0.77$, $P<0.001$) and at 0.6 to 0.9 m depth ($y = 2.20x + 1.36$; $R^2 = 0.39$, $P<0.05$).

Nitrate showed high temporal variation ($P<0.001$, Table 5.2) with a clear seasonal pattern exhibiting sharp increases and declines during both winter seasons (Fig. 5.5e). The concentrations of NO_3^--N ranged from 0 to 4.24 mg L^{-1} under PG and from 0 to 5.93 mg L^{-1} under RG, and were affected by the interaction between renovation and sampling date ($P<0.0001$). The concentrations under RG were elevated until 25th August 2009 (1.2 years following renovation). Moreover, there was a positive relationship between NO_3^--N in the groundwater and TON concentrations in soil extracts at 0.6 to 0.9 m depth ($y = 1.35x + 0.024$; $R^2 = 0.39$, $P<0.05$) and also between TON in groundwater and TON extracted from the soil at 0.6 to 0.9 m depth ($y = 1.42x + 0.02$; $R^2 = 0.41$, $P = 0.05$).

The levels of NO_2^--N were very low, lower than 0.28 mg L^{-1}, but still influenced by the interaction between renovation and sampling date ($P<0.0001$, Table 5.2).

5.3.5 N losses to groundwater

Annual losses of all N species from PG and RG are presented in Table 5.3. Losses of DON were not affected by grassland renovation, but were considerably higher ($P<0.0001$) in 2008/09 than in 2009/10. In contrast, annual losses of NH_4^+-N, also unaffected by renovation, were higher ($P<0.05$) in 2009/10 than in 2008/09. Losses of oxidised N species (NO_3^--N, NO_2^--N) were influenced by an interaction between renovation and sampling year ($P<0.05$); the losses from RG were greater than those from PG and the difference was more pronounced in 2008/09 than 2009/10. Despite this, the losses of DON represented 77.6% and 57.1%, and NH_4^+-N represented 6.6% and 19.0% of overall N losses in 2008/09 and 2009/10, respectively. The overall annual N losses were not affected by grassland renovation, however the values were noticeably lower ($P<0.001$) in the 2009/10 (16.9 to 18.4 kg ha^{-1}) compared with 2008/09 (22.9 to 24.6 kg ha^{-1}; Table 5.3).

5.3.6 N_2O emissions

The hourly N_2O fluxes from PG and RG from January to December 2009 are shown in Fig. 5.6. The N_2O fluxes were episodic in nature with small pulses throughout the year ($P<0.0001$). Occasional short-term negative peaks were observed in both treatments. The instantaneous fluxes ranged from -72 to 382 μg N_2O m^{-2} h^{-1} for PG and from -72 to 788 μg N_2O $m^{-2}h^{-1}$ for RG. The treatments differences were hard to distinguish in the first few weeks of measurements. The highest hourly N_2O emissions were measured on 17th March in both grassland treatments, shortly after commencement of grazing (between 14th February and 8th March in selected paddocks) when soil temperature was 8.47°C and volumetric soil moisture content at 0.05 m depth was 0.65 g cm^{-3}. The mean hourly N_2O fluxes from RG were 44.59 ± 89.49 μg N_2O m^{-2} h^{-1} and were found to be significantly higher compared with fluxes from PG (23.66 ± 47.71 μg N_2O m^{-2} h^{-1}, $P<0.0001$). The fluxes from RG measured on 1st October 2009 (1.3 years following renovation) were still significantly higher than those from PG (Fig. 5.6). The estimated annual fluxes of N_2O from PG and RG were 1.32 ± 2.66 and 2.49 ± 4.99 kg N ha^{-1}, respectively.

5.4 Discussion

5.4.1 Climatic and edaphic data

The years of the study had exceptionally high rainfall compared with previous years. This resulted in higher soil moisture content, higher annual ER and longer drainage seasons (between 108 and 115 days). High soil moisture conditions led to long periods of anoxic conditions of the soils. It is likely that these conditions promoted reduction biochemical processes while mineralisation rates were reduced. Depth to the watertable on site was low (therefore unsaturated zone was thin) and, despite fluctuations, remained close to the surface throughout the study. Vertical travel time to groundwater was estimated to be within a single drainage season (Fenton et al. 2009, Necpalova et al., 2012b). Such time lag allows for accurate examination of the impact of land use change on groundwater concentrations (which take a certain time to migrate vertically to groundwater and thereby affect nutrient concentrations). The watertable fluctuations across the site were consistent in recharge and also seem to have been consistent across the site. Therefore biochemical processes in the soil rather than dilution during vertical migration in the unsaturated zone and mixing in shallow groundwater controlled N concentrations in groundwater.

5.4.2 Soil N pools

Grassland soils contain from 5 to 15 t TN ha^{-1} in the root zone (Ryden, 1984); more than 90% of this N is present in an organic form. Ploughing and reseeding of PG in the present study caused a strong and sudden decrease of topsoil TN. While there has been a number of studies reporting substantial losses of TN following long periods of cultivation (Keeney and Bremner, 1964; Tiesses et al., 1982; Tiessesn and Stewart, 1983; Dalal et al., 1986; Post and Mann, 1990); e.g. Mikhailova et al. (2000) observed a significant reduction in TN to a depth of 1.3 m in the 50 years following continuous cultivation with a 45 to 53%

reduction observed in the top 0.1 m, studies investigating the effect of renovation of PG on soil TN content are very rare. It is generally accepted that disruption of soil aggregates increases soil aeration, exposes stable, adsorbed SOM within micro- and macro- aggregates to rapid microbial decomposition (Six et al., 2002, 2004). The depletion of TN due to grassland destruction in the present study took place almost entirely (72%) in the first four months following ploughing. Since there was no temporal variability observed in TN content in a 1.7 year period following ploughing, there was no evidence of apparent recovery of TN to previous levels. The magnitude and duration of the change indicated that renovation had a significant and long term effect on soil quality and sustainability on this site. Although C:N ratio of organic matter in the topsoil was slightly lower compared with a mean value for soils in Ireland (11.3; Brogan, 1966), it was within a range reported for grassland topsoils (Jenkinson 1988; Ammann et al.,2007). The fact that it did not change following renovation indicate that both C and N were depleted to the same extent (Post and Mann, 1990).

Soil SON and SIN pools are mainly controlled and influenced by similar processes, and in the same way as TN pool. Greater content of SON compared with SIN in this study was likely a feature of PG age (Murphy et al. 2000) and high clay content (Velthof et al. 2010). The C:N ratio of soluble organic matter was only slightly lower compared with values reported for PGs on a clay loam soil (Hassink 1994; Jones and Willett 2006). The seasonal pattern of SON was similar to that observed in other studies (Jensen et al. 1997; Murphy et al. 2000; Ros et al. 2009).

Grassland renovation slightly decreased topsoil SON; however the content under both grassland treatments still followed the same seasonal pattern with the greatest difference in September 2009 (15 months after ploughing). We expected that SON would temporarily increase as a result of decomposition of recalcitrant SOM and decay of grass residues like in studies of Bhogal et al. (2000) and Murphy et al. (2007), who showed that grassland renovation significantly increased topsoil SON contents over a 10 month period following grassland renovation. The decrease in this study was likely a result of accelerated mineralisation of exposed SON (Six et al. 2002, 2004). The magnitude and intensity of temporal changes indicated that SON is not dynamic (Mengel et al. 1999; Murphy et al. 2000) and the residual effect of renovation on SON may last for more than a season (i.e. 1.7

years). Similar results of a slight decrease or unaffected SON in clay soils following renovation were reported from Netherlands (Velthof at al. 2010; Smit and Velthof 2010) and Scotland (Davies et al. 2001). The reason for the different behaviour of SON is not clear and therefore the mechanisms of the release, decomposition, and transport of SON in grassland soils need further investigation.

Grassland renovation in the current study did not have an effect on SIN at any sampling depth. In most cases, ploughing of grassland leads to substantial increase of SIN in the soil profile (100 to 400 kg N ha^{-1} y^{-1}) for several weeks to months in the first year following ploughing (Van der Weerden et al. 1999; Davies et al. 2001; Mori and Hojito 2007, Vertès et al. 2007; Velthof et al. 2010) as a result of mineralisation of grass residues incorporated into soil layer and exposing SOM to microbial respiration (Davies et al. 2001). The lack of response or not detecting the increase in the current study could be attributed to the fact that the first soil sampling was carried out four months after renovation. Hence, it was assumed that there must have been a substantial release, particularly due to sudden decrease in TN, although, the release disappeared partly as a result of uptake by new sward (Velthof et al. 2010), and by physical and biochemical processes. The groundwater monitoring during uncharacteristically wet July and August 2008 with 308.6 mm of cumulative rainfall (Fig. 5.2a) suggested that some of the SIN content was washed out from the soil profile before commencement of the soil sampling (Fig. 5.5c,d,e), however, these losses could not fully account for the net SOM mineralisation following ploughing. Another possibility is that high soil organic C (4.48%) on site induced suitable conditions for denitrification during wet months and removed any TN lost in excess of N uptake and N leaching to groundwater. From a very clear seasonal pattern of TON, it is apparent that the size of SIN pools was also influenced by vertical leaching. Leaching to the deeper soil layers occurs only when the amount of rainfall exceeds evapotranspiration (Murphy et al. 2007), which was in the period from July to January due to exceptionally wet years (Fig. 5.2c). The TON content considerably increased at each soil depth in the soil profile during spring and summer months and started to decrease at the beginning of the drainage season until it got completely washed out at the end of the year. For this reason, the TON content in 0 to 0.9 m soil layer at the end of July (Fig. 5.2c, beginning of the drainage season) could provide some indication on the magnitude of NO_3^--N leaching from clay loam soils to groundwater during the following winter.

5.4.3 N concentrations and N losses to groundwater

A number of studies on the effect of grassland renovation on NO_3^--N leaching losses have been carried out (e.g. Scholefield et al. 1993; Adams and Jan 1999; Bhogal et al. 2000; Davies et al. 2001; Shepherd et al. 2001; Ball et al. 2007; Seidel et al. 2007; Velthof et al. 2010). These studies reported a wide range of leaching losses (100 to 300 kg NO_3^--N ha^{-1} y^{-1}) in the first year following renovation, mainly due to large differences in experimental conditions (soil type, SOM, N management, grassland age).

The concentrations and losses of TON from RG in the present study were greater than from PG; although, the magnitude was several times lower in comparison with previous results. In the first year, renovation resulted in a loss of 4.95 kg of NO_3^--N compared with 2.39 kg NO_3^--N from PG. In addition, the NO_3^--N did not exceed the maximum allowable concentration of 11.3 mg NO_3^--N L^{-1} for groundwaters set by the Groundwater Directive (European Parliament and Council 2006) at any occasion during the sampling period. Dramatic and inconsistent peaks in NO_3^--N during winter seasons provided evidence of substantial physical or biochemical processes taking place in the unsaturated zone. High reduction potential of the soils on site due to anoxic conditions, high soil pH, and high soil organic C content (Table 5.1) likely led to exhaustion of NO_3^--N via DNRA (Hill 1996, Stepniewski and Stepniewska 2009) or denitrification (Jacobs and Gilliam 1985; Lowrance 1992). These biochemical processes may have reduced TON produced by oxidation of exposed SOM and incorporated residues and thus reduced the water quality responses to grassland renovation.

A significant two way interaction of renovation and sampling date on N concentrations of DON, TON (NO_3^--N, NO_2^--N) and also a significant effect of two way interaction of renovation and sampling year on annual losses of TON (NO_3^--N, NO_2^--N) indicated that the extent of the effect of renovation on the magnitude of N losses changed over time. From the time courses it is clear that the effect was more pronounced in 2008/09 than 2009/10, decreased as a function of time and remained significant for up to 1.2 years following renovation (Fig. 5.5). Previous studies reported that the residual effect may remain significant for one growing season (Bhogal et al. 2000; Shepherd et al. 2001) or for several years (Roberts et al. 1989; Davies et al.2001; Laurent et al. 2004, Mori and Hojito 2007) depending on the grassland age (Eriksen 2001; Vertès et al. 2007).

The interaction had also an effect on DON concentration; however, from the statistical analyses and time course (Fig. 5.5b) it is apparent that the effect of sampling date was notably more important than the effect of renovation. This denotes that DON concentrations and annual losses to groundwater, likewise in the case of NH_4^+-N, were independent of grassland renovation. This contradicts to the findings of Bhogal et al. (2000) who showed that significant leaching of DON may occur after ploughing of grassland. On the other hand, DON concentrations and losses in the present study were high (mean of 2.1 mg L^{-1}) and dominant (64.4% of TDN) to the other N species. High DON losses from grazed grasslands have been previously reported (Dick et al. 2000). The reported values were highly variable and ranged from 0.3 kg DON $ha^{-1}y^{-1}$ in a grass clover system (Saarijarvi et al. 2004) to a maximum of 127 kg DON $ha^{-1}y^{-1}$ in a pasture following the application of urine (Wachendorf et al. 2005; Van Kessel et al. 2009). The increased DON losses on this site may be attributed to the presence of legumes in the swards (Oelmann et al. 2007), application of organic manures (Murphy et al. 2000) or reduced mineralisation associated with high soil moisture conditions (Trasar- Cepeda et al. 2000; Aitkenhead-Peterson et al. 2002; Stepniewski and Stepniewska 2009). Although, there has not been a limit set up for DON concentrations in the groundwater under EU law, DON may be an important pathway of NO_3^--N pollution of waterbodies, as it may be ammonified and nitrified in the waters.

