

Impact of Agricultural Management on Risks of Nitrate Leaching in Crop Rotations with Potatoes and Cereals



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Abstract

There is concern about increased nitrate levels in drinking water due to potential impacts on human health. At the same time there are also concerns about the environmental impact of increased levels of nitrate in surface water systems; the increased amount of nitrate in surface water can cause eutrophication. It has become almost axiomatic that nitrate which comes from agriculture soils is one of the main drivers of the increased nitrate levels in water. Arable agriculture is considered to be one of the main sources of nitrate due to high rates of nitrogen fertiliser or manure application, non-synchronous application of fertiliser with crop demand and inappropriate management of soil and water. Therefore minimise nitrate losses from agriculture soils could help to reduce nitrate level in ground and surface waters.

This PhD study aims to improve the recommendations that are available to farmers to minimise nitrate leaching from arable rotations under UK conditions by investigating the impact of typical agricultural management practices on the risks of nitrate leaching in crop rotations with potatoes and cereals.

- ❖ Chapter 2 presents a critical literature review which integrates current understanding of soil nitrogen cycle, water movement at field scale and crop nitrogen use efficiency (potato and cereals).
- ❖ Chapter 3 provides a full description of Nafferton Farming Systems Comparison Experiment including the location and field trial design. The cropping history in the organic and conventional rotations grown Nafferton Factorial Systems Comparison Trial (NFSC) together with details of the plots and their management is also presented.
- ❖ Chapter 4 reports a study of the effect of autumn-applied composted cattle manure and winter wheat variety on the overwinter leaching of nitrate. 8 winter wheat varieties with two rates of composted manure or no manure application (4 replicates) were grown in plots. The amount of soil mineral N in the soil profile was measured in early spring 2011. The results showed that there was no effect

of winter wheat variety or application of composted cattle manure on NO_3^- -N leaching, where the wheat was sown in late autumn.

- ❖ Chapter 5 reports a study of the effects of crop management practices (year, crop protection, fertility management, rotation and potato variety) on the nitrate at risk of leaching. Soil nitrate was measured through the growing season (2010-2012) and after potato and cereal harvest (PHSNi) in NFSC. Higher soil mineral nitrogen content accumulated in top 0-30 cm than subsoil (30-90 cm) in both experiments. The results showed that there was no significant difference between PHSNi where inorganic fertiliser or composted manure had been applied at recommended rates. There was no significant effect of year, potato variety and crop protection treatment on PHSNi content after potato and cereal crops. However, PHSNi after potato was higher than after cereal harvest. There was an interaction between potato variety and sample depth with higher nitrate deeper in the profile with the earlier harvested variety. Crop rotation did not affect the PHSNi content in 2010 but there was a significant effect in 2011. These results confirm that effective crop/ soil management (such as applying recommended rates of fertiliser) can reduce nitrate leaching risk.
- ❖ Chapter 6 reports a study of the soil physical properties affecting water transport within the site. Three soil profiles were dug and described. Intact soil cores were collected and used to measure soil water content at 0.05, 2 and 15 bars, total porosity and saturated hydraulic conductivity (K_s). Soil water retained (at 0.05, 2 and 15 bars) increased and total porosity, macroporosity and saturated hydraulic conductivity (K_s) decreased with depth as sand content decreased. The use of pedotransfer functions to estimate the soil moisture characteristic curve gave good estimates of the soil water content at 2 and 15 bar but the predicted and measured data were not in agreement for the intact soil cores at lower suction (0.05bar). These results confirm that total soil porosity, macroporosity, the soil moisture characteristic curve and water movement are strongly related to soil texture.
- ❖ Chapter 7 reports a study of hydrological pathways in the soil profile using bromide, which is a conservative tracer for nitrate movement. Field experiments were conducted on plots within NFSC, porous ceramic cups were installed at 30 and 60 cm depth in selected plots in spring 2011 and overwinter 2012-2012. Bromide was surface applied. Soil solution samples were collected during the

experiment and soil samples were taken to estimate bromide recovery were taken at the end of the experiment. The data shows that bromide (about 12-20%) moved laterally as well the main transport as vertically through the soil profile. Lateral transport of bromide may have result from the measured decline in the macroporosity and increase in clay content with depth (Chapter 6). Both piston flow and preferential flow were responsible for the transport of surface applied bromide downward through the soil profile. Over one drainage season, the results from this study show that soluble compounds present at the soil surface in autumn (where non-adsorbed by the soil matrix) may be leached out of the rooting zone overwinter. Up to 20 % of any soluble compounds in surface applied fertiliser or manure (e.g. nitrate) may be transported quickly (50 mm drainage) by preferential flow to 60 cm. This suggests that nitrate may move below 60 cm following only small amounts of drainage and hence there is a risk of significant nitrate losses for fertiliser applied early in spring.

- ❖ Chapter 8 integrates the findings of the experimental work described in Chapters 4-7 to evaluate the existing information on nitrate leaching from arable rotations that is available to farmers and makes proposals for improvements to current recommendations, if needed. In general, the findings supported the recommendations on the management of the agricultural nitrogen cycle, e.g. matching N applications with crop N requirements; not applying N fertiliser when soil is waterlogged, has cracks or fissures or before heavy rain. However, the recommendations and supporting information do not fully describe the effect of the soil type and/or the factors driving water movement in and through the soil profile. Therefore I recommend that more guidance is needed for farmers to support their understanding of the impacts of soil type (including characteristics of subsurface horizons) and drainage systems on water movement in and through the soil profile so that they can better identify areas with a high risk of nitrate losses via leaching and adapt their management appropriately.

In the conclusion, the achievements of this PhD study are evaluated with reference to the original aims and objectives. Then recommendations for further work to develop the understanding of nitrate leaching in arable rotations are made.

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1 Introduction

1.1 Introduction

Around 50 % of the European population lives in an area where the nitrate level in water is above 25 mg NO₃⁻ l⁻¹ (Grizzetti *et al.*, 2011), and 20% in areas with a level of nitrate that is already above the recommended rate of 50 NO₃⁻ l⁻¹ set in the Nitrate Directive (EC, 1991) and the Drinking Water Directive (EC,1980). A high level of nitrate in drinking water may cause methaemoglobinaemia in new born babies and has also been linked to an increased risk of stomach cancer (Ward *et al.*, 2005). However, on the basis of the data that is currently available, high nitrate concentrations in drinking water are not well correlated with the risk of stomach cancer and methaemoglobinaemia. Perhaps more importantly, nitrate in surface water also can lead to eutrophication; algal blooms, oxygen depletion and changes in species competition are still observed in several European water bodies (Bouraoui and Grizzetti, 2014).

A large proportion of the land in the UK is under the management of farmers; (Defra, 2013) reported that 4.9 million hectares were under arable and horticultural production in 2013. About 118,500 hectares of land was planted to potato crops in the UK in 2011(Potato Council, 2011). Sustained high yields in arable crops depend on the input of nitrogen in fertilisers or manure (Kirchmann and Bergstrom, 2001). However the increase of nitrate levels in surface and ground waters seems to have occurred simultaneously with an increase in agricultural production and changes in land use patterns (Kirchmann and Bergstrom, 2001). The economic and environmental sustainability of arable cropping systems is therefore dependent *inter alia* on the availability and efficient use of nitrogen within the crop rotation. Nitrate losses via leaching may be affected by a range of agricultural management practices, including crop, target yield, crop variety, previous crop, fertiliser type, crop protection and management of crop residues. The way in which agricultural management largely control the levels of nitrate in the soil at risk of loss, and the physical soil properties,

which control drainage is known. However the interaction between them is less understood.

A large amount of work has been carried out to derive management recommendations for farmers to optimise yield and to minimise nitrogen losses (Cuttle, 2007). Recommended management practices to minimise nitrate leaching include among others: optimal fertiliser application to match crop requirements, not applying fertilisers at times when there is a high risk of drainage. However, research studying the interactions between agricultural management practices at the crop rotation level (such as those which take place in commercial farm systems) is much less common than studies on the impact of single practices.

This study aims to investigate some factors which drive the nitrate losses particularly the interaction between agricultural management and the physical soil properties, which control drainage therefore the overall aims to improve the recommendations that are available to farmers to minimise nitrate losses via leaching from arable rotations under UK conditions by investigating the impact of typical agricultural management practices (and their interactions) on the risks of nitrate leaching in crop rotations with potatoes and cereals.

1.2 Objectives

- 1-** Present a critical literature review which integrates current understanding of soil nitrogen cycle, water movement at field scale and crop nitrogen use efficiency (potato and cereals).
- 2-** Determine the effect of autumn-applied compost and winter wheat varieties on overwinter nitrate leaching by measuring the amount of mineral N in the soil profile in early spring.
- 3-** Investigate the effects of crop management practices (year, crop protection, fertility management, crop rotation and variety choice) on the nitrate at risk of leaching by measuring soil nitrate content in the soil profile after potato and cereal harvest.
- 4-** Increase understanding of the hydrological pathways leading to nitrate leaching in the experimental field at Nafferton farm by using bromide tracer and measurement of soil physical properties.
- 5-** Evaluate the existing information on nitrate leaching from arable rotations that is available to farmers and improve current recommendations, if needed.

CHAPTER

2

2 Literature Review

Nitrate (NO_3^-) is a naturally occurring oxidised anionic form of nitrogen. The anion is the conjugate base of nitric acid, consisting of one central nitrogen atom surrounded by three identically bonded oxygen atoms carrying an overall charge of -1. Almost all inorganic nitrate salts are soluble in water at standard temperature and pressure and consequently nitrate is commonly found in ground and surface waters, in soil solution and in the vacuolar solution of plants (Addiscott, 2005).

2.1 Effects of nitrate on human health and in the environment

2.1.1 Nitrate and Human Health

Nitrate generally occurs in both drinking water and food, therefore nitrate enters the human body through the food chain. An increased level of NO_3^- in drinking water (whether supplied from surface or ground water) has been linked to two human medical problems: methaemoglobinaemia (blue-baby syndrome) and stomach cancer (Knobeloch *et al.*, 2000; Fewtrell, 2004; Powlson *et al.*, 2008). Consequently maximum safe levels of nitrate in drinking water have been set worldwide of $50 \text{ mg NO}_3^- \text{ l}^{-1}$ (Grizzetti *et al.*, 2011).