The concentrations of NH_4^+-N were high as well and comprised more than 49.9% of DIN in the groundwater. This in conjunction with depleted NO_3^- concentrations across the farm, inherent properties (high C content) and high reduction potential (anoxic conditions, high pH) of the soils on site indicated a substantial biochemical production of NH_4^+ via DNRA (Francis et al. 2007; Kartal et al. 2007; Stepniewski and Stepniewska 2009).

Good agreement between the SIN (TON, NH_4^+-N) in soil solution and DIN (TON, NH_4^+-N) in groundwater pointed out that the KCl extraction of soil samples at the depth of the local watertable provides comparable results of inorganic N leaching from heavy clay loam soils. The concentrations of TON and NH_4^+-N in groundwater were 1.4 and 2.2 times higher than those in the soil solution at the same depth, respectively. This denotes that KCl extracted only 45% of NH_4^+-N and 71% of TON. The lack of correlation between DON and SON suggested that the size of soil organic N pools strongly depend on the methodologies used (Jones and Willett 2006; Ros et al. 2009). It has been reported that N leached as DON represented only 2 to 10% of the SON extracted from the same soil (Murphy et al. 2000). This was not the case in the present study, since there was no evidence that the concentrations of DON were lower than SON. This leads to the conclusion that SON and DON are two diverse N pools of different size and likely different composition (Murphy at el. 2000; Ros et al. 2009).

Since ER caused a similar recharge in 2008/09 and 2009/10, the volume of rainfall draining through the root zone each year could not be responsible for year to year variation in DON and NH_4^+-N losses. Consequently, higher DIN (NH_4^+-N, NO_3^--N, NO_2^--N) and lower DON concentrations in 2009/10 must have been a result of enhanced deamination and ammonification of DON followed by further oxidation. Both years of the study received almost the same amount of rainfall, but the second year was slightly drier due to higher soil temperature and thus higher evapotranspiration rates. This likely increased mineralisation rates in the soil profile and led to greater DIN leaching in 2009/10.

5.4.5 N_2O emissions

Nitrous oxide originates from nitrification and denitrification processes in the soil, and its release is generally enhanced by moist conditions and presence of NO_3^--N and NH_4^+-N (e.g. Velthof et al. 1996). Soil moisture directly regulates diffusity and O_2 exchange between the soil and the atmosphere (Davidson and Schimel 1995) and thus has a considerable control over oxygen-dependent biochemical processes. Nitrification is the dominant source of N_2O under oxic conditions (WFPS<60%) and denitrification is the predominant source under anoxic conditions (WFPS>60%; Davidson 1991). After grassland ploughing and residue incorporation, the NH_4^+-N mineralised from the residues and SOM is quickly nitrified and consequently increases NO_3^--N. Additionally, an increased C supply stimulates rapid microbial respiration and O_2 consumption, thereby developing anoxic sites (Christensen et al. 1990; Luo et al. 1999; Baggs et al. 2000; Akiyama et al. 2004; Jones et al. 2005). For this reason, the N_2O emissions from the RG are partially attributed to both nitrification and denitrification processes (Mori and Hojito 2007). There has been a number of GHG studies published on the effect of ploughing up of grassland followed by reseeding with higher yielding grass species, maize or the other cereals (Baggs et al. 2000, Estavillo et al. 2002; Yamulki and Jarvis 2002; Pinto, et al. 2004; Ball et al. 2007). However, there have been only a few studies reporting N_2O emissions following grassland renovation. Davies et al. (2001) showed that ploughing of grass-clover grassland on a clay loam soil increased N_2O emission for several weeks and cumulative N_2O emissions from RG ranged from 0.1 to 1.2 kg N ha^{-1} over a 7 week period. In Netherlands, the N_2O emissions following renovation of non-fertilized PG on a clay loam soil were higher in spring (14.4 kg N $ha^{-1}y^{-1}$) than in autumn (7.9 kg N $ha^{-1}y^{-1}$) and the emissions from undisturbed PG were only 0.8 kg N $ha^{-1}y^{-1}$ (Velthof et al. 2010). Grassland renovation on loamy soils in Japan resulted in N_2O emissions of 3.7 kg N_2O-N ha^{-1} compared with a control of 1.9 kg N_2O-N ha^{-1} over a 67 day period (Mori and Hojito 2007). Ploughing of poorly drained grassland in Canada in spring resulted in 12 kg N_2O-N ha^{-1} y^{-1} (MacDonald et al., 2011).

The fluxes measured in the present study were lower than fluxes reported earlier. The magnitude of the N_2O emissions was most likely influenced by high soil moisture content and high soil pH on site (approximately 6.6). It has been reported that as anoxic conditions increase, the percentage of N_2O in denitrification products decreases until N_2 is the major gas evolved (Davidson 1993; Ruser et al. 2006). Besides this, the pH value under anoxic conditions tends to increase (even over two units) through affecting the solubility of numerous nutrients and metals (Stepniewski and Stepniewska 2009). Numerous studies concluded that if the pH of a soil is higher than 6, denitrification would emit less N_2O as a result of a lower $N_2O/(N_2O + N_2)$ product ratio (Weier and Gilliam 1986; Van der Weerden et al. 1999; Liu et al. 2010; Cuhel and Simek 2011; Senbayram et al. 2012). Stevens and Laughlin (1998) reported that an increase of one pH unit lowered the mole fraction by 0.2. It was also found that at pH of 6.5 the smaller proportion of the gaseous N was emitted as N_2O compared to more acid conditions (Granli and Bockman 1994). This suggests that denitrification and nitrification in the RG in the present study were likely enhanced by grassland renovation, but most of N_2O was reduced to N_2, and this led to a small but still significant difference in N_2O losses between the treatments. The fluxes from RG measured 1.3 years following renovation were still significantly higher than fluxes from PG. The peak in N_2O emissions from RG in the present study occurred in response to commencement of grazing, whilst a similar, albeit smaller, response was observed from PG as well. At this time the temperature was above 8°C so the organic C and N inputs originating from animal excreta were probably mineralising rapidly. In addition, the turning out of the animals to the grassland may have led to increased topsoil moisture content as a result of soil compaction by grazing animals. This suggested that the effect of renovation on N_2O emissions could be strengthened by the effect of grazing.

The amount of BNF by clover in non-fertilized paddocks in Solohead in 2008 and 2009 estimated using a mechanistic empirical model (Humphreys et al., 2008a) varied from 112 to 134 kg N $ha^{-1}y^{-1}$(Necpalova et al. 2012a). The N in ploughed-in phytomass (stubble and roots) amounted to 297 kg N ha^{-1} y^{-1} (Necpalova et al. 2011). The quantity of N excreted during grazing by livestock calculated as Powell et al. (2006) ranged from 82.2 to 95.2 kg N ha^{-1} y^{-1} (Necpalova et al. 2012a). Therefore, the annual N input to RG was approximately within the range of 504.5 and 513.0 kg N ha^{-1} y^{-1}. The N lost as direct N_2O represented 0.49% of the N input, which is less than the average of 1.6% found for five European sites by Petersen et al. (2005). Another 4.8 and 4.9% of the total N inputs were leached to groundwater in the first year following renovation. This resulted in the ratio of 6.78 between N leaching and N_2O-N emissions. Although, the overall losses following grassland renovation at Solohead Research Farm due to net SOM mineralisation were high (> 3 t N ha^{-1}), the losses via N leaching and N_2O emissions were low (27.1 kg N ha^{-1} y^{-1}). The ratio suggests that renovation had a greater impact on the groundwater quality than the quality of the air.

5.5 Conclusions

Ploughing and reseeding of PG decreased topsoil TN and SON, increased TON leaching to groundwater and the gaseous losses of N_2O from the soil surface as a result of soil disturbance, enhanced mineralisation of SOM and incorporated grass residues followed by nitrification and denitrification. The effect of renovation remained significant for more than 14 months following ploughing and decreased as a function of time. The rate of topsoil TN loss indicated that renovation on a clay loam soil had a significant and long term effect on soil quality and sustainability on this site. The overall losses following grassland renovation due to net SOM mineralisation were high (>3 t N ha^{-1}), however, the proportion lost via N leaching and N_2O emissions was low (27.11 kg N ha^{-1} y^{-1}). This was likely a result of inherent properties (high soil C), reduction potential (high soil pH) and predominantly anoxic status of the soils on site during the study period, which likely promoted reduction biochemical processes such as DNRA and complete denitrification, and consequently led to reduction of NO_3^--N and N_2O losses. The N losses via N_2O were much lower than losses via N leaching; i.e. grassland renovation on a clay loam soil had a greater impact on the groundwater quality than the quality of the air. The results of this study also report that KCl extraction of soil samples at the depth of a local watertable provides a comparable results of inorganic N leaching from a heavy clay loam soil, although, this does not apply to the results of organic N.

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Table 5.1 Soil properties under permanent (PG) and renovated grassland (RG) in the top 0.3 m at Solohead Research Farm. All values are means of at least three determinations with standard deviations in parentheses.

	PG		RG	
Clay (%)	28.3	(3.1)	28.3	(3.1)
Sand (%)	36.7	(6.4)	36.7	(6.4)
Silt (%)	35.0	(3.5)	35.0	(3.5)
Bulk density (g cm^{-3})	1.09	(0.16)	1.02	(0.21)
Particle density (g cm^{-3})	2.52	(0.15)	2.44	(0.20)
Total porosity (%)	58.7	(6.5)	58.3	(5.9)
CEC (Meq/100gDM)	25.4	(2.3)	25.4	(2.3)
pH	6.60	(0.2)	6.56	(0.3)
Total N (%)	0.48	(0.05)	0.41	(0.05)
Total inorganic C (%)	0.09	(0.03)	0.08	(0.04)
Total organic C (%)	4.48	(0.52)	3.75	(0.44)
Organic matter (%) †	6.55	(0.84)	5.44	(0.78)
C:N	9.34	(0.27)	9.23	(0.32)

† calculated from loss on ignition results (%) using the Ball's equation: OM = (0.476*loss on ignition) - 1.87 (Ball, 1964)

Table 5.2 Mean concentrations (mg L^{-1}) of N species in groundwater under permanent and renovated grassland from August 2008 to February 2010.

	August 2008 - February 2010		P value		
Mg L^{-1}	Permanent (SE)	Renovated (SE)	Cultivation	Date	Cultivation x Date
Total N	2.95 (0.12)	2.93 (0.09)	NS	<0.0001	<0.001
Dissolved organic N	2.18 (0.10)	2.01 (0.08)	NS	<0.0001	<0.001
C:N ratio	12.49 (0.65)	14.28 (0.87)	NS	<0.0001	NS
Ammonium N	0.38 (0.04)	0.35 (0.03)	NS	<0.0001	NS
Nitrite N	0.01 (0.00)	0.01 (0.00)	<0.05	<0.001	<0.0001
Nitrate N	0.41 (0.02)	0.59 (0.03)	<0.05	<0.0001	<0.0001

Table 5.3 Mean annual losses (kg $ha^{-1}y^{-1}$) of N species to groundwater from permanent and renovated grassland.