Methaemoglobinaemia (blue-baby syndrome) is the name given to the effect of a reduction in the ability of the haemoglobin in red blood cells to carry oxygen (Gupta *et al.*, 1999; Manassaram *et al.*, 2010). The actual mechanism requires nitric oxide to be formed from nitrate; in the presence of nitric oxide haemoglobin is oxidised to methaemoglobin decreasing the amount of haemoglobin available to bind oxygen and resulting in reduced oxygen levels in the human body (Gupta *et al.*, 1999; Addiscott and Benjamin, 2004; Manassaram *et al.*, 2010). Methaemoglobinaemia mainly affects babies younger than six months old and has occurred when the water used to prepare infant formula milk comes from a source contaminated with NO_3^- (Comly, 1945;

Sharon Skipton 1986; Gupta *et al.*, 1999; Knobeloch *et al.*, 2000). However NO_3^- may not be the only factor causing methemoglobinemia, Addiscott and Benjamin (2004) re-interpreted the early studies to show that gastroenteritis resulting from bacteria in well water stimulated nitric oxide production in the gut and that reacted with oxidised haemoglobin in blood to convert it into methaemoglobin (Hegesh and Shiloah, 1982; Fewtrell, 2004; Addiscott, 2005). In addition there were no increases in cases recorded during the time of growing nitrate concentrations in surface and ground water were increasing and no cases recorded when formula milk was made with tap water (Addiscott and Benjamin, 2004; Addiscott, 2005).

High NO_3^- concentrations in ground water used as drinking water have been linked to some cases of stomach cancer (Correa *et al.*, 1976; Knobeloch *et al.*, 2000; Fewtrell, 2004). The key cancer causing agent is nitrite which reacts with certain amine groups to form carcinogenic N-nitroso compounds in the stomach (Knobeloch *et al.*, 2000; Fewtrell, 2004). Bacteria in the human gut are capable of reducing nitrate to nitrite, thus providing the link to nitrate consumed in food and water. However, a study conducted in Yorkshire, northern England, failed to confirm a relationship between nitrate exposure and stomach cancer (Barrett *et al.*, 1998). Fraser and Chilvers (1981) did not find a relationship between stomach cancer and the use of nitrate fertiliser in rural areas in England and Wales. Similarly in the Netherlands no relationship was found between nitrate exposure and stomach cancer where populations used tap water with different nitrate levels (Zeegers *et al.*, 2006).

The possible beneficial effect of nitrate on the human body have also been widely considered; it has been proposed that nitrate can kill *Salmonella*, *E. coli* and other organisms that cause bacterial gastroenteritis and also kill harmful bacteria and fungus in the mouth (Avery, 1999; McKnight *et al.*, 1999; Addiscott and Benjamin, 2004; Addiscott, 2006). Hence understanding the metabolism mechanism of the ingested nitrate is very important for complete assessment of both the harmful and useful effects on human health (Addiscott and Benjamin, 2004).

2.1.2 Eutrophication

In surface water ecosystems the nutrient cycle is finely balanced (Howarth, 2008). Nitrate and phosphate are important limiting factors for living cells in these surface water ecosystems (Davidson *et al.*, 2012; Warwick *et al.*, 2013). Eutrophication occurs when inputs of nutrients (usually as a result of human activity) exceeds the current

ecosystem requirement and therefore disrupt the nutrient cycle (Burt *et al.*, 1993; Davidson *et al.*, 2012).

It has become almost axiomatic that nitrate which comes from agriculture (arable and pasture soils) is one of the main causes of surface water contamination (Table 2.1). Due to the large amounts of supplementary nitrogen which are added to agricultural soils in inorganic fertilisers and manure, agricultural soils represent a major nitrate input to surface waters compared with semi-natural grasslands and forests where the load and export are low (Burt *et al.*, 1993). Nitrate enters surface water either dissolved in drainage (leaching) or as a result of surface runoff from agricultural fields (Davidson *et al.*, 2012). The main effects of eutrophication on the ecosystem of surface waters were summarised from Rabalais and Nixon (2002) and (Camargo and Alonso, 2006) as follows:

- Increase biomass and production of phytoplankton.
- Decrease water transparency and light accessibility.
- Rapid growth decreases oxygen levels.
- Changes in species composition of phytoplankton and decreased overall species diversity.
- Changes in species composition of zooplankton, invertebrates, fish and decreased overall species diversity.
- Changes in the food chain of fresh water and coastal marine ecosystems.
- Increase growth of blue green algae (sometimes leading to toxic blooms).
- Uncontrolled growth of some organisms can pose a potential risk to human health and other water animals.

Table 2.1 Nitrogen contribution to surface waters from non-point source in the USA
(Burt *et al.*, 1993)

Non-point source	Nitrogen load (MTy ⁻¹)
Arable	4.3
Pasture	2.5
Forest	0.3
Urban runoff	0.15
Rural road	0.0005
Small feedlots	0.17
Landfill	0.026

2.1.3 Nitrous Oxide (N₂O) Emission

Nitrous oxide (N₂O) is a greenhouse gas and it has also been shown to breakdown ozone in the stratosphere, hence increasing concentrations of N₂O are a significant environmental concern (Kool *et al.*, 2010; Milne *et al.*, 2011). At a global scale, agricultural activities account for about 60% of the anthropogenic N₂O emissions (Vilain *et al.*, 2012). In the UK it has been estimated that 73 % of N₂O emissions come from arable soils (Milne *et al.*, 2011).

N₂O is produced in the soil during the microbial processes of aerobic nitrification and anaerobic denitrification (Smith and Conen, 2004). For nitrification, NO₃⁻ is the main product following sequential oxidation of ammonium ions; for denitrification NO₃⁻ forms the terminal electron acceptor and hence is a key substrate. Factors that influence these two processes will influence on the amount of N₂O emitted from the soil, (these factors are described in more details in sections 2.3.2.2 and 2.3.3.2). During denitrification, reduction of N₂O to N₂ reduces the environmental impact of the process and the balance of gases emitted depends on soil structure and soil water content (Burt *et al.*, 1993). Reduced N₂O emissions can be achieved by reducing the amount of nitrate in the soil profile when soils are likely to be anaerobic through increasing the efficiency of inorganic N fertilisers, improving soil drainage and reducing soil compaction (Cameron *et al.*, 2013).

2.2 Water movement through agricultural soils

There are a number of interacting processes which control water movement through agricultural soils (Figure 2.1). Changes in precipitation, evapotranspiration, soil surface slope, landscape position, vegetation type, soil and hydrological characteristics all interact to influence the movement of water into the soil profile and through the profile to ground and surface waters (Bathke and Cassel, 1991; Rowell, 1994). The study of water movement through agricultural soils is complicated, not only because of the large number of interacting processes and driving factors above and below-ground (Rowell, 1994) but also because of their variability in time and space (Bruce *et al.*, 1985).

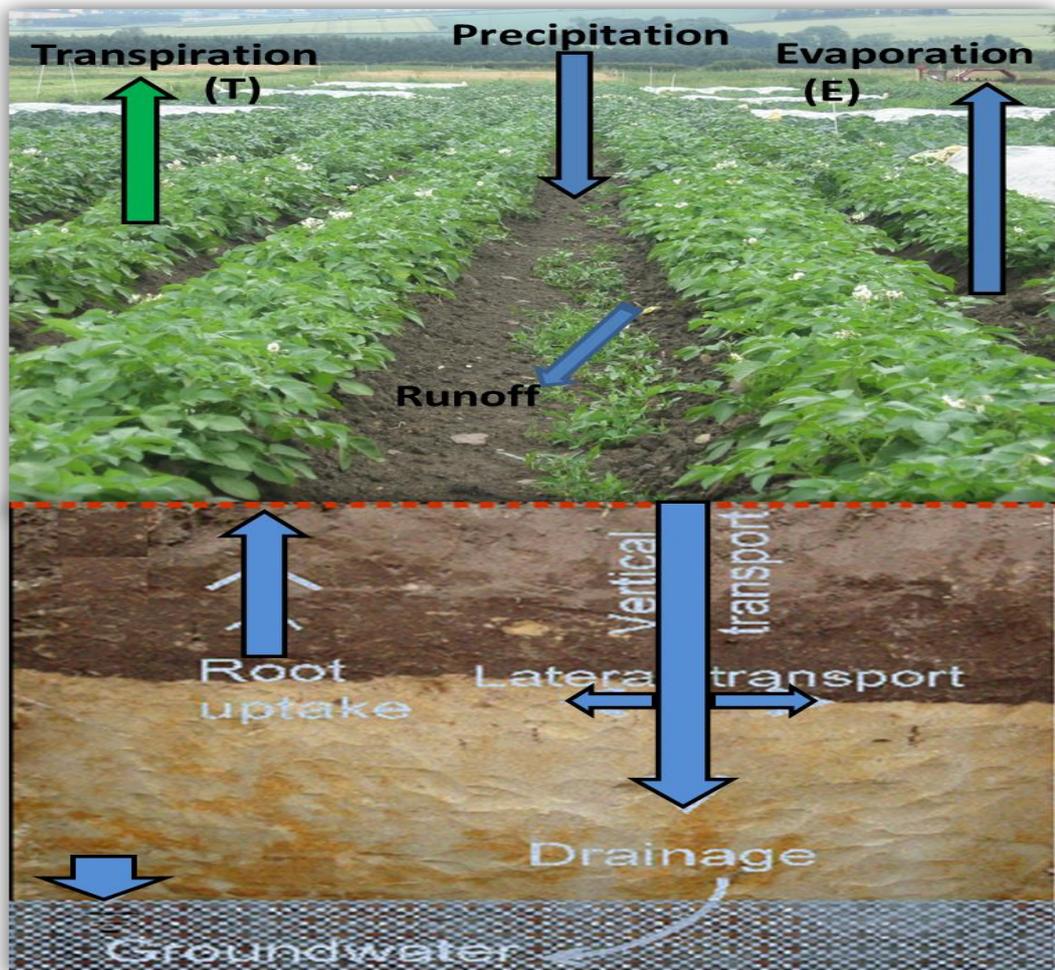


Figure 2.1 Schematic diagram showing the interacting processes which control water balance in agricultural soils.

2.2.1 Water balance at the soil surface

Precipitation, evapotranspiration and irrigation are the major processes whose interactions control water balance at the soil surface (Figure 2.1).

2.2.1.1 Precipitation (P)

The amount of precipitation at any site is controlled by meteorological factors. Precipitation (rain, snow) is the major input of water to most agricultural soils; hence accurate measurement of precipitation is needed for water balance analysis (Bruce *et al.*, 1985). Rain varies considerably from place to place in terms of intensity and timing (Faurès *et al.*, 1995).

Precipitation is usually measured directly in the field using a tipping bucket gauge, this tool allows both the amount and intensity of rainfall to be collected and recorded accurately (Kampf and Burges, 2010). However, wind direction and speed, drop size, sample location which is related to topography, and slope may also affect collection and measurement of rainfall (Goodrich *et al.*, 1995).

2.2.1.2 Irrigation (I)

Irrigation is the application of water to arable crops where the crop water requirements are not able to be met by rainfall. Hence irrigation is mostly applied in arid and semi-arid areas, where the level of rainfall is low, or when seasonal droughts occur (Nachabe *et al.*, 1999). Because the crop water requirements differ with crop growth stages and weather situations, adjusting the time and amount of irrigation is important. This irrigation scheduling can be estimated using a water balance method, using parameters such as initial soil water content in the root area, precipitation, available water capacity and evapotranspiration (Hillel, 1998).

2.2.1.3 Evapotranspiration (ET)

Evapotranspiration is the term used for the combined processes whereby water is transported from the soil-plant system to the atmosphere by means of the processes of evaporation from the soil surface and transpiration through plants (Allen *et al.*, 1998).

Different evaporation rates from soil are the result of differences in soil type and environmental conditions. Radiative heat in surface soil transforms water from the liquid phase to the gas phase; water will be lost from the soil if the vapour pressure in the air over the soil is less than the vapour pressure at the soil surface (Hillel, 1998). Vapour pressure is controlled by meteorological factors i.e. radiation, wind velocity, humidity and air temperature. For evaporation to continue the soil surface needs to be resupplied with water either by rain or by upward movement from the horizons beneath the soil surface (Blight, 2005). Where there is very shallow groundwater, soil moisture content may never limit evaporation; however under normal conditions, movement of water to the soil surface limits evaporative losses.

When the soil surface is covered by plants, the loss of water from the soil to the atmosphere is mostly through plant tissue (transpiration). Transpiration occurs as result of the vapour pressure gradient between the dry atmosphere and water saturated leaf cells (Allen *et al.*, 1998). Plant roots extract water from the soil and transmit it via xylem to above-ground plant tissue. Consequently plants can dry the soil to significant depths depending on the vegetation type. The rate of evapotranspiration (ET) is expressed in mm (millimetres) per unit time (hourly, daily, monthly or yearly) which reports the amount of water that is lost from a cropped surface soil.

There are wide range of factors that have significant effect on the rate of ET including: 1) weather conditions for instance solar radiation, air temperature, humidity, wind speed; 2) crop parameters including crop type, the level of growth, and density; and, 3) environmental conditions like soil properties, slope and latitude (Temesgen *et al.*, 2005). Because of these factors and their interaction it is not easy to predict actual ET, therefore a step-by-step process has been widely proposed (Allen *et al.*, 1998; Temesgen *et al.*, 2005), which first calculates ET_0 (reference evapotranspiration) from the climate factors only, using standard crop and soil properties kept constant through time. Then crop coefficients (K_c) are used to modify ET_0 to calculate the actual ET (ET_c) for a certain crop / growth stage (Allen *et al.*, 1998).

The Food and Agriculture Organisation (FAO) recommend use of the Penman-Monteith equation for prediction of ET_0 (FAO56), despite this equation has higher data requirements than other methods (Table 2.2). After comparing a number of methods for prediction of ET_0 Alkaeed *et al.* (2006) found that FAO56-PM based on the Penman-Monteith equation is currently used and is considered to be a standard method .

Table 2.2 Comparisons of ET_0 methods and their parameters needed.

Variables Methods	Air temperature	Humidity	Wind speed	Radiation	No of daylight hours	Saturation vapour pressure
FAO56-PM	required	required	required	required		required
Thornthwaite	required				required	
Hargreaves	required			required		
Hamon	required				required	
Rs-based radiation	required	required		required	required	
Rn-based radiation	required	required		required	required	

ET_0 is estimated from weather data using the FAO56-PM method as follows:

$$ET_0 = \frac{0.408\Delta(Rn - G) + \gamma \frac{900}{T + 273} u_2 (e_s - e_a)}{\Delta + \gamma(1 + 0.34 u_2)}$$

Where:

ET_0 is reference evapotranspiration [mm day^{-1}],

Rn is net radiation at the crop surface [$\text{MJm}^{-2} \text{day}^{-1}$],

G is soil heat flux density [$\text{MJm}^{-2} \text{day}^{-1}$]

T is average daily air temperature at two meters height [$^{\circ}\text{C}$],

u_2 is wind speed at two meters height [m s^{-1}],

e_s is saturation vapour pressure [kPa],

e_a is actual vapour pressure deficit [kPa],

$e_s - e_a$ is saturation vapour pressure deficit [kPa],

Δ is slope of the vapour pressure curve [$\text{kPa}^{\circ}\text{C}^{-1}$],

γ is psychrometric constant [$\text{kPa}^{\circ}\text{C}^{-1}$].

The main weakness of FAO56-PM is high data demand (Table 2.2) where the data required are not available in many areas especially measuring the radiation and humidity, and if the data can be found, they may not be very accurate. Alternative methods can be used when the data are not complete. If a complete set of climate data is not available then the Hargreaves method gives a reasonable estimate (Droogers and Allen, 2002; Alkaeed *et al.*, 2006) with only minimum and maximum temperature data.

Crop coefficients (crop factor) are then used to calculate the actual evapotranspiration ET for a particular crop and these coefficients depend on crop variety, growth stage and density (Allen *et al.*, 1998; Temesgen *et al.*, 2005). Applying K_c in agriculture land is easier than forests and semi-natural ecosystems because vegetation is generally more uniform.

2.2.2 Movement of water across the soil surface - infiltration and runoff

Infiltration is the process of water entry from the soil surface into the soil profile (Hillel, 1998). The source of the water can be rainfall, irrigation or from snowmelt. Understanding soil infiltration and the factors, which affect it, is very important for management of crop water supply, irrigation and soil erosion (Liu *et al.*, 2011). Rainfall /irrigation amounts and intensity, together with surface vegetation and soil characteristics affect infiltration rates (Hillel, 1998). Once water reaches the soil surface, some part of the water may evaporate before infiltration can occur when the rain/irrigation amounts are small or at low intensity; timing and the distribution of rainfall or irrigation will determine the amount of water penetrating the soil surface (Hillel, 1998). The intensity of the rainfall also has an effect on the infiltration rates (Léonard *et al.*, 2006).

When the infiltration capacity of the soil is higher than the rainfall intensity, all water will enter the soil profile, however if the infiltration capacity is less than rainfall intensity then water will accumulate at the soil surface or run off. Runoff may occur because of high rainfall intensity (even where soil is unsaturated) or where precipitation falls on an impermeable or saturated soil surface (Entekhabi and Eagleson, 1989). Soil properties also play an important role in determining the infiltration rate. Soil surface conditions also can influence the balance between infiltration and runoff (Kargas *et al.*, 2012). Increased soil surface porosity will lead to increased infiltration, whereas a compacted topsoil will reduce water infiltration into the soil profile (Hillel, 1998).

The initial soil moisture content in the surface horizons when the rain or irrigation starts has a significant effect as it will determine how much the soil can store. Where soil pores are already largely saturated the capacity of the soil to absorb more water is reduced (Lange *et al.*, 2011). Infiltration capacity is the key factor determining surface runoff; soils with high infiltration capacity usually have low runoff even if the soil is wet, on the other hand soils with low infiltration capacity usually have high runoff,

especially when the soil is wet (Follett, 2008). Soil characteristics, such as soil texture, influence infiltration capacity because the texture affects the stability of surface soil structure and hence the water movement into the soil profile (Hillel, 1998). Increasing gradient can increase the amount and speed of the surface water runoff (Follett, 2008). Surface runoff may be responsible for transporting chemicals from agricultural fields to surface water as well as increasing the risk of flooding (Fiener *et al.*, 2011).

2.2.3 Water balance in the soil profile

Any change in the water storage (Δs) for a defined site (extent and depth) for a specific period of time (year, month, week, day) can be described by a simple water balance equation:

$$\text{Change in water storage } (\Delta s) = \text{water in } (P+I+U) - \text{water out } (ET+R+D)$$

When water inputs exceed outputs, soil storage is positive and soil moisture will increase; if the opposite occurs then soil moisture will decrease. In agriculture, runoff is generally considered small (therefore negligible), and when the groundwater is far beneath the surface then the upward movement of the water into the root zone is also considered to be negligible, if there is no irrigation and no water enters the soil profile laterally, then the water balance equation can be further simplified to consider only **P** as input and, **ET** and drainage (**D**) as the only water outputs from the soil profile (Hillel, 1998). Drainage will depend on the water balance at the surface ($P + I - ET$) and any change in water storage. Under UK temperate conditions, **D** generally occurs between the winter and early spring, in that time **ET** is very low as no crops are growing or they are in the early stages of growth (Hillel, 1998). Where water drains beneath the reach of plant roots in the next growing season, then this can allow recharge of groundwater or discharge to surface waters (Hillel, 1998)

Xu *et al.* (2011) measured water balance in Wolong in China and showed how these processes interacted with one another. For example, small amounts of rainfall (5-15 mm) entered the soil and temporarily increased soil moisture at depth of 0 to 10 cm, however this increase was rapidly reversed due to evapotranspiration. Whereas heavy rainfall (for example a rainfall event of 28 mm) significantly increased soil moisture content to nearly saturated at the depth of 0 to 10 cm and 85% saturation between 10 and 40 cm for 3 days and preferential flow to depth was observed through macropores

in the soil profile (Xu *et al.*, 2011). El-Hendawy *et al.* (2008) also applied the water balance model to soil layers showing that if the soil water storage capacity was lower than the amount of water which was applied in each irrigation event then water moved through the layer i.e. drainage occurred. Understanding of these interactions and prediction of the rate and the amount of drainage is critical for agricultural management and to understand the downward movement and losses of nutrients via leaching (Stone *et al.*, 2011).

The water balance model can be used for irrigation scheduling (Hillel, 1998) and for prediction of soil water content or drainage (Stockdale, 1999). However, use of the water balance model can oversimplify consideration of water movement in soil unless very short time steps and/or thin soil layers are used within the defined soil system. Such applications are critically dependent on the data availability; most often meteorological data is available only at a daily timestep.

Both field measurements and determinations on soil samples in the laboratory are possible to measure soil water content; several methods have been reported in the literature to measure soil water content, a summary of these methods are reported in (Table 2.3). The gravimetric method is very common method, which consists of collecting soil core samples and determining the mass of water that is lost during drying at 105 °C. This direct method is easy to apply, but relies on the collection of soil core samples which can be time consuming, costly, and can be difficult to use with rocky soils (Hillel, 1998).

Table 2.3 *Methods to measure soil water content and water potential (Dobriyal et al., 2012).*

Methods		Measured parameters	scale	Precision
Direct	Gravimetric method	Mass water content	small	good
	Neutron moisture probe	Volumetric water content	small	good
	TDR	Volumetric water content	small	good
	Capacitance and FDR	Volumetric water content	small	low
Indirect	Gamma ray	Volumetric water content	small	low
	Remote sensing	Soil surface moisture	big	low
	Capacitance sensor	Volumetric water content	small	good
	Ground penetrating radar	Volumetric water content	big	good

Soil water potential (Ψ) is the measurement of the energy that water contains (Brady, 1990), this can be expressed as atmospheric pressure equivalents with units such as bar or as centimetre of water (Table 2.4). Measures of water potential are not absolute measures but only differences between potential at two different points. The forces acting on water in soil include gravity, osmotic forces and capillary forces (surface tension and adhesion) which are strongly related to pore size. Large pores exert lower capillary forces than small pores; pores in soil are therefore often divided by size into macropores in which soil can move easily and micro-pores where water is held strongly. The soil water potential value is considered to be zero when the soil is saturated and negative when the soil is unsaturated.