	August 2008 - February 2009		February 2009 - February 2010		P values		
	Permanent (SE)	Renovated (SE)	Permanent (SE)	Renovated (SE)	Cultivation	Year	Cultivation x Year
Total N	22.9 (1.49)	24.6 (1.43)	18.4 (2.21)	16.9 (2.39)	NS	0.001	NS
Dissolved organic N	18.6 (1.01)	18.2 (0.64)	10.5 (0.97)	9.6 (1.32)	NS	<0.0001	NS
Ammonium N	1.85 (0.50)	1.30 (0.12)	3.15 (0.82)	3.56 (1.35)	NS	<0.05	NS
Nitrite N	0.04 (0.01)	0.12 (0.03)	0.09 (0.02)	0.08 (0.03)	<0.05	NS	<0.05
Nitrate N	2.39 (0.34)	4.95 (0.99)	4.13 (0.58)	4.11 (0.83)	<0.05	NS	<0.05

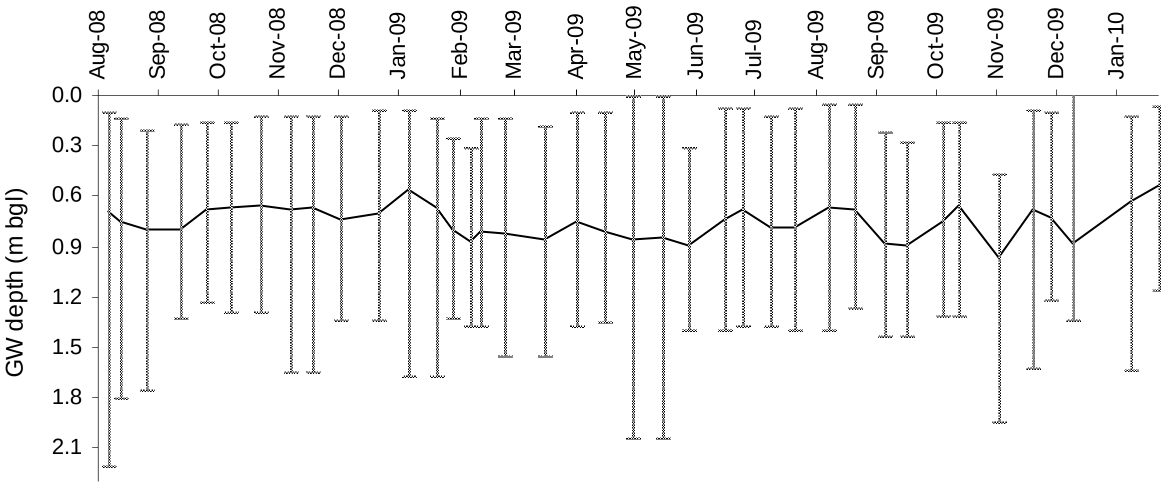


Fig. 5.1 Temporal variation of ground watertable depth from August 2008 to February 2010. Vertical bars represent the maximum and minimum below ground level (bgl).

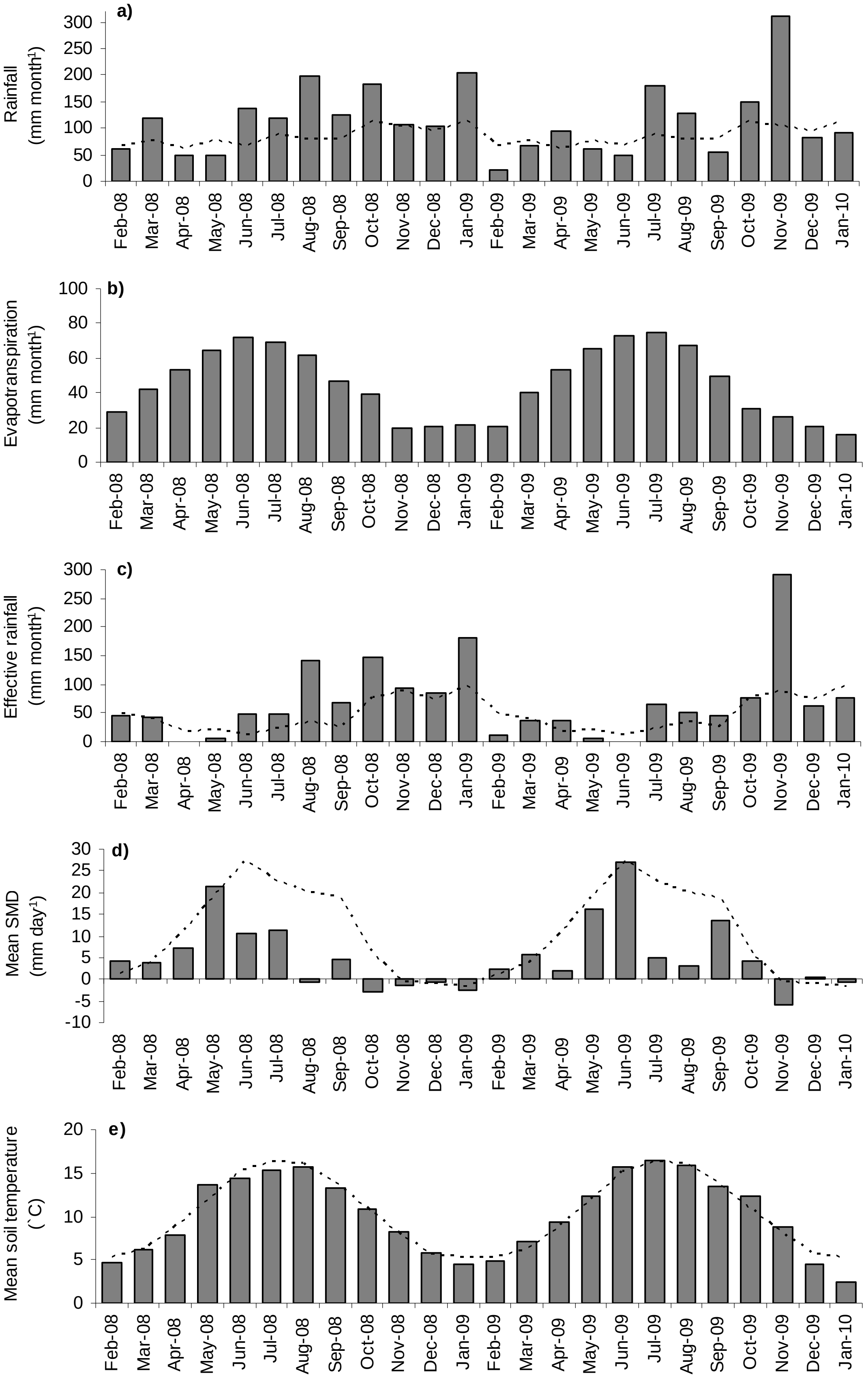


Fig. 5.2 Meteorological data at Solohead Research Farm from February 2008 to February 2010: a) monthly rainfall (mm month^{-1}), b) monthly evapotranspiration (mm month^{-1}), c) monthly

effective rainfall (mm month^{-1}), d) monthly mean soil moisture deficit (SMD, mm d^{-1}) and e) monthly mean soil temperature (°C) at 0.05 m depth. Dashed line represents a 10 year mean.

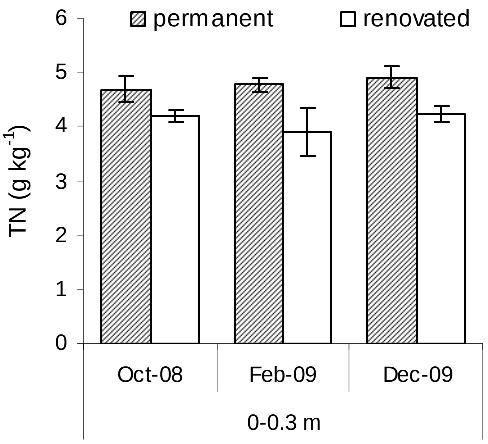


Fig. 5.3 Soil total N content (TN, g kg^{-1} soil) under permanent and renovated grassland at 0 to 0.3 m depth. Error bars are ± SE.

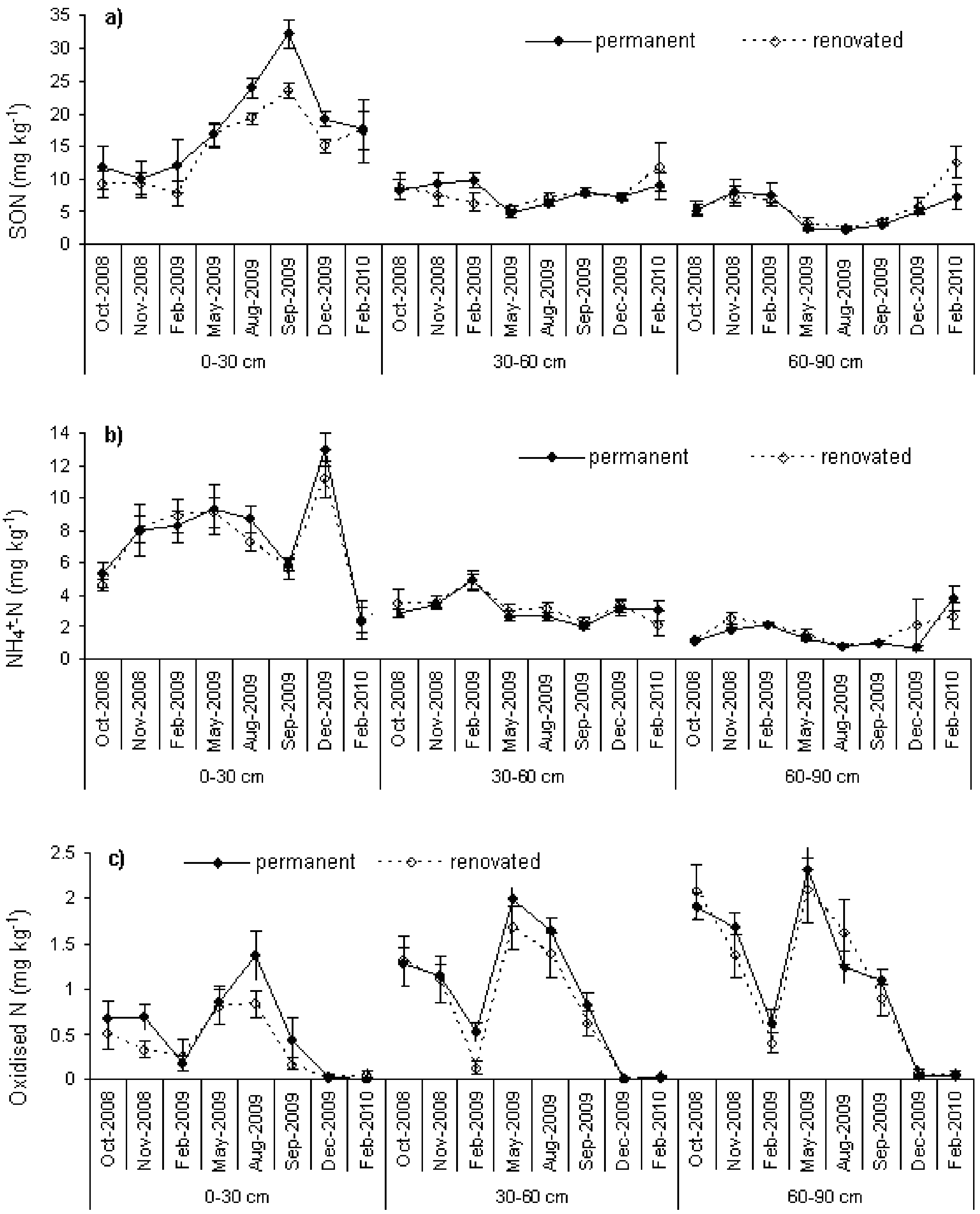
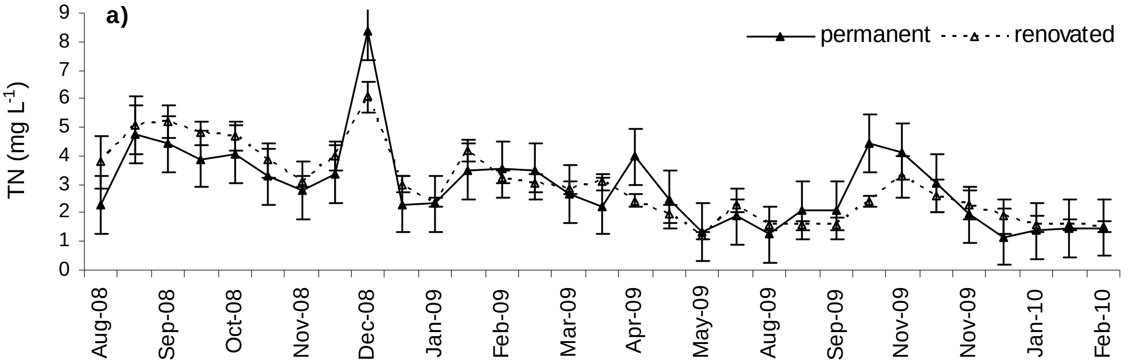
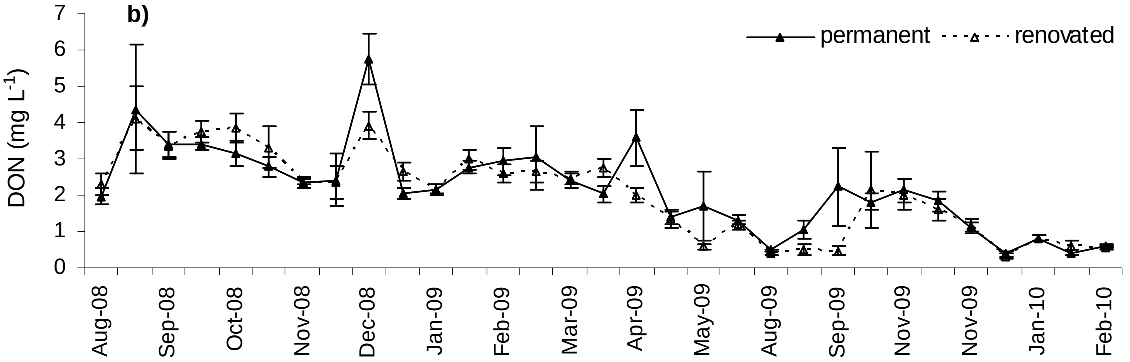
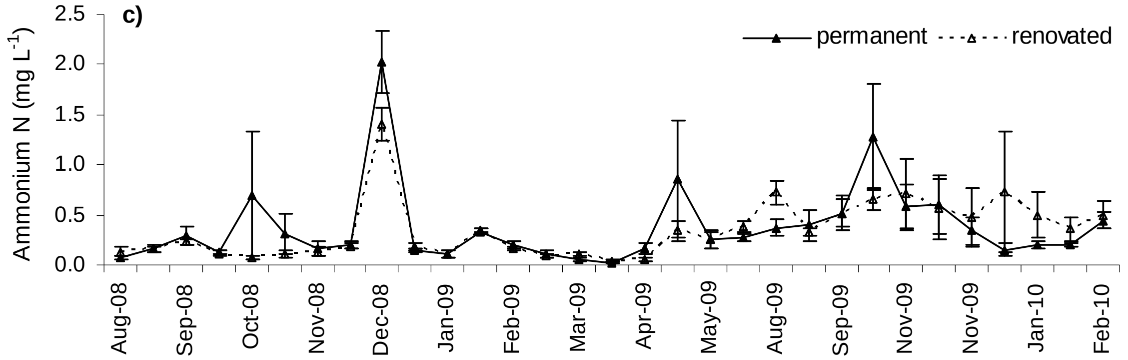
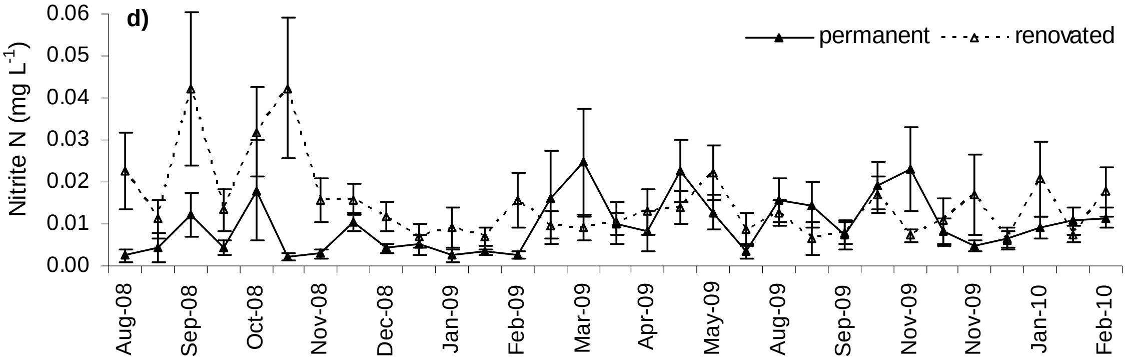