Total soil water potential can therefore be calculated as the sum of:

$$\Psi_t = \Psi_g + \Psi_p + \Psi_o$$

Where Ψ_t is the total water potential,

Ψ_g is the gravitational potential,

Ψ_p is the matric potential, and

Ψ_o is the osmotic potential.

Table 2.4 Soil water potential units and their relationship, 10 bar are equal to one megapascal (Brady, 1990).

Height of water (cm)	Soil water potential (bars)	Soil water potential (MPa)
0	0	0
10.2	-0.01	-0.001
102	-0.1	-0.01
306	-0.3	-0.03
1,020	-1.0	-0.1
15,300	-15	-1.5
31,700	-31	-3.1
102,000	-100	-10.0

Tensiometers have been commonly used to measure water potential in the field, the maximum suction that can be measured is 100 kPa which is equivalent to 1 bar (Hillel, 1998). The equipment is easy to use in both unsaturated and saturated soil, however installation of tensiometers requires good hydraulic contact with the soil without disturbing the soil profile; when a soil becomes very dry results are inaccurate (Dobriyal *et al.*, 2012).

The soil moisture characteristic curve describes the relation between the water potential and soil moisture content in a particular soil; soil structure and the volume, size and continuity of soil pores are the main factors driving the relationship (Hillel, 1998). At any soil water potential, the amount of water held in the soil pores at equilibrium will represent the size and the volume of the water-filled pores and also the amount that is adsorbed to the surface of soil particles, since these are all a function of the suction (Hillel, 1998). The soil moisture characteristic curve can be used for several applications for example to predict water fluxes or evaporation (Hillel, 1998), and to plan irrigation management (Bittelli and Flury, 2009). Pedo-transfer functions can be used to estimate the soil water release curve; most of these pedo-transfer functions were developed by identifying the key soil properties (texture, bulk density, organic matter) which predicted the water release curve obtained using pressure plates (Rawls *et al.*, 1982).

In the laboratory, the soil moisture characteristic curve is usually determined by measuring the soil water content at a range of deliberately applied suctions using a

tension plate or sand table method at low suction and by pressure plates at higher suction values (Hillel, 1998).

Some questions have been raised about the possible errors caused by incomplete equilibration at low water potential. Madsen *et al.* (1986) compared the pressure plate and thermocouple psychrometer to determine water potential and found that water potential which was determined with the pressure plate was double the water potential when determined with a thermocouple psychrometer. It has been reported that the main causes of the errors are the loss of hydraulic contact between the soil sample and the plate and/or soil dispersion which cause blocking of the pores in the plate (Bittelli and Flury, 2009). Sand tables also have problems including air locks in the sand bath or in the tubes, and the loss of water by evaporation (Hall *et al.*, 1977). It has been suggested that disturbed soil samples may not represent the actual structure and the pore size distribution of the soil in the field, therefore Hillel (1998) recommended the use of undisturbed soil core samples (intact cores). At higher suction values, soil water retention is dependent on soil texture and not affected by the soil structure therefore using disturbed soil samples is possible. Soil sample thickness has also significant influence on the method; soil samples with large thickness increase the time required for equilibration.

Two water potentials are recognised as having particular relevance to water movement and plant growth; these are wilting point and field capacity. When soil pores are completely filled with water then the soil is saturated. However, once water inputs cease the force of gravity will rapidly empty large pores, which are subject to free drainage as capillary forces on the soil water are weak. Once drainage has ceased (usually considered to take a couple of days) the soil moisture content at that water potential is known as **field capacity** (FC) (Figure 2.2). Consequently water, which occupies soil pores between saturation and the field capacity, is considered as unavailable water, because this water is readily lost by drainage (Hillel, 1998).

Field capacity therefore represents the highest water content that soil can hold. Water content at field capacity is usually larger in soil containing more clay compared with soil that contains more sand (Hillel, 1998). In clay soils, the average pore size is smaller than in sandy soils, which increases the capillary forces holding water in soil preventing drainage.

Under field conditions, evaporation from the soil and transpiration by vegetation creates suction in the soil profile and this is able to empty soil pores and move water by acting against capillary forces (Hillel, 1998). The presence and activity of the vegetation is a major influence on the soil moisture content, plant roots extract water to meet their requirements to maintain cell turgor during transpiration processes. It has been suggested that 2 bar represents the lower limit of easily available water for plant growth (Giddins, 2004). Eventually, the soil becomes so dry that only very small pores hold water, consequently the hydraulic conductivity becomes unable to transfer moisture from the soil pores to the plant roots; the soil has reached *the wilting point* (WP) (Figure 2.2). A value of -15 bar has been reported as water potential for soil water content at wilting point (Rowell, 1994). Any amount of water held in the soil profile between the wilting point and the field capacity is known as *plant available water* (PAW) (Figure 2.2), which is the total amount of water in the soil available for extraction by plant roots (Dobriyal *et al.*, 2012).

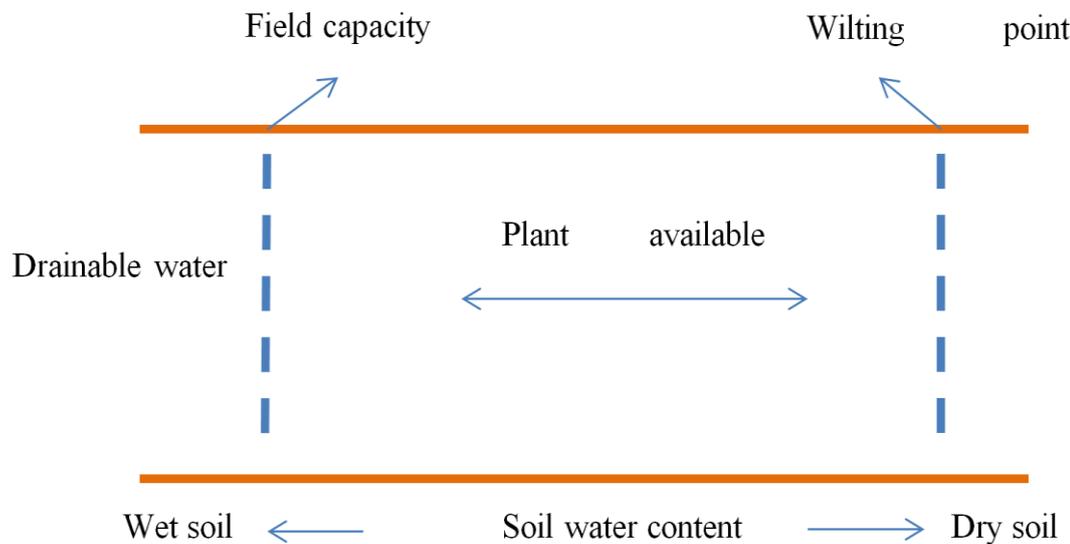


Figure 2.2 Soil water content states (Sands, 2001).

2.2.4 Movement of water within the soil profile

Water potential varies from one place to another in the soil profile or laterally within a field. A difference in water potential between two points in the soil profile encourages soil water to move from an area where the total soil water potential is higher to an area with lower soil water potential, equalising the water potential gradient (Hillel, 1998). Kinetic force is the other driving force but it is usually ignored because the water velocity in the soil profile is very low (Hillel, 1998). When the soil pores are filled mostly with water, i.e. between saturation and field capacity, saturated flow occurs, driven mostly by the force of gravity. However, for most soils this takes place only for a few weeks/days at a time. During unsaturated flow only small soil pores hold and transmit water, as the large pores are already filled with air (Hillel, 1998).

The rate of water movement is related to the total potential gradient (hydraulic gradient) which is the difference in total potential between two points divided by the distance between those points, and hence the rate soil water will flow (q ; $\text{cm}^3 \text{ water cm}^{-2}$) in the soil profile can be calculated as follows, using the equation known as Darcy's law:

$$q = K * (\text{potential gradient})$$

where K is the hydraulic conductivity which has units equivalent to velocity e.g. cm day^{-1} (Brady, 1990; Rowell, 1994; Hillel, 1998).

Hydraulic conductivity depends on the size and continuity of the pores which are carrying the water as it moves ; these properties are affected by soil properties such as texture, structure, moisture, and their heterogeneity within the soil (Xu *et al.*, 2011). Because different soil pores are filled with water at different soil moisture contents (see Section 2.2.3), hydraulic conductivity increases with increase in soil moisture content, whereas K_s significantly decreases as soil moisture changes from saturated to wilting point (Hillel, 1998). Measurement of K_s can take place in situ (Guelph parameter, velocity permeameter, disk permeameter, double-tube) or in the laboratory using intact cores (constant or falling head permeameter) (Mohanty *et al.*, 1994).

The saturated hydraulic conductivity (K_s) is very important hydraulic parameter for drainage; it quantifies the rate of water flow in a saturated soil (Hu *et al.*, 2012b). The value of K_s is a constant for each soil. Different K_s values have been reported between

soils, due to differences in soil texture and structure (Hillel, 1998). In sandy soils, K_s is between 10^{-4} to 10^{-5} m s^{-1} and in clay soils K_s is between 10^{-6} to 10^{-9} m s^{-1} (Hillel, 1998). Hu *et al.* (2012b) observed that during the dry season K_s increased due to the development of some vertical cracks, and also that increases in worm activity and the decay of plant roots increased the K_s , probably due to the holes and channels that are created. Clay soil with good structure can also have a large K_s compared with structureless clay soils, which may be unable to maintain spaces between their particles and as result have reduced infiltration rates and decreased permeability (Dane *et al.*, 2002). K_s is often higher where soil organic matter is higher; organic matter can stabilise soil aggregates and hence increase macroporosity and pore continuity (Lado *et al.*, 2004).

Soils are commonly not saturated in the vadose zone (Hillel, 1998) and the unsaturated zone acts as a link between the surface soil and ground water (Nielsen *et al.*, 1986). During unsaturated flow in soils, water moves through the meso- and micro-pores from areas of higher (negative) to lower matric potential (more negative); as water potential falls, water moves in smaller and smaller pores. Therefore unsaturated hydraulic conductivity K_s is not a constant but depends on the soil moisture content. The unsaturated hydraulic conductivity is considered one of the most important hydraulic parameters for transport of water and dissolved solutes towards plant roots through the soil profile. The tension infiltration method have been used widely in both field and laboratory to measure unsaturated hydraulic conductivity; other methods include instantaneous profile and steady-flux methods (Hillel, 1998).

2.2.5 Water movement from soil to ground water and surface waters

Initially drainage will cause water to move downwards through the soil profile under the influence of gravity. The depth where the pore space is permanently filled, or saturated, with water is known as the saturated zone and the top of this zone is called the water table. The water table may be within the soil or it may be hundreds of metres below. In many soils, there may also be significant lateral movement of water if the soil is located on a slope or has an impermeable layer preventing (or restricting) water moving downwards (Hardie *et al.*, 2012). Water may then move directly from soil into surface water – streams, rivers or lakes. The movement of soil water to ground and surface water is governed by many factors. Both soil and geological properties, hydraulic conductivity and water potential, the distribution of permeable and impermeable layers

influence movement of water from any field into the ground or surface water (Sullivan and Krieger, 2001). Land use and management can potentially influence downward water movement, for example ploughing the soil can increase permeability of the surface soil, fallow periods can increase soil water storage and drainage compared with continuous cropping (Grismer, 2013).

In agricultural soils, when the natural drainage cannot transmit all the water from the root zone and water accumulates, aeration is restricted in the root zone and can cause yield loss in the crops. In these systems, artificial drainage is often used to lower the perched water table below the upper layers of the soil and extend the unsaturated layer so that oxygen is more available to crop roots and to support microbial activity (Mostaghimi *et al.*, 1989). The soil will also have more pore volume available for water infiltration as large pores will be empty (Hillel, 1998). Surface drainage removes the water from the land as it infiltrates the soil using deep and narrow field ditches; whereas, subsurface drainage remove water after infiltration and movement through the soil through buried pipes; agricultural drainage of either type increases the connectivity of the field to surface water systems (Brady, 1990; O'Connell *et al.*, 2007).

Where there is high ground water with good hydraulic gradients between the saturated area and the soil profile, ground water can also supply water to the soil profile and become a major source of the water for plant uptake; however this is relatively uncommon in UK arable soils. Drainage of soil water to the groundwater is mostly dependent on the porosity and the permeability of subsurface layers i.e. their hydraulic conductivity. Ground water can also supply and receive water to surface water, ground water can move in lateral direction (Sullivan and Krieger, 2001). These lateral movements can be in either direction - into the surface water when the groundwater table is higher than the level of the surface waters and back into the groundwater when the level of the ground water is lower than the surface waters (Chen and Hu, 2004).

When the ground water table is close to the soil surface, then recharge of the water from snow melt or rain is fast and may take only hours or days. This fast recharge can carry some pollutants from the surface land and from the soil profile to ground water (Grismer, 2013; Jang *et al.*, 2013). Under temperate conditions an increase in the recharge usually occurs in autumn and winter when increased drainage causes the water table to rise; in summer time, increased temperatures and growing vegetation increase evapotranspiration which reduces drainage and hence the recharge (Scanlon *et al.*, 2002;

Jang *et al.*, 2013). The downward movement of water is usually controlled by the permeability and the thickness of the underlying geology materials which can have a significant effect on the water depth and speed (Grismer, 2013).

2.3 Nitrogen balance of agricultural land

2.3.1 N inputs

2.3.1.1 N Deposition

N is added to the land surface through the processes of both wet and dry deposition, N deposition is usually dominated by ammonia (NH₃), nitrogen dioxide (NO₂) and nitric acid (HNO₃) (Trebs *et al.*, 2006). The sources of this N include emissions from industry and intensive livestock farms and the extent of the deposition at any site is related to the proximity of the site to the source and to weather factors including wind and precipitation. It is likely that both conventional and organic agriculture receive similar inputs of various forms of nitrogen wet and/or dry deposition (Webb *et al.*, 2000a). For example Webb *et al.* (2004) have estimated that the N input from precipitation at sites in UK was between 7-20 kg N ha⁻¹ y⁻¹.

2.3.1.2 Nitrogen Fixation

Biological N fixation by soil microbes, especially where they form symbiotic relationships with plants, can provide a large N input to the soil-plant system (Addiscott *et al.*, 1991; Stockdale and Brookes, 2006), Free living N fixing bacteria fix about 15 kg N ha⁻¹ year⁻¹, cyanobacteria 7-80 kg N ha⁻¹ year⁻¹ but the main input to agricultural systems results from the Rhizobium-legume symbiosis which can contribute 24 -584 kg N ha⁻¹ year⁻¹ (Shantharam and Mattoo, 1997). In crop rotations legumes may be grown for grain (e.g. beans and peas), grown as forage (e.g. red and white clover). Typically in the UK estimated N fixation by red clover, white clover and beans were 240, 200 and 150 kg N ha⁻¹ year⁻¹ respectively (Berry *et al.*, 2003).

2.3.1.3 Fertiliser

The input of N from fertiliser represents the main source of N to agricultural soils; a large amount of N fertiliser is usually applied to meet the N requirements of crops with high yields. The addition of N to arable soils most commonly take places as inorganic fertiliser (mineral nitrogen; Table 2.5). Organic inputs such as animal manures (liquid

and solid manures), green manures and composts (Addiscott, 2005; Munoz *et al.*, 2005; Cameron *et al.*, 2013) are considered in the following section.

Table 2.5 Type of fertiliser and their chemical formula and the amount of available N in them (adapted from Addiscott, 2005b).

Fertiliser	Formula	% N
Solids		
Ammonium nitrate	NH_4NO_3	34
Ammonium sulphate	$(\text{NH}_4)_2\text{SO}_4$	21
Calcium nitrate	$\text{Ca}(\text{NO}_3)_2$	16
Sodium nitrate	NaNO_3	16
Urea	$\text{CO}(\text{NH}_2)_2$	46
Mono-ammonium phosphate	$\text{NH}_4\text{H}_2\text{PO}_4$	12
Di-ammonium phosphate	$(\text{NH}_4)_2\text{HPO}_4$	20
Liquids/solutions		
Liquified ammonia	NH_3	82
Ammonia in water	$\text{NH}_3/\text{NH}_4\text{OH}$	25

2.3.1.4 Organic manures

Nitrogen added in organic manures is found in a number of different forms which vary in their availability for plant uptake. Often N is in complex organic forms which are not readily available to the plants and is released slowly during decomposition within the soil which may extend over some seasons (Cameron *et al.*, 2013). The rate of mineralisation of these organic forms varies largely due to the different chemical composition of the materials which manures contain (Burt *et al.*, 1993; Heinrich and Pettygrove, 2012; Cameron *et al.*, 2013), including undigested feedstuffs, rumen products and gut micro-organisms. Nonetheless most organic materials also contain some readily available mineral N which rapidly enters the soil solution and which may be taken up by plants or, if there is large amount of rainfall, soluble organic N and nitrate can be lost through leaching (Cameron *et al.*, 1996; Chambers *et al.*, 2000).

One of the key advantages of composting animal manure (and other wastes) before application to land is to convert their nutrients into more stable organic forms. Composted materials can also be handled and stored more easily and spread more uniformly as a result. In addition effective composting also kills pathogens and weed seeds (Eghball, 2000; Lim *et al.*, 2010; Escudero *et al.*, 2012). Repeated application of

compost is therefore often observed to increase the stable organic matter pool in the soil and hence improve soil structure and water holding characteristics, which can influence N dynamics in the soil (Webb *et al.*, 2000b; Diacono and Montemurro, 2010).

It is important to know the amount of N that organic manures can provide to current and subsequent crops (Webb *et al.*, 1997; Eghball, 2000; Qiu *et al.*, 2012) (Table 2.6). The availability of N from organic manures depends on many factors, for composts this includes: input materials, (especially C/N ratio), storage and/or composting method, decomposition rate and duration of composting (immature or mature compost), the time of compost application and soil properties (Webb *et al.*, 2000b; Amlinger *et al.*, 2003). Consequently estimates of the availability of N from compost in the first year of application vary; Amlinger *et al.* (2003) reported that 5 to 15 % of applied N was available whereas Diacono and Montemurro (2010) reported a slightly higher initial supply of 15-20% total N applied. Eghball (2000) reported that around 11% of the organic N was available from composted manure and 21% from non-composted manure from the same source during the first season after application; lower N availability from the composted manure was attributed to the losses of N which had been mineralised during the composting processes and before the application (Escudero *et al.*, 2012). Other studies attributed the difference to immobilisation of N by micro-organisms during the composting process which then reduces nutrient availability on application (Amlinger *et al.*, 2003). In subsequent years, 2 to 8% of the remaining compost N pool has been found to be mineralised (Amlinger *et al.*, 2003; Diacono and Montemurro, 2010). Rates of compost applied depend on many factors including: availability of composted material, any legal restrictions (e.g. within Nitrate Vulnerable zones), the crop type and growth stage, the composition of the compost and the environmental conditions such as rainfall (Escudero *et al.*, 2012).

Some disadvantages from the use of compost include cost of installation and management, require bulking agent, large area required for storage and operation and continuous use of compost may led to high level of residual N which may increase the risk of nitrate losses via leaching (Escudero *et al.*, 2012).

Table 2.6 Predicted total N and plant available N in manures and compost at typical application rates adapted (Berry *et al.*, 2002).

Manure	Application rate (ton or m ³ ha ⁻¹)	Total N (kg N ha ⁻¹)		Plant available N (kg N ha ⁻¹)	
		Conv.	Org.	Conv.	Org.
Fresh cattle	25	150	125	38	14
Stored cattle	25	150	125	15	6
Cattle slurry	25	75	63	38	22
Poultry	10	160	-	80	-
Compost green waste	10	120		1--8	

2.3.2 N transformations in the soil

2.3.2.1 Mineralisation and immobilisation

Soil organic matter is comprised of all the organic substances that are present in the soil and result from the growth and death of plants, animals and soil microorganisms (Diacono and Montemurro, 2010). It has been estimated that the topsoil in arable soils can contain between 2000 and 6000 kg N ha⁻¹ within the organic matter (Powlson, 1993). The amount of organic matter in the soil depends on the amount of organic materials that enter the soil and the rate of the decomposition of these materials (Johnston *et al.*, 2009). Decomposition of organic matter is largely driven by the activity of soil heterotrophic microorganisms, which use the organic materials as an energy source, and the breakdown can take period of days or weeks (Powlson, 1993). However some organic materials can be resistant to decomposition due to their chemical composition (Stockdale *et al.*, 1997), due to physical location (Powlson, 1993) or a combination of physical and chemical stabilisation processes in the soil (Diacono and Montemurro, 2010). Organic matter decomposition is controlled by a range of factors including temperature, soil water content and chemical composition of the crop residue (Diacono and Montemurro, 2010).