Fig. 5.4 Temporal variation of soil a) soluble organic N, b) ammonium N and c) oxidised N content (mg kg^{-1}) at three different depths under permanent and renovated grassland. Error bars are ± SE. The treatment means of SON at 0 to 0.3 m depth are significantly different ($P<0.05$).


a)
TN (mg L^{-1})
0
1
2
3
4
5
6
7
8
9
permanent
renovated
Aug-08
Sep-08
Oct-08
Nov-08
Dec-08
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Aug-09
Sep-09
Nov-09
Nov-09
Jan-10
Feb-10


b)
DON (mg L^{-1})
0
1
2
3
4
5
6
7
permanent
renovated
Aug-08
Sep-08
Oct-08
Nov-08
Dec-08
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Aug-09
Sep-09
Nov-09
Nov-09
Jan-10
Feb-10


c)
Ammonium N (mg L^{-1})
0.0
0.5
1.0
1.5
2.0
2.5
permanent
renovated
Aug-08
Sep-08
Oct-08
Nov-08
Dec-08
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Aug-09
Sep-09
Nov-09
Nov-09
Jan-10
Feb-10


d)
Nitrite N (mg L^{-1})
0.00
0.01
0.02
0.03
0.04
0.05
0.06
permanent
renovated
Aug-08
Sep-08
Oct-08
Nov-08
Dec-08
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Aug-09
Sep-09
Nov-09
Nov-09
Jan-10
Feb-10

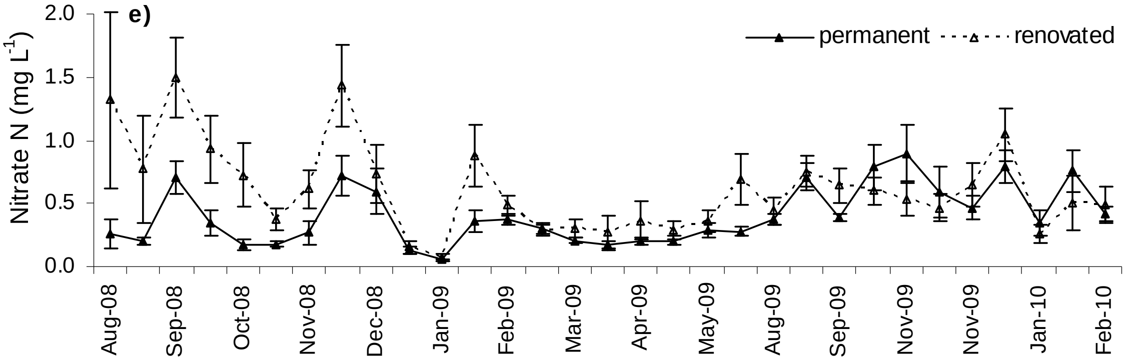


Fig. 5.5 Temporal variation of concentrations (mg L^{-1}) of a) total N (TN), b) dissolved organic N (DON), c) ammonium N, d) nitrite N and e) nitrate N in groundwater under permanent and renovated grassland. Error bars are ± SE.

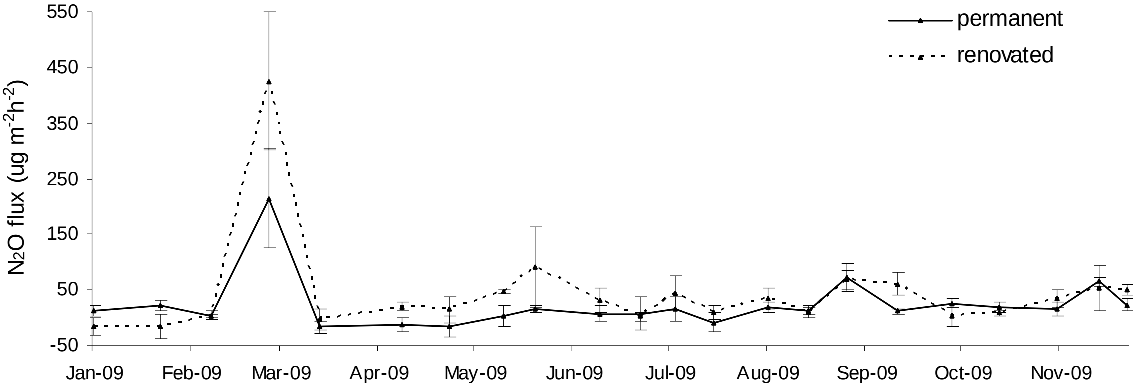


Fig. 5.6 Hourly N_2O fluxes (μg m^{-2} h^{-1}) from permanent and renovated grassland. Error bars are ± SE

6. Changes in soil organic carbon in a clay-loam soil following ploughing and reseeding of permanent grassland under temperate moist climatic conditions

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Necpalova M., Casey I.A., Fitzgerald E., Humphreys J. (2011) Changes in soil organic C in a clay-loam soil under permanent and cultivated grassland. In: Book of abstracts of the Research day 2011, Waterford Institute of Technology, 13. April 2011, Waterford, Ireland, p. 99.

Necpalova M., Li, D., Lanigan, G., Casey I.A., Fitzgerald E., Burchill, W., Humphreys J. (2011) Changes in soil organic carbon in clay-loam soil under permanent and cultivated grassland under oceanic climatic conditions. In: Proceedings of the British Grassland Society 10th Research Conference in Belfast 20- 21. September 2011.

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Abstract

This study investigated changes in soil organic carbon (SOC) in a poorly drained clay-loam soil under (i) permanent grassland (PG) over seven years and (ii) after ploughing and reseeding of PG over 2.5 years. The experimental area was divided into four blocks with four paddocks per block. Bulked soil samples from PG per block were taken to a 0.3 m depth on five occasions between 2004 and 2011. In 2008, one paddock per block was ploughed, reseeded and sampled as above on the last four occasions. The SOC was determined by dry combustion. Renovation decreased SOC ($P<0.05$) by 32.2 t ha^{-1} in 2.5 years following ploughing and the difference developed almost entirely (86%) in the first four months following ploughing. Renovation had no effect ($P>0.05$) on the above-ground phytomass productivity, standing root and stubble phytomass. Therefore heterotrophic respiration of soil microbial biomass and dissolved organic carbon leaching were considered to be mechanisms responsible for SOC loss form renovated grassland. There was no evidence of recovery in SOC to previous levels during the study period. These results could have substantial consequences in the context of climate change. A simple linear regression indicated a tendency for PG to accumulate SOC, although, the increase was not significant.

Keywords: soil organic carbon, permanent grassland, ploughing, renovation

6.1 Introduction

Soil organic carbon (SOC) plays a key role in the global carbon (C) cycle. Agricultural soils, particularly grassland soils act as an important C reservoir (Schimel et al., 1995; Jones et al., 2006; Fontaine et al., 2007). Grasslands are one of the world's most widespread land cover types and comprise approximately 40.5% of the earth's terrestrial land area, excluding the areas of permanent ice cover (White et al., 2000), 22% of the land area of Europe (Soussana et al., 2007) and 53% of the land area of Ireland (Eaton et al., 2008). Apart from many important functions related to water, air quality, erosion and biodiversity, they represent a significant component of the global C cycle (Jones et al., 2006). Worldwide, the surface soils of temperate grassland store around 295 Gt of SOC (Bolin and Sukumar, 2000). While it is well known that grassland ecosystems have a high SOC content and are a potential sink or source of C (Arshad et al., 2004; Bronson et al., 2004; Soussana et al., 2007; Rogiers et al., 2008), SOC storage and dynamics in grassland soils vary across studies for a variety of reasons, depending on local climatic and other site specific conditions (i.e. site heterogeneities, productivity of the ecosystems, soil type) as well as on the type of land use history and land management practices (Post et al., 2000; Leifeld et al., 2005).

It has been often observed in practice that yields and quality of permanent grassland (PG) decrease during ageing, because of sward deterioration (i.e. compaction, poor drainage, sward composition, weed invasion, soil acidification or erosion) following extreme weather conditions and/or bad management (Velthof and Oenema 2001). For this reason, the managed grasslands are occasionally renovated (ploughed up and reseeded) in order to maintain or increase the sward productivity (Velthof et al. 2010), reduce weeds, maintain clover content (Humphreys and Lawless 2008) or to introduce new pasture species and varieties (e.g. high sugar grasses). Ploughing of grassland leads to physical disruption of aggregates, increased soil aeration and consequently exposure of stable and adsorbed soil organic matter (SOM) within micro- and macro- aggregates to rapid microbial respiration (Six et al. 2004; Buss et al. 2005; Velthof et al. 2010). In addition, the disruption also decreases soil moisture, increases maximum soil temperature and thus accelerates mineralisation process (Lal 2004). For this reason ploughing of grassland, particularly of long term grassland with a substantial SOC pool may temporally lead to important carbon dioxide (CO_2) emissions. Rising concentrations of greenhouse gases (GHG) in the atmosphere are of worldwide concern. By signing the Kyoto Protocol in 1997, governments of 37 industrialized countries agreed to reduce the emissions of the GHG on average by 5% against the levels from 1990 over a five years period (2008-12). Ireland is committed to limit GHG emissions by 13% in the period 2008 to 2012, and by 25 to 30% in the period 2012 to 2020 compared with 1990 levels. As part of international efforts to stabilize atmospheric GHG concentrations, signatories of the Kyoto protocol are also committed to establish national inventories of the SOC content and its changes. The inventory systems are being developed, but to date national-scale measurement based inventories have not been able to clearly attribute the changes in SOC to specific land use or climatic effects (Smith et al., 2007). Consequently, there is a strong need for accurately quantifying the effects of different management practices on SOC content.

Soil profile accumulation or depletion is predominantly dependent upon the ability of the soil to stabilise C, the physical protection of C within soil aggregates, the lability of C added to the soil and on balance of inputs (e.g. photosynthesis, organic matter (OM) inputs) and losses (e.g. ecosystem respiration, product exports, leaching and erosion), management practices and climate variations that alter the balance between inputs and outputs in the soil (Saggar and Hedley, 2001; Freibauer et al., 2004; Schipper et al., 2010). The magnitude of change following a land-use change after a certain time period is generally quantified as the differences in SOC content between plots under new land use and that under unchanged management (Ellert et al., 2001, Schipper et al., 2010). So far, the impact of land use or management on SOC have been focused on changes following afforestation of grassland (Guo and Gifford, 2002; Laganiere et al., 2010), conversion of grassland to cropland (Johnston, 1986; Strebel et al., 1988; Guo and Gifford, 2002; Lal, 2002; Ogle et al., 2005), forest to grassland or cropland (Murty et al., 2002) and management of cropland (Senthilkumar et al., 2009). The studies on the effect of grassland management practices such as ploughing and reseeding of long term PG on SOC and their potential contribution to CO_2 emissions of under humid Irish conditions are lacking.