Mineralisation is the name given to the processes during which N in organic forms is transformed by soil microorganisms to inorganic forms (usually ammonium), the rate of

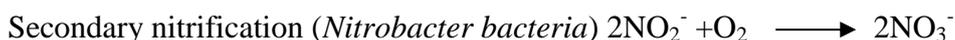
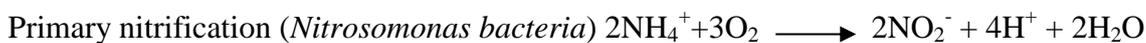
this process is strongly linked to rates of organic matter decomposition. Immobilisation is the opposite processes during which microorganisms take up simple forms of N and convert them to more complex organic forms (Burt *et al.*, 1993). In fact within the soil both mineralisation and immobilisation proceed simultaneously (Robertson and Groffman, 2007) and it is the balance between the two processes which is usually considered to estimate the N being released from soil organic matter (or added organic materials) which will be available for crop growth or at risk of loss (Shepherd *et al.*, 1996).

A key factor controlling the balance between mineralisation and immobilisation is the relative availability of carbon and nitrogen in the decomposing material, which is indicated by the C:N ratio. A low ratio of C:N (so the amount of N is high) results in net mineralisation and therefore increases the plant available forms of N in the soil. Materials that have higher relative N content include legumes residues and animal slurry. In contrast, materials with high C:N ratio (so the amount of N is low) lead to net immobilisation (e.g. wood chips, straw). Where materials have good amounts of available C but low N contents, soil microorganisms will utilise any available inorganic N from the surrounding soil and, as result, reduce the amount of nitrate present (Burt *et al.*, 1993; Powlson, 1993).

As well as organic matter composition, the rate of mineralisation is affected by a number of environmental factors including soil temperature, soil water content and soil pH (Burt *et al.*, 1993). Temperature has a major effect on all biological processes; increases in the temperature therefore increase rates of mineralisation (Powlson, 1993; Mitchell *et al.*, 2000; Mitchell *et al.*, 2001). In the field, during the winter mineralisation is usually limited, in spring time mineralisation rates start to increase as the soil temperature become warmer. Mineralisation rates are also restricted if water availability is low (Powlson, 1993; Webb *et al.*, 1998) but rates will also be inhibited due to anaerobicity, if water content becomes too high (Kemmitt *et al.*, 2008).

2.3.2.2 Nitrification

Nitrification is the process by which soil microorganisms oxidise ammonia (NH_3/NH_4) into nitrate (Stockdale *et al.*, 2002; Stockdale and Brookes, 2006; Robertson and Groffman, 2007). The reactions involved in the process are:



(Sánchez-Monedero *et al.*, 2001).

One of the main factors controlling the nitrification process is availability of NH_4^+ which is the main substrate of the process. Hence an increase in the quantity of NH_4^+ present in the soil can increase the rate of nitrification, but if the rate of decomposition and N mineralisation in the soil is low or the immobilisation of ammonium is high, then nitrification rates will be slowed (Burt *et al.*, 1993). Hence the factors that have an effect on the production of NH_4^+ will eventually affect nitrification (Robertson and Groffman, 2007). The ratio of nitrification to immobilisation (showing the balance of processes affecting ammonium availability) has been found to provide an indicator of the likely potential of NO_3^- leaching from arable soils (under certain conditions), but the ratio is not reliable in soils that have a significant residue of unused fertiliser (Stockdale *et al.*, 2002). In addition the aeration status of the soil is an important factor controlling the processes, as nitrification is an oxidative process and a lack of aeration means that the nitrification processes stop (Sánchez-Monedero *et al.*, 2001; Robertson and Groffman, 2007). In addition, soil microorganisms, which show facultative anaerobism, will use the nitrate present in the soil as source of oxygen (denitrification, see Section 2.3.3). The rate of nitrification is also affected by soil moisture content, low soil water content may reduce the nitrification processes by reduce microbial activity (Stark and Firestone, 1995). Rates of nitrification can also be controlled through the addition of chemical nitrification inhibitors and such inhibitors may be used to increase fertiliser use efficiency when N is applied in NH_4^+ form (Cameron *et al.*, 2013).

2.3.3 N Removal

2.3.3.1 Crop uptake

The amount of N taken up by crops can be different due to the crop species and cultivar (Munoz *et al.*, 2005). The crop N demand is also determined by environment and management and can be affected by several factors include length of growing season, pest and disease and the supply of other nutrients (Angus, 2001; McPharlin and Lancaster, 2010). Consequently the seasonal pattern of N uptake is also related to growth but peak N uptake may precede peak growth. Vos (1999) showed that about 80% of the total N in some potato varieties was taken up 20 to 60 days after emergence. Crops are then able to store N within their tissues to support later growth and development. The amount of N taken up and the resulting crop N content can be different between years at the same site, which probably results from different patterns of growth driven by differences in weather conditions (Olf *et al.*, 2005). During spring, crops are able to absorb the mineral N that is produced by mineralisation (Powlson, 1993). However where mineralisation continues after the rates of crop uptake decline or after crop harvest, accumulation of a large amount of mineral N occurs in the soil.

N is mainly taken up from mineral N pools in the soil solution (NO_3^- and NH_4^+) (Masclaux-Daubresse *et al.*, 2010). Crop species have been shown to express a preference between N forms for uptake; for example, potato biomass was increased when N fertiliser contained both nitrate and ammonium compared with fertiliser containing ammonium alone, indicating that NO_3^- is the first choice for potato roots (Munoz *et al.*, 2005).

Chien *et al.* (2009) reported that only 51% of N fertiliser applied to cereals was recovered by the crop; in the case of potato crops the recovery can be between 33 to 56% (Venterea *et al.*, 2011). N uptake by potato plants is function of the root properties (Glass, 2003; Kristensen and Thorup-Kristensen, 2007). The potato crop is considered to be a poor N hunter due to the fibrous shallow root system (Yamaguchi and Tanaka, 1990; Peralta and Stockle, 2002; Munoz *et al.*, 2005); 67% of potato root are found in the top 20 cm depth (Munoz *et al.*, 2005). Yamaguchi and Tanaka (1990) measured total length, dry weight, surface area and root volume of potato roots and found that all these characteristics were lower in potato than in wheat, maize and soybean. As result of the root characteristics of potato, the long-time needed for development stages with low

N uptake and relatively low total N uptake achieved at harvest, the risk of nitrate losses in association with cultivation of this crop is relatively high (Munoz *et al.*, 2005; Shrestha *et al.*, 2010).

2.3.3.2 Denitrification

Denitrification can be seen as the last step in the N cycle as fixed N is returned to the atmosphere in gaseous form as nitrogen (N₂) and/or nitrous oxide (N₂O) gases (Robertson and Groffman, 2007). N₂O contributes to stratospheric ozone destruction and it is also a greenhouse gas (Burt *et al.*, 1993; Phillips, 2008). Denitrification takes place under anaerobic or partially anaerobic conditions (Powlson, 1993). Consequently one of the main factors affecting the rate of denitrification is oxygen, soil microbes which normally use oxygen as an electron acceptor will use a nitrate ion as substitute when oxygen is absent (Phillips, 2008). The availability of NO₃⁻ is also key, hence an increase in the amount of soil nitrate can increase the rate of denitrification. Denitrification can start immediately after the application of large amounts of nitrate in fertiliser; for example, high rates of denitrification have been reported in irrigated crops following fertiliser application (Phillips, 2008). Under British climate conditions, the losses of nitrate through denitrification are most common when the soil is warm after heavy rainfall with nitrate supplied from fertiliser (spring, early summer) and/or from the mineralisation of crop residues in autumn (Burt *et al.*, 1993).

2.3.3.3 Ammonia Volatilisation

Ammonia (NH₃) volatilisation is the loss of gaseous ammonia from the soil surface and it is considered a significant route for loss of N from soil following application of fertiliser such as urea or manures (Webb *et al.*, 2006; Cameron *et al.*, 2013). After applying urea in fertiliser or animal urine, hydrolysis takes place to form ammonium carbonate which can be converted to ammonium and ammonia gas (Bouwman *et al.*, 2002; Cameron *et al.*, 2013). Emission rates depend both on the environmental conditions and soil characteristics. High pH of the soil solution can enhance ammonia production, while temperature, ammonium concentration, soil water content and rainfall will also affect rates of volatilisation (Webb *et al.*, 2005; Cameron *et al.*, 2013).

Different management practices can be used to minimise ammonia volatilisation including: using fertiliser with a urea inhibitor coating and placement of the fertiliser

below the soil surface (Bouwman *et al.*, 2002; Cameron *et al.*, 2013) or replacing urea with ammonium nitrate (Webb *et al.*, 2006).

2.3.3.4 Nitrate leaching

The amount of NO_3^- losses via leaching from the soil depends on the concentration of NO_3^- present in the soil solution and the amount of drainage that occurs through the soil profile over a certain period of time (Cameron *et al.*, 2013). The key processes determining the nitrate concentration in soil at any time are those driving the N balance as discussed previously in this section. The factors affecting drainage have been discussed above (Section 2.2). Other factors include, soil type, crop variety, previous crop/crop rotation, crop residues, target yield and harvest time (Shrestha *et al.*, 2010) and these are discussed further in Section 2.4.

2.4 Impact of agricultural management practices on losses of nitrate via leaching

2.4.1 Crop rotation:

In arable farming systems, crops are usually grown in rotation where different crops are grown in sequence. Crop rotation is an important tool to control weeds, pests and diseases in both conventional and organic farming systems, and also can affect soil physical properties often through the accumulation of organic matter in soil (Stockdale *et al.*, 2001; Watson *et al.*, 2002a). In an organic rotation it is important to include crop phases that increase the soil nitrogen content, as well as phases where crops use the accumulated N (Watson *et al.*, 2002a). Legumes such as beans, red clover, white clover plants residues are the main fertility building crops that supply N and other nutrients to the subsequent crops in organic rotations (Stockdale *et al.*, 2001; Watson *et al.*, 2002a). The amount of N fixed by these plants depends on several factors including plant varieties, management and weather conditions. Similar factors affect N availability to the subsequent crops (Watson *et al.*, 2002a).

Soil NO_3^- -N content is influenced by crop rotation (Cameron *et al.*, 2013). For example, Soon and Clayton (2003) reported that after 8 years of crop rotation, soil nitrate of sandy loam soil were higher where beans was the preceding crop when compared with plots where cereals had been grown continuously. A similar result was also reported in sandy loam soil; Thomsen *et al.* (2001) found there were higher losses of soil nitrate via leaching where cereals followed beans than where cereals followed a cereal crop.

Crops with a high N demand such as potato are usually grown after legume crops in organic rotations for instance beans (Munoz *et al.*, 2005), the legume crop residue is capable of supplying N to the subsequent crop in the rotation. However the availability of N from legume residues is usually less than that of applied inorganic fertiliser, this is due to the dependence on the decomposition and mineralisation rate of the legume N residue (Soon *et al.*, 2001). Despite the importance of the legume crop residues in supplying the N to subsequent crops which can reduce the need for inorganic fertiliser, N released by legumes can also be at risk of leaching under certain conditions, for example areas with high rainfall, sandy soil and high mineralisation (Munoz *et al.*, 2005). Boehm *et al.* (2009) compared conventional crop rotations (including inorganic and organic fertiliser) with organic crop rotations (including organic fertiliser) and found that the organic crop rotations significantly increased both soil mineral N and nitrate leaching. In the organic rotation legume residues incorporated into sandy soil resulted in higher post-harvest soil mineral N (62 kg N ha^{-1}) and increased soil nitrate leaching through the winter period compared with plots receiving inorganic fertiliser in the conventional crop rotation (23 kg N ha^{-1}).

2.4.2 Crop protection

Crop protection can have significant effects on the amount of NO_3^- -N remaining in the soil after crop harvest. Healthy crops may take up and utilise soil and fertiliser N more efficiently, whereas in crops infected with disease the soil N uptake may be reduced, yield depressed and soil NO_3^- -N after harvest may therefore increase (Kristensen and Thorup-Kristensen, 2007). Macdonald *et al.* (1997) concluded that the efficiency of N fertiliser uptake by winter wheat was reduced when the crop was infected by disease, as result residual fertiliser and soil NO_3^- -N was increased. Dilz (1988) found a positive significant relationship between poor crop growth and soil NO_3^- -N found after crop harvest which is at risk of leaching. Where herbicides are not used or used at reduced levels, weed growth may increase which can limit crop yields; however in such circumstances the total plant (crop and weed) uptake of N will be similar (or perhaps even higher) and so there may be no effect on the overall risk of nitrate leaching.

2.4.3 Fertiliser

Fertiliser applied during the growing season is not strongly at risk of leaching as drainage during this period is low and crop demand for N is high. However, this is affected by the crop type, e.g. potato crops require large amount of N fertilisers in early stage of their growth when the roots are still small and the soil is still often moist enough for drainage to occur (Jenkinson, 2001). As result when N is supplied in excess of potato demand in early growth stages, soil NO_3^- can be lost via leaching. In addition, the amount of N taken up by the crop more than 3 months after emergence may not be directly used for tuber production but is used to support the canopy (Vos, 1999). Consequently applying split N fertiliser applications can increase tuber yield and reduce N losses (Errebhi *et al.*, 1998; Vos, 1999; Munoz *et al.*, 2005). However each split application should be sufficient enough for each stage's growth. When sufficient N fertilisers are applied using split application in the first half of the season, N will accumulate in the potato biomass and then be will transported to the tubers during the second stage of the growing season, as result the N fertiliser applied during the late stage growth (when soils are wetting up again) can be minimised (Vos, 1999).

Application of an excessive amount of N fertiliser is one of the main causes of NO_3^- losses. Applying N fertilisers at rates exceeding the amount required by the crops can reduce crop recovery of the applied N fertiliser and increase the losses of NO_3^- via leaching in the following winter season (Goulding, 2000; Shrestha *et al.*, 2010) (Figure 2.3). Chaney (1990a) examined the effect of seven rates of N fertilisers (ammonium nitrate) applied to winter wheat at eight sites in eastern England on the amount of nitrate present in the soil after harvest and found that, the highest amount of NO_3^- was found in plots receiving the highest rate of fertiliser. About 50% was found in the top 30 cm and 30% in the depth between 30-60 cm and 20 % between 60 and 90 cm depth; Chaney (1990a) concluded that the amount of NO_3^- remained in the soil increased markedly with fertiliser rate when the optimum N rate for yield has been exceeded.

Another main source of nitrate losses via leaching is the mineralisation of the organic N outside the crop growing period (Cameron *et al.*, 2013). Mineralisation of soil organic N may led to large losses via leaching when there is no crop growing to remove the nitrate from the soil (Shrestha *et al.*, 2010). Macdonald *et al.* (1989) applied ^{15}N labelled fertilisers to 11 winter wheat crops at recommended rates in spring in England, and reported that no more than 4% of the labelled fertilisers remained as inorganic N in

the soil at harvest, whereas most of the mineral nitrogen that left in the soil was unlabelled which indicates that it was derived from mineralisation of soil organic nitrogen and not from the applied fertilisers. In another experiment they also found that the amount of soil inorganic nitrogen remaining at harvest in wheat plots that received no N fertiliser was about the same as the amount found in other plots which had received N fertiliser at a rate of 234 kg N ha⁻¹ (Macdonald *et al.*, 1989). Campbell *et al.* (1993) pointed out that only small differences were found in NO₃⁻ losses (spring wheat, Canada) in plots receiving no N fertiliser compared with plots receiving nitrogen application at rates equal to or less than the optimum.

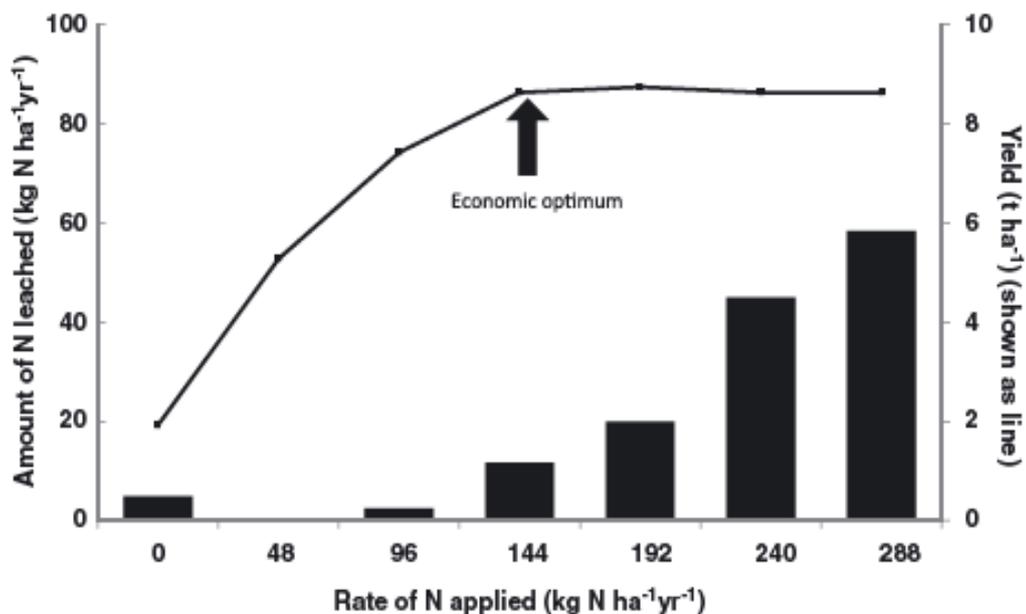


Figure 2.3 N leaching from the Broadbalk Experiment at Rothamsted Experimental Station from (Goulding, 2000).

In the UK at the beginning of the autumn after harvest, the soil is often still warm enough to encourage mineralisation and nitrification, the presence of actively growing crops may take some of the residual NO₃⁻, however a significant amount of NO₃⁻ will remain in the soil (Addiscott, 1996a). Between 15 and 25 % of the labelled N fertiliser applied in spring remained after crop harvest in organic forms Macdonald *et al.* (1997).

Hart *et al.* (1993) found that leaching of NO_3^- from cereal crops usually came from mineralisation of the organic N that was present in the soil organic matter, crop residues and any unused N fertiliser. The risk of NO_3^- losses via leaching may also be increased if the crops leave larger residues of N in the subsoil as a result of shallow rooting systems (Munoz *et al.*, 2005). Cameron *et al.* (2013) considered that the slow release of the N from the manure such as plant manure or animal manure can lead to a higher risk of leaching per unit N applied, because some of the organic N in the manure can be released by mineralisation during the time when the crop is absent or when the crop has a low rate of growth. The time of manure application is also important, the greatest risk of leaching occurs if the manure is applied in early autumn where the soil is warm and there is enough soil moisture which can enhance mineralisation of the organic N and increase the risk of losses via leaching from the soil profile over winter (Cameron *et al.*, 2013). Consequently in the UK, inorganic N fertiliser application now rarely takes place in autumn due to the high leaching risk and low N use efficiency of such applications (Jenkinson, 2001).

Several studies have investigated the effect of applied compost on nitrate leaching, however the results can be different. For example Mallory and Griffin (2007) after 13 years of experiments reported that the amount of residual NO_3^- was less in plots that received compost than in plots that received inorganic fertiliser, the lower accumulation of the nitrate was attributed to the low release of N from the compost. A higher amount of NO_3^- was leached from compost plots compared to inorganic fertiliser plots when 390 kg N ha^{-1} of compost was applied compared with 348 kg N ha^{-1} of inorganic fertiliser (Cameron *et al.*, 2013). However results from long term application of compost to different soil types showed that applied compost resulted in lower or equal NO_3^- losses via leaching compared with applied inorganic N fertilisers (Hartl and Erhart, 2005; Erhart *et al.*, 2007). Nevens and Reheul (2003) in a 4 years experiment found that a higher amount of applied compost did not increase NO_3^- -N in soil at harvest compared with a smaller amount of inorganic N fertiliser. However, continuing mineralisation of the compost organic N after crop harvest may be responsible for differences in residual NO_3^- (Habteselassie *et al.*, 2006).

2.4.4 Agricultural practices used to minimise losses of nitrate via leaching

The amount of nitrate present after crops have been harvested can be reduced by planting cover/catch crops in late summer so they take up as much nitrate as they can.

Minimising the period of time between harvest and sowing the next crop/catch crop helps to reduce the amount of nitrate loss via leaching (Jenkinson, 2001). There are several methods for reducing N losses in systems using fertiliser (Di and Cameron, 2002; Munoz *et al.*, 2005; Goulding *et al.*, 2008; Kay *et al.*, 2009; Dungait *et al.*, 2012) these can be summarised as follows:

- 1- The input of N fertiliser should match crops need to reduce the residual NO_3^- from the fertilisers in the soil after harvest.
- 2- Using split application method for N fertilisers.
- 3- Using a nitrification inhibitor to slow down the release of NO_3^- from applied fertilisers.
- 4- Growing cover crops in winter can reduce N losses via leaching through uptake the soil nitrate that at risk of leaching.
- 5- Planting early crops to reduce the time of bare soil.
- 6- Spring cultivation instead of autumn cultivation for spring crops can reduce the losses of N that are produced by mineralisation of N from organic matter. This N will be available for the following growing crops that are planted soon after. cultivation, whereas autumn cultivation can encourage the losses of N.
- 7- Increase N plant uptake through control of the amounts of irrigation, disease and pests.
- 8- N fertiliser should be applied during the period when the potential for leaching is low.

2.5 Methods of measuring nitrate and its loss from soils

2.5.1 Soil core sampling

Sampling soil cores is a direct method to measure the concentration of soil mineral N in the soil profile. Soil samples are collected in the field and then soil nitrate is extracted and measured in the laboratory.