The objectives of the study were to quantify changes in SOC content on a poorly drained clay-loam soil under (i) PG used for dairy farming in southern Ireland over seven years and (ii) after ploughing and reseeding of PG over two and a half years. In order to compare the levels of C inputs through phytomass and C losses through leaching in permanent and renovated grassland (RG), the above-ground phytomass productivity, root standing phytomass and dissolved organic carbon (DOC) leaching were investigated.

6.2 Material and methods

6.2.1 Site description

The study was conducted on a dairy research farm in Solohead, in Ireland (52˚51'N, 08˚21'W) from October 2004 to January 2011. The local climate is humid temperate oceanic with a long potential growing season from February to mid of December. During the last 10 years the site received on average 1018 mm of annual rainfall and this resulted in a mean annual effective rainfall (ER) of 552 mm. Mean growing season length based on a soil temperature above 5ºC at 5 cm depth (Parson, 1988) was approximately 305 days. Annual grass production rates over the last 10 year period ranged between 14.6 and 16.9 t dry matter (DM) ha^{-1}. The farm has been under PG used primarily for grazing and to a lesser extent for silage production for more than 50 years. Prior to this study all the paddocks were ploughed and renovated between 1985 and 1995.

The predominant soils are poorly drained Gleys (90%) and Grey Brown Podzolics (10%) with a clay loam texture and low permeability (28.3% clay, 35% silt). The soils have a high buffering capacity with CEC of 25.4 cmolc kg^{-1}. The mean SOC and total nitrogen (N) content at 0 to 0.3 m depth is 4.48% and 0.48%, respectively with a corresponding soil bulk density (BD) of 1.09 g cm^{-3}. Elevation on site ranges from 148.5 to 155.5 m Above Ordnance Datum (AOD). Depth to bedrock (Cappagh White Devonian Sandstone Formation (Archer et al., 1996)) on site is uneven ranging from 5 to 10 m. Overlying quaternary till contains a perched watertable (depth of 0 to 2.2 m below ground level (bgl)). The watertable is shallowest during the winter season. Although a number of ditches (4 m bgl) and tile drains (1.8 m bgl with spacing of 25 m) were installed between 1960 and 1995 across the farm to improve the drainage on site by lowering the watertable (Gleeson, T., 1997, personal communication), much of the farm still remains seasonally wet, waterlogged or flooded due to impeded drainage.

Mean annual rainfall, soil moisture deficit and soil temperature at 0.1 m depth for the period from January 2004 to December 2010 were 1055 mm, 10.7 mm day^{-1} and 9.8 ºC, respectively. The highest monthly rainfall occurred from October to January and the lowest was recorded between March and June. Rainfall exceeded evapotranspiration over seven or eighth months, typically from August until March. Mean annual ER was 588 mm with a peak in January. While the annual rainfall in 2008 and 2009 was exceptionally high and exceeded a ten year mean by 21 and 27% respectively, the annual rainfall in 2010 was only 857 mm. Uncharacteristically wet weather conditions in 2008 and 2009 were also evident from water filled pore space records at 0.05 m depth indicating complete soil saturation (≥100%) during 14 months.

6.2.2 Experimental design and treatments

During 1999, the area of the farm (52 ha) was divided into 8 blocks, each area of approximately six hectares. Four of these blocks were assigned into this experimental study (24 ha). Each block was divided into four paddocks (>1 ha). From 2004 to 2011, the farm was under typical grassland management as described in Table 6.1. The pasture was dominated by perennial ryegrass (76%, *Lolium perenne* L.) with white clover (24%, *Trifolium repens* L.) and was allocated to livestock in a rotational grazing system. The RG treatment was established in June 2008, when one paddock in each block was grazed or cut off to a height of 0.05 m, inversion ploughed to a depth of approximately 0.2 m and sown with a seed mixture containing perennial grass and white clover.

6.2.3 Soil organic carbon

Soil samples from PG were taken in October 2004, October 2008, February 2009, December 2009 and January 2011. The RG was sampled on the latter four dates. At each sampling, fifteen cores per paddock were taken randomly using a Geonor MCL3 hydraulic auger (Geonor A/S, Olso, Norway) to a depth of 0.3 m bgl. Samples were bulked to a composite sample per block. Immediately after sampling all plant material and stones were removed manually, the soil cores were oven dried at 40°C, crushed, sieved (2 mm) and analysed for total C (TC), total inorganic C (TIC) and total N content by dry combustion at 1300 ºC using a LECO CN-2000 elemental analyzer. Subsamples analysed for TIC were pre-treated by heating at 450 ºC and SOC concentration was then estimated by the difference between TC and TIC.

6.2.4 Soil bulk density

Soil BD was measured using the cylinder core method (Blake and Hartge 1986) in August 2008. Four replicate samples were taken at six random locations from both, PG and RG. A steel cylinder (internal d = 0.046 m; L = 0.05 m) was hammered into the soil sufficiently to fill the inner cylinder without any soil compression at required depth. Soil cores obtained by empting the cylinders were examined for signs of shattering or compression. On return to the laboratory, the samples were dried at 105°C and weighed prior to BD determination.

Soil organic carbon content was calculated on an equivalent mass basis as the product of SOC concentration, BD and the layer depth.

6.2.5 Root, stubble and herbage phytomass

Root standing phytomass was sampled using a Dutch hand augur in September 2010. Sets of cores were obtained for PG at six random locations and for RG at three random locations around the farm. Prior to taking the soil cores, the herbage phytomass within a square of 0.5 m^2 was cut using a Gardena hand-shears (Gardena, Accushears, Ulm, Germany) to a height of 0.05 m. Soil cores (d = 0.06 m) were taken at depths of 0 to 0.15 and 0.15 to 0.3 m. Following storage in a refrigerator (4°C) the cores were soaked in a tap water for approximately 30 minutes. Roots were separated from the soil by washing with running water through a 1 mm sieve and were picked out with forceps. The washed roots (>1 mm) were oven dried at 40 ºC for 24 h prior to DM determination. Hence, root material in the current context refers to the root material extracted as described above, which included dead material. The stubble phytomass (0 to 0.05 m) was measured at the same locations; samples were taken from each of the topsoil cores by harvesting the herbage to ground level using a scissors. The DM was determined as above. During the grazing period, pre-grazing herbage in each paddock was measured by cutting four random strips (each 5 m × 0.55 m wide) using a HRH-536 lawn-mower (Honda®, Georgia, U.S.A.) at a cutting height of 0.05 m. The cut herbage was bulked, weighed and DM was determined by drying a sub-sample as described above. The aboveground phytomass productivity was obtained as a sum of pre-grazed herbage masses from the whole grazing season and stubble phytomass. The root, stubble and herbage subsamples taken for chemical analyses were milled through a 0.5 mm sieve prior analyses for TC content by dry combustion at 1050 ºC using a LECO CN-2000 elemental analyzer. The C phytomass storage was estimated from its C content.

6.2.6 Dissolved organic carbon in groundwater

Dissolved organic C leaching was investigated through sampling of shallow groundwater (0 to 2.2 m bgl) as described by Necpalova et al. (2012). Estimated vertical travel time through the unsaturated zone to groundwater ranged between 0.21 and 0.57 years at different locations around the farm (Necpalova et al., 2012). Unfortunately due to organisational reasons the concentrations were for the first time determined in March 2009 and then on another eighth occasions until January 2010. Dissolved organic C was measured by chemiluminescence after catalytic combustion at 720°C using a Shimadzu TOC-VCPH analyzer with an ASI-V autosampler. The losses from each treatment were estimated by multiplying the mean concentrations recorded on the sampling date with the volume of ER between two sampling occasions with an assumption that the DOC concentrations recorded in the groundwater were representative of concentrations in the ER reaching the piezometer screen.

6.2.7 Statistical analyses

Statistical analyses were performed using the SAS software, version 9.01 (SAS Institute Inc., Cary, North California, USA). Normality distribution of residuals was tested with PROC UNIVARIATE. Transformation of variables was not required in any case. Soil organic C, C:N ratio of OM were analysed using a two way analysis of variance (PROC MIXED). The time factor such as sampling date was entered as a repeated measure with a compound symmetry covariance structure and the other factors (renovation and renovation × sampling date interaction) were entered as fixed effects. Similarly DOC concentrations in GW between PG and RG were subjected to a repeated measure model ANOVA (PROC GLM). A one-way analysis of variance (PROC MIXED) was used to examine the differences in aboveground productivity, standing root phytomass and DOC annual losses between PG and RG. Post hoc treatment comparisons were made according to Tukey and Bonferroni. Simple linear regression analysis (PROC REG) was used to estimate the annual change in SOC under PG as a function of time. The slope of this regression line reflects the rate of C accumulation on a horizontal land area basis. In addition, the differences in SOC under PG and associated C:N ratios over time were also examined using a one-way analysis of variance (PROC MIXED).

6.3 Results

6.3.1 Effect of grassland renovation on BD and SOC content

Grassland ploughing and renovation had no effect on BD at 0 to 30 cm depth. Mean BD under PG and RG was 1.09 and 1.02 g cm^{-3}, respectively. The RG treatment was established in June 2008. But because SOC content has not been measured immediately before ploughing, the content from October 2004 was considered as a reference value for the comparisons (Fig. 6.1). Grassland renovation decreased SOC content ($P<0.05$) in upper 0.3 m of the soil profile. There was no effect of a sampling date on SOC content in a two and a half year period following ploughing (June 2008 to January 2011). During this period, a long term mean change in SOC between PG and RG represented a loss of 32.2 C t ha^{-1} or, in other words, a 22% reduction of topsoil SOC compared with PG. This difference developed almost entirely during the first four months following renovation (from June to October 2008). Since grassland renovation had no effect on topsoil BD, the effect on SOC content was largely caused by the effect on SOC concentrations. The C:N ratio of SOM was not affected by the grassland renovation or the sampling date during the study period (Fig. 6.2).

6.3.2 Effect of grassland renovation on aboveground and belowground phytomass

The root standing phytomass in upper 0.3 m of the soil profile under PG and RG estimated on DM basis amounted to 15.99 and 14.90 t ha^{-1}, respectively, with no significant difference between the treatments (Table 6.2). The major part of the root phytomass under both treatments (91% and 96%) was located in the upper 0.15 m of the soil profile and decreased rapidly at 0.15 to 0.30 m depth. Although, the C content of roots (26% to 36%) was low; the root phytomass under PG and RG stored 4.16 and 4.23 t C ha^{-1}, respectively (Table. 6.3). Since the standing root phytomass was measured only on a single occasion, the below-ground productivity for the site and root litter C inputs to SOM via root mortality could not be estimated on the basis of the available data.

There was also no difference in above-ground phytomass productivity between the grassland treatments (Table 6.2). The mean annual above-ground productivity of PG and RG obtained as a sum of pre-grazing herbage masses and stubble was estimated at 11.2 and 12.2 t DM ha yr^{-1} containing 4.81 and 5.18 t C ha^{-1} yr^{-1}, respectively. Stubble phytomass (<0.05 m) of PG and RG amounted to 2.15 and 2.63 t DM ha^{-1} with C storage of 0.87 and 1.01 t ha^{-1}, respectively (Table 6.2). The C content of stubble and herbage (38% to 43%) was considerably higher than C content of roots. Overall, grassland ploughing and reseeding had neither an effect on standing root and stubble phytomass sampled 15 months after grassland renovation nor above-ground phytomass productivity during two grazing seasons following grassland renovation, their C storage and associated C:N ratio (Table 6.2).

6.3.3 Effect of grassland renovation on DOC leaching to groundwater

The rainfall for the whole sampling period from March 2009 to January 2010 was 716 mm of which 545 mm drained to the groundwater as an ER. There was a significant two way interaction ($P<0.001$) between the effect of renovation and the sampling date on DOC concentration and its corresponding C:N ratio in the shallow groundwater. The DOC concentration under PG ranged from 0.2 to 70.9 mg L^{-1} (mean = 13.6 mg L^{-1}, SD = 12.25) with corresponding mean C:N ratio of 12.2. The concentrations under RG were recorded within the range of 0.13 and 67.6 mg L^{-1} (mean = 10.7 mg L^{-1}, SD = 9.48) with a mean C:N ratio of 15.7. The annual DOC leaching losses to groundwater from PG and RG from March 2009 to January 2010 were not significantly different and were estimated at 74.0 and 62.4 kg ha^{-1}, respectively (Table 6.2).

6.3.4 SOC change over time under permanent grassland

The slope of regression line indicated a tendency for SOC to increase over time, $y = 2.13x + 136.5$ (x represented the year), although this increase was not significant ($R^2 = 0.07$, $P>0.05$). The sampling date had no effect on topsoil SOC content over the entire study period. Also, C:N ratio of the SOM remained stable around 9.3 (SD = 0.26) without significant variation between the years (Fig. 6.2).

6.4 Discussion

6.4.1 Effect of grassland renovation on C inputs to soil organic matter

In grazed grasslands, C inputs enter SOC pool in the form of either above-ground litter, root phytomass or animal excreta (Bol et al., 2004). The levels of C inputs under PGs are usually high because of the perennial nature of the plants and also high belowground growth allocation (Loiseau and Soussana, 1999). Ploughing of grassland induces the death of most of the living plans that form this ecosystem (Vertes et al., 2007) and supplies soil with large amounts of phytomass residues with relatively low C:N ratio (between 15 and 25; Six et al., 2002). For this reason, higher C inputs were expected following ploughing and renovation of PG.

The above-ground productivity measured throughout two grazing seasons on site, at 11.2 and 12.2 t DM ha^{-1} yr^{-1} was comparable with 12.5 t ha yr^{-1} (Guo et al., 2008) and 13.0 t ha^{-1} yr^{-1} in a synthesis of field data for grassland ecosystems (Hui and Jackson, 2006) and did not differ between PG and RG in both years. Hence, it is likely that there were similar inputs of herbage C to the soil.

In general, the main input of C comes from roots (exudates and dead roots; Steele et al., 1997; Six et al., 2002). Since, the root systems are subject to simultaneous growth, senescence and decay, an accurate determination of below ground productivity has proven to be difficult (Aerts et al., 1989; Gill and Jackson, 2000; Milchunas and Lauenroth, 2001), especially with grazing animals present (Vertes et al., 2007). The focus of this study was mainly to compare the root phytomass between PG and RG and thus the potential C inputs originated from roots to corresponding SOC pools. For this reason, the comparison of root phytomass was based only on a single core sampling occasion and was representative of a root standing phytomass grown 15 months after cultivation. The measured quantities in both treatments were comparable with values reported for PGs (Eriksen and Jensen 2001; Vertes et al., 2003) and the pattern of their vertical distribution followed the pattern reported in other studies (Janssens et al., 2002; Claus and George 2005). However, there was no difference in the root phytomass between PG and RG and consequently, the C inputs originated from dead roots and exudates were likely not to differ as well. In addition, the rotational grazing management practiced on the farm likely resulted in a similar deposition of C through animal excreta between PG and RG.

6.4.2 Effect of grassland renovation on SOC content

The losses of SOC supported the hypothesis that grassland renovation causes strong and sudden decrease of SOC in the soil profile. Post et al. (2000) reported that the decrease in SOC can be attributed to reduced inputs of OM, increased decomposability of phytomass residues, and cultivation effects that decrease the amount of physical protection to decomposition. Since the measured C inputs in this study did not differ between the treatments, the decrease in SOC content following grassland renovation must have been attributed to the soil disturbance by ploughing.

It is generally accepted that disruption of soil aggregates increases soil aeration, exposes stable, adsorbed SOM within micro- and macro- aggregates to rapid microbial decomposition and thus causes substantial ecosystem losses (Elliott 1986; Augustin et al., 1996; Kasimir-Klemedtsson et al., 1997; Reicosky et al., 1999; Six et al., 2002; Vertes et al., 2003; Lenhart et al., 2007). A number of studies have published rapid losses of SOC following a conversion of temperate grassland to cultivated use (Tiessen et al., 1982; Mann, 1986; Burke et al., 1989; Schlesinger and Andrews, 2000; Slobodian et al., 2002; Schnitzer et al., 2006); e.g. Strebel et al. (1988) measured losses of up to 100 t ha^{-1} of SOC (57%) in 4 years following conversion of PG to arable land. However, there has been a few studies referring on the effect of ploughing and renovation of grassland on SOC dynamics; e.g. Eriksen and Jensen (2001) measured soil respiration directly using a dynamic chamber method during the first three months following ploughing of an old grass-clover pasture in grass-arable rotation on a sandy soil (sand 56.5%). Their results showed that cultivation caused losses of 1.2 t CO_2-C ha^{-1} over a three month period compared with undisturbed grassland. The magnitude of losses in the present study was several folds higher compared with their findings. This could be attributed to the fact that PG on site was based on a heavy clay loam soil and has been accumulating SOM for many years under unchanged management.

The difference in SOC in the present study developed almost entirely (86%) in the first four months following ploughing. This is in agreement with previous cultivation studies (e.g. Vertes et al., 2007).

Although the DOC losses measured in the present study after March 2009 did not increase as a result of grassland renovation, they could have been a considerably increased from June 2008 to March 2009. Consequently not only heterotrophic respiration of soil microbial biomass (mineralisation), but also DOC leaching was considered to be a potential pathway responsible for the SOC loss from the RG. The rate of SOM decomposition is controlled by the chemical composition of SOM, edaphic, climatic and hydrological conditions (Post et al., 2001). The C:N ratio of SOM in this study did not change following renovation and was within the range reported for grassland topsoils (Jenkinson 1988; Ammann et al.,2007), however, was slightly lower compared with a mean value for Irish soils (11.3; Brogan, 1966). On the basis of available SOC data from four sampling occasions spanning a period of two and a half years, the relationships with the hydrological and climate variables could not be fully investigated. Despite this, there was a weak relationship found between SOC change and soil temperature ($P = 0.06$; $R^2 = 0.87$, ´data not presented´) indicating that the process of mineralisation of SOM following renovation may have been enhanced by higher temperature during summer months (June to October).

Since there was no effect of a sampling date on SOC content in this study in a two and half year period following ploughing, there was no evidence of apparent recovery of SOC to previous levels. The SOC depletion was much faster following grassland destruction than the build-up of SOC in the years immediately after renovation. This is in agreement with Rasmussen et al. (1998), who reported that after 50 years following ploughing, the SOC levels reached only 50% of the previous content. Consequently, a further research is required to determine the ability of the PG to restore a high level of soil quality on this site.

6.4.3 SOC change over time under permanent grassland

Despite the fact that SOC content under PG in this study was observed over a seven years period and successive monitoring involved bulking a large number of soil cores ($n = 45$) per replicate to overcome spatial heterogeneity, the SOC content exhibited a high spatial and temporal variation. The spatial heterogeneity could have been associated with the fact that some paddocks were renovated in 1985 and 1995 and the SOC levels were still restoring the previous contents. On the other hand, the year to year variation might have been caused by extremely wet weather conditions in the 2008 and 2009 and extremely dry conditions in 2010. Considering this uncertainty, it was not possible to detect a change in SOC under PG within this study period. The statistical approach using a simple linear regression indicated a tendency of PG in Solohead to act as a sink for CO_2 at a rate of 2.1 C t ha^{-1} yr^{-1} between 2004 and 2011; although this was not significant.

The SOC accumulation in temperate grasslands is generally promoted by (i) high clay content (Wang et al., 2003; Jones and Donnelly, 2004; Mestdagh et al., 2006), which physically stabilizes SOM on clay surfaces and protects labile SOM from decomposition (Post et al., 2001; Guggenberger and Kaiser, 2003; Lal,2004; Swanston et al., 2005; von Lutzow et al., 2006); (ii) high soil moisture content causing limited aeration and leading to lower decomposition (Jones et al., 2006; Mestdagh et al., 2006; Hutchinson et al., 2007, O`Brien et al., 2010); (iii) low temperatures also leading to lower SOC decomposition (Freibauer et al., 2004; Hutchinson et al., 2007) (iv) high primary production and thus high C inputs to the soil (Campbell et al., 2001; Jones and Donnelly, 2004); (v) increased intensity and pattern of rainfall events (Springob and Kirchmann,2003; O`Brien at al., 2010) (vi) high groundwater tables promoting higher phytomass production by easing moisture limitation during summer (Vertes et al., 2003, Phelan et al., 2012); (vii) intermittent water logging, impeding decomposition processes (Davidson and Lefebvre, 1993). The watertable depth and volumetric soil moisture content were recorded only during two years of the study so the correlations between local hydrological settings and SOC accumulation rates could not be statistically analysed. Despite these statistical limitations, it is hypothesized that PG in Solohead acts as a strong CO_2 sink, especially due to poorly drained conditions on the farm. For this reason, measurements extended over a longer time are needed to fully investigate the extent of SOC accumulation on the site.

6.5 Conclusions

In this study, we evaluated the impact of ploughing and renovation of PG on SOC dynamics in a clay loam soil. The results indicated that grassland renovation significantly decreased topsoil SOC content, resulting in 22% reductions compared with PG. The major difference in SOC (86%) due to grassland destruction developed in the first four months following ploughing. Heterotrophic respiration of soil microbial biomass (mineralisation) and DOC leaching were considered to be potential pathways responsible for the SOC loss. For this reason, these results could have substantial consequences in a context of climate change.

We also investigated the changes in SOC under PG under moist conditions. Although, the edaphic (poorly drained heavy structured) and climatic conditions in Solohead are expected to support high rates of accumulation, the rates of sequestration reported in this paper were not statistically significant. And therefore further research is required in order to fully evaluate the rate of SOC sequestration under PG on this site.

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Table 6.1 Grassland management at Solohead Research Farm from 2004 to 2009.

	Livestock density LU ha^{-1}	Grazing days per year	Annual herbage intake by livestock (t ha^{-1})	Annual N input through biological N fixation (kg N ha^{-1}) †	Annual N input in fertilizer (kg N ha^{-1})	Annual slurry application (m^3 ha^{-1})
2004 [a)]	2.2	254	11.9 - 12.6	14-129	84-224	73
2005 [a)]	2.2	250 - 256	12.0 - 12.9	10-113	89-219	68 – 67
2006 [a)]	2.2	251 - 255	10.2 - 11.5	11-87	99-240	62 – 68
2007 [b)]	2.1	225 - 237	9.9 - 11.2	60	90	55
2008 [c)]	1.59 - 2.1	220 - 237	9.9 - 11.3	71-109	0-90	24 – 25
2009 [c)]	1.59 -2.1	217 - 237	9.9 - 11.2	58-170	0-90	25 – 27

[a)] Humphreys et al., 2009
[b)] Humphreys et al., 2010
[c)] Humphreys et al., 2010, Keogh et al., 2010
† estimated according to an empirical model, based on herbage yield and white clover content (Humphreys et al., 2008).

Table 6.2 Aboveground and belowground phytomass, and dissolved organic carbon (DOC) losses to groundwater from permanent (PG) and renovated grassland (RG) at Solohead Research Farm in 2008 and 2009.

	PG		RG		Statistic	PG		RG		Statistic
	Dry mass (t ha^{-1})	SE	Dry mass (t ha^{-1})	SE	P value	C (t ha^{-1})	C:N	C (t ha^{-1})	C:N	P value
Aboveground primary productivity:										
Utilized phytomass > 0.05 m	9.08	0.32	9.60	0.38	0.419	3.94	16.50	4.17	16.50	0.419
Stubble < 0.05 m	2.16	0.53	2.63	0.33	0.672	0.87	18.63	1.01	20.70	0.744
Belowground standing phytomass:										
0 - 0.15	15.17	4.15	14.57	3.77	0.946	3.87	16.16	4.11	19.45	0.913
0.15 - 0.30	0.82	0.19	0.33	0.10	0.243	0.29	25.70	0.12	29.59	0.247
Roots 0 - 0.30	15.99		14.90			4.16		4.23		
DOC leaching						0.07	12.20	0.06	15.70	0.302

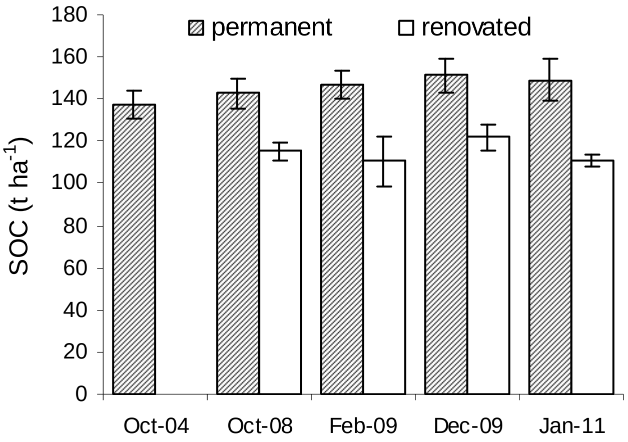

Fig. 6.1 Soil organic carbon (SOC) at 0 to 0.3 m depth under permanent and renovated grassland on four sampling occasions after grassland renovation compared with SOC levels from October 2004. Error bars are ± SE. Means across the treatments are significantly different on the basis of analysis of variance ($P = 0.005$) and the Tukey test; means across sampling dates are not significantly different ($P>0.05$).

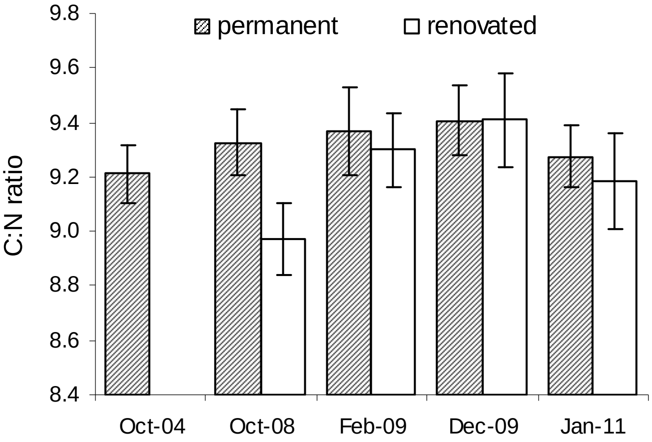

Fig. 6.2 C:N ratio of soil organic matter at 0 to 0.3 m depth under permanent and renovated grassland on four sampling occasions after grassland renovation compared with C:N ratio from October 2004. Error bars are ± SE. Means are not significantly different on the basis of analysis of variance (P>0.05).

7. Discussion and conclusions

7.1 General discussion

7.1.1 Climatic and edaphic data

The years of the study had exceptionally high rainfall compared with previous years. This resulted in higher soil moisture content, higher annual effective rainfall (ER) and longer drainage seasons. High soil moisture conditions led to long periods of anoxic conditions of the soils with considerable reduction potential, which likely promoted reduction biochemical processes such as dissimilatory nitrate (NO_3^-) reduction to ammonium (NH_4^+) (DNRA) and denitrification while mineralisation rates were reduced. Depth to the watertable on site was low (therefore unsaturated zone was thin) and, despite fluctuations, remained close to the surface throughout the study. Vertical travel time to groundwater was estimated to be within a single drainage season (Fenton et al. 2009; Necpalova et al., 2012) and allowed for an accurate examination of the impact of land use or grassland management on groundwater concentrations. The water table fluctuations across the site were consistent in recharge and also seem to have been consistent across the site. Therefore biochemical processes in the soil rather than dilution during vertical migration in the unsaturated zone and mixing in shallow groundwater controlled N concentrations in groundwater.

7.1.2 Effect of a dairy production system involving grazing over the winter

In order to assess N utilisation and to evaluate the potential impact of grazing over the winter on the environment compared with conventional practices, soil surface balances (SSBs) were calculated for each paddock within three dairy production systems (ES-100N-early spring calving with an input of 100 kg N ha^{-1}; ES-0N - early spring calving with an input of 0 kg N ha^{-1}; LS-0N- late spring calving with and input of 0 kg N ha^{-1}). The biological N fixation (BNF) was the most important N input to soil component of ES-0N and LS-0N systems. The application of synthetic fertilizer at a rate of 100 kg ha^{-1} in ES-100N reduced the amount of N fixed through BNF by 46% as a result of clover content reduction. Since BNF in ES-0N and LS-0N replaced an equivalent quantity of synthetic fertilizer, all the systems showed similar rates of herbage uptake and thus herbage production. The SSBs revealed that the land component of the systems generated N surpluses from 113 to 161 kg N ha^{-1} y^{-1} without significant variation between the systems and years of the study. This suggests that grazing over the winter in LS-0N did not create an extra environmental pressure on the soil component on an annual basis in comparison with early calving systems (ES-100N and ES-0N). The surpluses and nutrient use efficiencies estimated in the present study were in accordance with results reported for SSBs on dairy farms in other European countries (Oenema et al. 2003; Van Beek et al., 2003; Steinshamn et al., 2004).

While soil surface surplus and N inputs positively influenced the size of total soluble N (TSN) and soluble organic N (SON) pools, they had no effect on the size of soluble inorganic N (SIN) pool, which is in contrast to the findings of Jarvis (1999), Grignani and Zavattaro (2000). This suggests that SIN content in clay loam soils results from a great number of interacting factors and simple relationships are not sufficient to explain the size of this pool in the soil profile.

Despite this, there was a hypothesis that soil SON, SIN and N leaching to groundwater would temporarily increase during the winter months since grazing over the winter leads to a substantial uneven deposition of highly concentrated excreta on the soil surface (Bakker et al., 2004; Decau et al., 2004; Hutchings et al., 2007), while grass growth and thus N uptake is temperature limited and significant ER occurs (Jewkes et al., 2007). There was an effect of a two way interaction between the system and sampling date on some N species in the soil profile and the groundwater (e.g. SON, TDN, DON, oxidised N and NO_3^{-}N), however, from more detailed analyses and time courses, it has become clear that the effect of the time and seasonal changes were noticeably more important than the effect of the dairy system operating on the soil surface. Consequently, the soil and groundwater N dynamics under all systems exhibited a similar intra-annual trend despite the differences in the time of supply (grazing season) and the form (i.e. synthetic fertilizer, BNF) of N inputs. This suggests that grazing over the winter which characterized the LS-0N dairy production system, did not affect the size and dynamics of soil N pools, its dynamics and did not create a greater environmental pressure on the groundwater quality compared to earlier calving dairy systems.

The lack of response or not detecting the inorganic N increase in the current study could be attributed to the fact that the variation in soil N and groundwater N was buffered by the biochemical processes related to inherent soil properties on site (e.g. physical structure, heavy texture, high soil pH, high soil organic C content), continuous anaerobic conditions during the study period and by the presence of a shallow groundwater table (0 to 2.2 m bgl) in the soil profile (Grignani and Zavattaro, 2000). High natural attenuation and denitrification capacity of these soils and the absence of significant responses of SIN and water quality to grassland managements on this site has been already reported (Humphreys et al., 2008b, Necpalova et al., 2012).

The effects of the dairy systems on N losses through leaching were based on their effects on N concentrations in the groundwater. Annual losses of all N species from the dairy production systems ranged from 19.3 to 22.9 kg N ha^{-1} y^{-1}. Higher DON losses from ES-100, due to higher DON concentrations compared with the systems receiving no fertilizer was attributed to higher stocking density of grazing animals in this system and thus to higher deposition of excreta over the treatment area. There was no evidence of higher annual N losses from the system involving grazing over the winter compared with earlier spring calving dairy production systems during both experimental years.

Furthermore, the annual nitrous oxide (N_2O) fluxes from the fertilized and ES-0N and LS-0N systems were also not significantly different and amounted to 6.4 kg N ha^{-1} y^{-1} (Li et al., 2011). This implies that the studied dairy production systems created similar pressure on the environment in terms of N leaching to groundwater and direct N_2O emissions from the soil surface. The unaccounted N ranged from 86.4 to 134.0 kg N ha^{-1} y^{-1} and on the fundamental basis of the N cycle was denitrified to dinitrogen gas (N_2), contributed to air pollution as ammonia and/or was accumulated to the soil organic pools.

7.1.3 Effect of grassland renovation on C and N cycle in the permanent grassland

Ploughing and reseeding of permanent grassland (PG) caused a strong and sudden decrease of soil organic carbon (SOC), total N (TN) and SON in the topsoil. It is generally accepted that disruption of soil aggregates by ploughing increases soil aeration, exposes stable, adsorbed soil organic matter (SOM) within micro- and macroaggregates to rapid microbial decomposition (Elliott 1986; Augustin et al., 1996; Kasimir-Klemedtsson et al., 1997; Reicosky et al., 1999; Six et al., 2002; 2004; Vertes et al., 2003; Lenhart et al., 2007).

A number of studies have reported rapid losses of SOC following a conversion of temperate grassland to cultivated use (Tiessen et al., 1982; Mann, 1986; Strebel et al.,1988; Burke et al., 1989; Schlesinger and Andrews, 2000; Slobodian et al., 2002; Schnitzer et al., 2006) or substantial losses of TN following long periods of cultivation (Keeney and Bremner, 1964; Tiesses et al., 1982; Tiessesn and Stewart, 1983; Dalal et al., 1986; Post and Mann, 1990; Mikhailova et al.; 2000); however, studies investigating the effect of PG ploughing and reseeding on SOM content are rare (e.g. Eriksen and Jensen; 2001, Bhogal et al., 2000). The magnitude of SOC and TN changes in the present study was several folds higher compared with findings previously reported. This could be attributed to the fact that PG on this site was based on a heavy clay loam soil and has been accumulating SOM for many years under unchanged permanent grassland management. The depletion of SOM due to grassland destruction took place almost entirely (72 to 86%) in the first four months following ploughing, which is in agreement with previous cultivation studies (e.g. Vertes et al., 2007). Since there was no temporal variability observed in SOM content following ploughing, there was no evidence of apparent recovery to previous levels during this study period. The magnitude and duration of the change indicated that renovation had a significant and long term effect on soil quality and sustainability on this site. Topsoil C:N ratio of SOM was within the range reported for grassland topsoils (Jenkinson 1988; Ammann et al.,2007), however, was slightly lower compared with a mean value for Irish soils (11.3; Brogan, 1966). The fact that C:N ratio did not change following renovation supported the finding that both C and N were depleted to the same extent (Post and Mann, 1990).

There was a hypothesis that SON would temporary increase as a result of decomposing a recalcitrant SOM or decaying grass residues like in studies of Bhogal et al. (2000) and Murphy et al. (2007). However, the slight decrease in this study was likely a result of mineralisation of exposed SON in the same way as exposed recalcitrant SOM pool. Similar results of a slight decrease or unaffected SON in clay soils following renovation were already reported (Davies et al. 2001; Velthof at al. 2010; Smit and Velthof 2010). The reason for the different behaviour of SON following PG renovation is not clear.

Despite the high net SOM mineralisation rate, SIN (with this sampling strategy) was not influenced by grassland renovation at any sampling depth. In general, ploughing of grassland leads to a substantial increase of inorganic N in the soil profile (100 to 400 kg N ha^{-1} y^{-1}) for several weeks to months in the first year following ploughing (Van der Weerden et al. 1999; Davies et al. 2001; Mori and Hojito 2007, Vertès et al. 2007; Velthof et al. 2010) as a result of stimulated decomposition and microbial respiration (Davies et al. 2001). The lack of response or not detecting the increase in the current study could be attributed to the fact that the first soil sampling was carried out four months after PG renovation. Another possibility is that high SOC soils (4.48%) on site induced suitable conditions for denitrification during wet months and removed any SOM lost in excess of N uptake and N leaching to groundwater.

This suggestion is also supported by low magnitude of the total oxidised N leaching losses to groundwater. A number of previous studies on the effect of grassland renovation on NO_3^--N leaching reported losses up to 300 kg NO_3^--N $ha^{-1}y^{-1}$ (Scholefield et al. 1993; Adams and Jan 1999; Bhogal et al. 2000; Davies et al. 2001; Shepherd et al. 2001; Ball et al. 2007; Seidel et al. 2007; Velthof et al. 2010). The NO_3^--N losses in this study were lower than 5 kg N ha^{-1}. High reduction potential of the soils on site (discussed above) likely led to exhaustion of NO_3^--N via DNRA (Hill 1996, Stepniewski and Stepniewska 2009) or denitrification (Jacobs and Gilliam 1985; Lowrance 1992) and thus reduced the water quality response to grassland renovation. Despite this, the effect of PG renovation decreased as a function of time and remained significant for 1.2 years following renovation, which is in agreement with other studies (Roberts et al. 1989; Davies et al.2001; Laurent et al. 2004, Mori and Hojito 2007). In contract to findings of Bhogal et al. (2000), the dissolved organic N (DON) and NH_4^+-N were not influenced by grassland renovation.

There has been a number of greenhouse gas studies published on the effect of ploughing up of grassland followed by reseeding with higher yielding grass species, maize or the other cereals (Baggs et al. 2000, Estavillo et al. 2002; Yamulki and Jarvis 2002; Pinto, et al. 2004; Ball et al. 2007). However, there have been only a few studies reporting N_2O emissions following grassland renovation (Davies et al., 2001; Mori and Hojito 2007; Velthof et al., 2010; MacDonald et al., 2011). The fluxes measured from renovated grassland (RG) in the present study were increased for 1.3 years, however, were lower than fluxes reported earlier. The magnitude of the N_2O emissions was most likely influenced by high soil moisture content and high soil pH on site (Weier and Gilliam 1986; Davidson 1993; Granli and Bockman 1994; Stevens and Laughlin, 1998; Van der Weerden et al. 1999; Ruser et al. 2006; Stepniewski and Stepniewska 2009; Liu et al. 2010; Cuhel and Simek 2011; Senbayram et al. 2012). It is assumed, that grassland renovation enhanced denitrification and nitrification rates, but the additional N_2O was almost entirely reduced to N_2. The peak in N_2O emissions from RG in the present study occurred in response to the commencement of grazing, which suggests that the effect of renovation on N_2O emissions was strengthened by the effect of grazing.

The N lost as N_2O represented 0.49% of the N input to RG, which is less than the average of 1.6% found for five European sites by Petersen et al. (2005). The other 4.8 to 4.9% of the total N inputs were leached to groundwater in the first year following renovation. This indicates that although the overall losses following grassland renovation at this site as a result of net SOM mineralisation were high (> 3t N ha^{-1}), the losses via N leaching and N_2O emissions due to high natural attenuation and denitrification capacity of the soils on site were low (27 kg N ha^{-1} y^{-1}).

7.2 Conclusions

1. Soil N balances and soil N dynamics in a clay-loam soil under Irish dairy production systems (Chapter 3)

i. Since BNF replaced an equivalent quantity of synthetic fertilizer, there was no difference in herbage production and potential for utilization by grazing or harvesting between the systems.
ii. The management of the systems resulted in a similar N surplus (143.6 kg N ha^{-1} y^{-1}) and N use efficiency (66%) at the soil surface level leading to a similar environmental pressure on the soil component on an annual basis.
iii. The correlation between grassland managements and soil N dynamics in the clay loam soil profile was difficult due to high natural buffering capacity of the soils associated with high soil organic C content, high soil pH, anaerobic conditions

and the presence of a shallow groundwater table, i.e. grazing over the winter period had no effect on the soil N dynamics on this site.

iv. Anaerobic reduction processes such as denitrification and DNRA probably ensured consistently low soil TON content. Consequently, the performance of grazing over the winter on these heavy clay loam soils did not create additional environment pressure via N losses to groundwater and N_2O emissions compared with conventional grazing systems.

v. The management factors such N input and N surplus influenced the dynamics of SON pool, while SIN dynamics was mainly affected by the hydrological factors and soil temperature, which are the most important factors controlling microbial activity, biochemical processes and leaching.

2. N leaching to groundwater from dairy production involving grazing over the winter on a clay-loam soil (Chapter 4)

i. Vertical travel time of approximately one drainage season due to a shallow watertable and high ER allowed correlations between nutrient losses and shallow groundwater nutrient concentrations within a small time lag period.

ii. The high natural attenuation and denitrification capacity of the soil due to high C and anaerobic conditions ensured low concentrations of nutrients making correlations difficult; i.e. grazing over the winter period had no effect on groundwater quality on this site.

iii. Any losses from the dairy production systems were likely reduced by biochemical processes which consequently resulted in increased NH_4^+-N levels. For this reason, DON and NH_4^+-N represented the highest proportion of N losses, presently migrating slowly towards receptors on site.

iv. Some of the spatial and temporal variation of N concentrations was explained by correlations with selected chemical and hydro-topographical parameters.

v. Strong correlations to NO_3^--N/Cl^- ratio and the distance of the sampling point from the closest receptor indicated presence of point sources of contamination and groundwater-surface water interactions on site.

3. Effect of ploughing and reseeding of permanent grassland on soil N, N leaching and nitrous oxide emissions from a clay-loam soil (Chapter 5)

i. Ploughing and reseeding of PG decreased topsoil TN and SON, increased TON leaching to groundwater and the gaseous losses of N_2O from the soil surface as a result of soil disturbance, enhanced decomposition of SOM and incorporated grass residues followed by nitrification and denitrification.
ii. The effect of renovation remained significant for more than 14 months following ploughing and decreased as a function of time.
iii. The rate of topsoil TN loss indicated that renovation on a clay loam soil had a significant and long term effect on soil quality and sustainability on this site.
iv. The overall losses following grassland renovation due to net SOM mineralisation were high (>3 t N ha^{-1}), however, the proportion lost via N leaching and N_2O emissions was low (27.11 kg N ha^{-1} y^{-1}). This was likely a result of inherent properties (high soil C), reduction potential (high soil pH) and predominantly anoxic status of the soils on site during the study period, which likely promoted reduction biochemical processes such as DNRA and complete denitrification, and consequently led to reduction of NO_3^--N and N_2O losses.
v. The N losses via direct N_2O were much lower than N losses via leaching; accordingly grassland renovation on a clay loam soil had a greater impact on the groundwater quality than the quality of the air.
vi. KCl extraction of soil samples at the depth of a local watertable provides a comparable results of inorganic N leaching from a heavy clay loam soil, although, this does not apply to the results of organic N in the extracts and groundwater.

4. Changes in soil organic carbon in a clay-loam soil following ploughing and reseeding of permanent grassland under temperate moist climatic conditions (Chapter 6)

i. Grassland renovation significantly decreased topsoil SOC content, resulting in 22% reductions compared with PG.
ii. The major difference in SOC (86%) due to grassland destruction developed in the first four months following ploughing.
iii. Heterotrophic respiration of soil microbial biomass (mineralisation) and dissolved organic C leaching were considered to be potential pathways

responsible for the SOC loss. For this reason, these results could have substantial consequences in a context of climate change.

iv. Although the edaphic (poorly drained heavy structured) and climatic conditions in Solohead are expected to support high rates of accumulation, the rates of sequestration reported in this paper were not statistically significant.

7.3 Recommendations for future research

- The years of the study had an exceptionally high rainfall compared with previous years, which resulted in lower herbage production, higher annual ER, longer drainage seasons, long periods of anoxic conditions, greater potential for N leaching, dissimilatory DNRA and denitrification. The environmental impact of winter grazing compared with conventional practices and also the effect of permanent grassland cultivation in the present study were investigated under highly moist climatic conditions. Nevertheless, the effects should be investigated under dryer climatic condition in the future.

- The biological N fixation (BNF) in stolon, roots and stubble in the present study was quantified using a mechanistic model based on a white clover production, a method that introduces a possible bias when used in SSBs. Therefore a comparison of BNF estimates with a directly measured data would be valuable.

- The atmospheric wet deposition of N was well quantified in the present study. Nevertheless, the dry atmospheric deposition of N was not investigated, which was found to significantly contribute to the atmospheric deposition of N in other studies.

- The SSBs of the three dairy production systems could be improved, if each studied system would have separate housing and storage premises and thus separate silage and slurry management.

- The SSBs revealed that the studied dairy production systems generated N surplus on the soil surface of 113 to 161 kg N ha^{-1}. The N fluxes to the groundwater and N_2O emissions to the air were quantified; however, some of the N surplus (from 86 to 134 kg N ha^{-1}) remained unexplained. Therefore, measurements of N_2 (e.g. using acetylene inhibition, He/O_2 system, ^{15}N incubation technique), ammonia emissions (e.g. micrometeorological technique) and N accumulation into soil organic pools are highly required on this site.

- There is a number of models which could provide a) an estimate of ammonia emissions (NARSES; Webb and Misselbrook, 2004), b) an estimate of N_2O/N_2 emissions (DNDC, Li, 2000; DayCent, Parton et al., 1998) or c) the whole N cycle in ruminant systems (NCYCLE, Scholefield et al., 1991; NGAUGE, Brown et al., 2005; SIMSDAIRY, del Prado et al., 2008; del Prado et al., 2011)

- Grazing over the winter that characterised the LS-0N dairy production system did not affect the soil soluble N pools and their dynamics in a clay loam soil and also the N concentrations in the shallow groundwater on this site. Nevertheless, the effect should be investigated on different soil types in the future.

- The absence of a significant SIN and SON response to grassland management on the soil surface in this study was attributed to the fact that the variation in the size of the pools has been buffered by the biochemical processes related to soil properties, continuous anaerobic conditions during the study period and to the presence of a shallow groundwater table in the soil profile. The correlations with climatic variables were established. To understand how the soil properties control the biochemical processes and soluble N dynamics in the soils on this site, the results of the future studies are advised to be correlated with the soil properties and groundwater depth.

- Similarly, on the basis of available data, it was not possible to investigate the correlations between soil parameters responsible for the control over the N concentrations in the groundwater. An investigation of these correlations is essential for future understanding of the soil biochemical processes on this site.

- In the present study, some of the spatial and temporal patterns in N concentrations in groundwater were explained by the correlations with a set of hydro-topographical parameters. A high explanatory power of the distance of the sampling point from the closest receptor indicated that the River Pope and local drains interact with the groundwater and cause a dilution at the groundwater-surface water interface when the watertable is very shallow. Therefore a comparison of N concentrations in the groundwater and in the receptor would be valuable.

- The mechanisms of the release, decomposition, and transport of SON and SIN in clay loam soils following PG renovation need further, more detailed investigation.

- The N_2O losses following grassland renovation were quantified in the present study. The magnitude of the results suggested that grassland renovation enhanced denitrification and nitrification in a clay loam soil, but most of the N_2O emissions was further reduced to N_2. For this reason, measurements of N_2 could help to explain the high rates of net SOM mineralisation following grassland renovation on this side.

- In general, the main input of C comes from roots (exudates and dead roots). The focus of this study was to compare the root standing phytomass in PG and RG grown 15 months after cultivation. The belowground net primary productivity and C inputs originated from dead roots and exudates to corresponding SOC pools were not quantified. These estimates were found to be an important element of C sequestration studies and could support to date findings on this site.

- Despite the fact that DOC losses were investigated during a year period, the quantification of DOC and also dissolved inorganic C to groundwater from clay loam soils following PG renovation need further, more detailed investigation.

- The rate of SOM decomposition is controlled by chemical composition of SOM, edaphic, climatic and hydrological conditions. On the basis of available SOC and TN data from four sampling occasions spanning a period of two and a half years, the relationships with the hydrological and climate variables could not be fully investigated; however, they would be considered as very important.

- There was no evidence of apparent recovery of TN and SOC to previous levels in the present study. Consequently, a further research is required to determine the ability of the PG to restore a high level of soil quality on this site.

- In the present study, there was an attempt to quantify SOC sequestration rates in a clay loam soil under PG on a basis of limited dataset spanning a period of 7 years. To reduce the high uncertainty related to year to year variation, more frequent measurements (e.g. annually) over a longer period are recommended.

- The present study investigated changes in SOC and TN content to a depth of 0.3 m. This sampling depth has been found as insufficient when the effect of land-use is investigated. For this reason, the future studies should take into consideration a core sampling at least to a 1 m depth.

- The SOC content in the present study was compared on an equivalent mass basis taking into account changes in soil bulk density. If the same approach is used in the future, it is advised to determine the soil bulk density along with SOM content on each sampling occasion.

- Due to poorly drained conditions, it is hypothesized that PG in Solohead acts as a strong CO_2 sink; however, the watertable depth and volumetric soil moisture content were recorded only during two years of the study period. Thus, the correlations between local hydrological settings and SOC accumulation rates could not be statistically analysed. For this reason, measurements extended over a longer time are needed to fully investigate the extent of SOC accumulation on the site

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Glossary of terms

Aerobic - an environment containing molecular oxygen; biodegradation or other process operating in the presence of molecular oxygen

Anaerobic - an environment containing no molecular oxygen; biodegradation or other process operating in the absence of molecular oxygen

Aquifer - saturated underground rock or sediment formation which is sufficiently permeable to allow the flow of water

Cation exchange capacity of soil is a measure of its ability to store ions in exchange with soil solution

Denitrification - anaerobic biological activity utilising nitrate as electron acceptor.
The end-product of respiration is usually nitrogen but intermediate formation of nitrite or nitrous oxide may be detected. Also termed nitrate reduction.

Effective porosity - the interconnected pore volume or void space in a soil/rock that contributes to fluid flow or permeability in an aquifer. Effective porosity excludes isolated pores and pore volume occupied by water adsorbed on clay minerals or other grains.

Eutrophication - the loss of trophic conditions, normally as a result of nutrient enrichment of an aquatic system by nitrogen or phosphorus

Evapotranspiration (ET) is a term describing the transport of water into the atmosphere from surfaces, including soil (soil evaporation), and from vegetation (transpiration).

Field capacity is the amount of soil moisture or water content held in soil after excess water has drained away by gravity after 24 hours.

Hydraulic conductivity - linear proportional constant from Darcy's law that. It is specific to the direction of flow. It depends on anisotropic porous materials.

Macropore - a large pore in a soil or other porous medium (generally created by root holes, worm holes or desiccation cracks amongst other processes)

Mineralisation - biodegradation that leads to the transformation of contaminants into inorganic end-products, such as carbon dioxide, water, methane, chloride ions

Nitrate reduction -denitrification

Nitrification -the oxidative conversion of ammonium to nitrate

Nitrogen cycle is the set of biogeochemical processes by which nitrogen undergoes chemical reactions, changes form, and moves through difference reservoirs on earth, including living organisms.

Particulate organic N (PON) includes small organisms (algae, bacteria, etc), both living and dead and fragments of organisms, that are not bound to mineral particles.

Soil porosity refers to the space between soil particles, which consists of various amounts of water and air.

Unsaturated zone -the zone between the land surface and the water table. It includes the soil zone, unsaturated rock and capillary fringe. The pore spaces contain water at less than atmospheric pressure, as well as air and other gases. Saturated bodies such as perched groundwater may exist within the unsaturated zone. Also called zone of aeration or vadose zone

Velocity - is a vector measurement of the rate and direction of motion or, in other terms, the rate and direction of the change in the position of an object.

Water deficit -the cumulative difference between the potential evapotranspiration and rainfall during a specified period in which the rainfall is the smaller of the two.

Appendix