The soil core method has been widely used to evaluate nitrate leaching from arable soils; the determination of nitrate concentrations is used to provide a mass balance of nitrate in the soil profile (Close *et al.*, 2003). Estimation of NO_3^- leaching in the UK using this method is based on the difference between the soil mineral nitrogen in a 90 cm soil profile at the end of the growing season (autumn) and that measured at the beginning of the next season (spring). Denitrification processes are assumed to be negligible and rates of mineralisation are assumed to be very low overwinter (Lord and

Shepherd, 1993); this is a reasonable assumption under UK conditions. Successive sampling of the soil profile measures changes in the soil nitrate concentration between the soil profile horizons over time. However, the soil core method provides only information about nitrate which is at risk of leaching and not the actual nitrate concentrations leaving the soil profile (Addiscott, 1990; Lord and Shepherd, 1993).

The soil core method is a simple technique, cheap and suitable for most soil types (Magesan *et al.*, 2007). Samples can be collected manually. However, the time needed for sampling can be reduced by using a hydraulic sampler. Care is always needed, if repeated samples are required, as any sampling can disturb the soil profile if samples are taken from the same site many times (Magesan *et al.*, 2007). Fresh soil should be used for extraction to minimise artefacts or losses of nitrate (Li *et al.*, 2012); soils are often stored cold ($< 4\text{ }^{\circ}\text{C}$) or frozen before extraction. Water can be used to extract NO_3^- but not NH_4^+ , whereas potassium-based salt solution can extract both (Carter, 1993). KCl salt is widely used to extract NH_4^+ and NO_3^- with high levels of efficiency; about 113% and 95% was recovered for NO_3^- and NH_4^+ respectively when extracted at a soil: solution ratio of 1:10 (Li *et al.*, 2012). 2 M KCl is usually preferred as the extractant because i) it is easy to prepare; ii) a quantitative amount of nitrate and ammonium is extracted; iii) biological activity is stopped in the extracts, hence the extracts can be stored for months before analysis (Cruz and Loução, 2002). However storing extracts above zero $^{\circ}\text{C}$ for long period of time can cause changes in the NO_3^- and NH_4^+ concentrations; however freezing at $-18\text{ }^{\circ}\text{C}$ had no significant effect on NO_3^- concentration, but if extracts have been frozen analysis should then start immediately after thawing (McTaggart and Smith, 1993; Li *et al.*, 2012).

2.5.2 Sampling soil solution – porous cups

Porous ceramic cups have been extensively used to collect samples of soil solution since first described by Briggs and McCall (1904). A water potential gradient is established when suction is applied within the cups, water flows from soil pores into the cups until the pressure in the cup and in the soil are equal (Grossmann and Udluft, 1991; Webster *et al.*, 1993; Curley *et al.*, 2011). Samples of soil solution can provide information about the spatial and temporal distribution of nitrate and its mobility and availability to plants and movement to surface or ground water (Litaor, 1988; Burt *et al.*, 1993; Curley *et al.*, 2011).

New porous ceramic cups are cleaned using diluted acid, followed by repeated flushing with distilled water before they are used in the field (Curley *et al.*, 2010; Curley *et al.*, 2011). In general it is advised that cups should be installed and left for some time before sampling starts and the first sampling should always be rejected to minimise the effect of possible adsorption on the surface of the ceramic cups (Grossmann and Udluft, 1991; Curley *et al.*, 2010). Care should be taken during cups installation to create good hydraulic contact between the cups and the soil, and also to minimise any disturbance to the surrounding soil. Porous cups can be installed horizontally, vertically and on an angle (Curley *et al.*, 2011); but the most common method of installation in arable soils is vertical (Lord and Shepherd, 1993; Webster *et al.*, 1993; Curley *et al.*, 2010; Curley *et al.*, 2011). Because of the small cross-sectional area of the cups, the samples collected only represent soil solution at one point in the field, however the use of replicate cup samplers can increase the representativeness of the samples collected (Litaor, 1988).

In order to capture the nitrate likely to leach to ground water, porous ceramic cups are usually installed below the depth of plant roots (Curley *et al.*, 2011), as cups placed in the root zone will sample nitrate which may be accessible for plant uptake. In the case of cereal crops, the required installation depth can therefore be as deep as 120 cm (Lord and Shepherd, 1993). The most common depth of installation is at 90 cm (Table 2.7) (Lord and Shepherd, 1993; Djurhuus and Jacobsen, 1995; Poss *et al.*, 1995; Zotarelli *et al.*, 2007; Wang *et al.*, 2012). Ninety cm is considered the limit of effective root growth, because only 3% of the total roots mass is found below 90 cm (Poss *et al.*, 1995); this depth also matches the common maximum depth of soil sampling for soil mineral nitrogen. However it is important to consider the hydrology of the site carefully, especially the characteristics of the subsoil when designing a sampling array for porous ceramic cups.

A range of factors which might affect the suction chosen to be applied include soil type and the amount of water sample needed for analysis (Curley *et al.*, 2011). The volume of the soil from which the cups extract solution is larger in a sandy soil than heavier soil, however determining the soil volume from which the soil water is removed is difficult (Addiscott, 1990; Addiscott, 1996b). The most common suction applied to collect soil solution samples is 50-80 KPa (Grossmann and Udluft, 1991; Lord and Shepherd, 1993; Webster *et al.*, 1993).

Table 2.7 Examples of studies using ceramic cups at different depths.

Reference	Location	Soil type	Crop	Cups depth (cm)	solute
Magesan <i>et al.</i> , (2007)	New Zealand	Silt loam	Ryegrass-white clover	45	NO ₃ ⁻
(Lord and Shepherd, 1993)	Nottinghamshire UK	Loamy sand	potato, wheat, peas	90	NO ₃ ⁻ / Br ⁻
Hatch <i>et al.</i> , (1997)	S.W.England	Clay loam	grass	10,30,60	NO ₃ ⁻
Poss <i>et al.</i> , (1995)	Charles Sturt Wales	Chromic Luvisol	wheat	12,25,90	NO ₃ ⁻
Wang <i>et al.</i> , (2012)	New Zealand	Silt loam/sandy loam	grass	35, 60	NO ₃ ⁻
Zotarelli <i>et al.</i> .,(2007)	Florida USA	Tavares sand	tomato	90	NO ₃ ⁻
(Lord and Mitchell, 1998)	England	Sandy soil	Spring wheat	90	NO ₃ ⁻
(Williams and Lord, 1997)	England	Silt clay loam	Fallow/grass	30,60,90	NO ₃ ⁻ / Br ⁻

The aim for measurements of nitrate leaching is to capture the soil solution moving under the influence of gravity i.e. mobile water (Litaor, 1988; Hatch *et al.*, 1997; Wang *et al.*, 2012). The flow of water from the soil into the cups is dependent on many factors including the suction in the cups, the water potential in the soil around the cup, the effectiveness of the hydraulic contact between the cups and the soil, and the level of the ground water (Curley *et al.*, 2011). Once the soil solution moves into the cups, the solution should be removed as soon as possible to avoid any possible changing in the nitrate concentration due to microbial transformations therefore knowing the amount of time needed to obtain the required volume of soil solution is critical to ensure the soil solution doesn't stay in the cups for longer than is necessary (Grossmann and Udluft, 1991).

To sample mobile water, samples should be collected regularly during any periods of drainage (Webster *et al.*, 1993; Curley *et al.*, 2011). To calculate nitrate leaching, the volume of drainage needs to be predicted separately; this is then multiplied by the nitrate concentration in the sample of the soil solution during each drainage period (Burt *et al.*, 1993).

Porous ceramic cups provide a direct *in situ* tool for sampling soil solution in agricultural soils and are easy to install and use. No large soil pits or extraction steps are required and consequently costs are relatively low (Wang *et al.*, 2012). Once installed porous cups can also be used routinely to collect repeated measurements from the same location (Webster *et al.*, 1993). However soil heterogeneity provides a major limitation to the use of porous cups. In sandy soil where the soil is assumed to be more homogeneous and is not subject to cracking, soil solution amounts and nitrate concentrations may be more consistent compared with soils which are more structured; the presence of macropores (cracks, small channels or holes) in these soils increases variability in soil solution samples between cups (Addiscott, 1990; Webster *et al.*, 1993; Addiscott, 1996b).

2.5.3 Sampling drainage water - lysimeters

Lysimeters can be used to measure nitrate leaching from the soil profile; in general these are blocks of soil which have been hydrologically isolated and from which drainage can be collected directly e.g. Islam *et al.* (2011). Two types of lysimeters have been proposed: disturbed lysimeters and undisturbed monolith lysimeters. Disturbed lysimeters use repacked soil columns usually in the laboratory (Lewis and Sjöström, 2010; Wang *et al.*, 2012), whereas undisturbed lysimeters seek to maintain the soil profile and use undisturbed soil taken from the field or isolated in a field plot (Burt *et al.*, 1993). Nitrate leaching is determined by collecting the volume of the sample leached at the base of the lysimeters under gravity, then analysing the samples for both NH_4^+ and NO_3^- ; the amount of nitrate leached is then calculated using the volume of the drainage (Islam *et al.*, 2011).

Lysimeters give a direct measurement of nitrate leaching from a known soil volume by capturing all the nitrate leached. Both inputs of water and fertiliser can be controlled, large soil volumes can be sampled and undisturbed soil cores allow the natural soil pore structures to be studied (Zotarelli *et al.*, 2007; Wang *et al.*, 2012). However, lysimeters are expensive and installation can cause soil disturbance. More significantly, the base of lysimeters introduces an artificial lower boundary, which can act as a free surface for water, which is different to field conditions where natural suction occurs (Burt *et al.*, 1993; Zotarelli *et al.*, 2007). Even when large field plots are hydrologically isolated, this does not mean that the plot outcome will represent all fields (Webster *et al.*, 1993).

2.5.4 Comparison of the three methods

Each of the methods described above has advantages and disadvantages especially when the soil is more heterogeneous, selection of an appropriate method will therefore need consideration of method of analysis, extraction method and cost (Addiscott, 1990; Burt *et al.*, 1993; Lord and Shepherd, 1993; Webster *et al.*, 1993; Addiscott, 1996b; Curley *et al.*, 2011). Different NO_3^- concentrations may be obtained when two methods are applied in the same place at the same time, however the variability of NO_3^- concentration usually results from the interaction of the distribution of crop residues and organic matter in the field and soil physical properties within the field (Addiscott, 1996b).

Several authors have conducted studies to compare the three methods soil core, porous ceramic cups and lysimeters for measuring nitrate leaching (Table 2.8). Differences do occur due to the presence of preferential flow which porous cups may miss (Wang *et al.*, 2012) and in soils where NO_3^- sorption occurs on the soil which is then recovered by soil extraction (Poss *et al.*, 1995). Webster *et al.* (1993) compared three methods of sampling nitrate and bromide leaching in sandy loam soils using porous ceramic cups, lysimeters and the soil core sampling technique, and found that the total amount of NO_3^- leached overwinter was not significantly different between the three methods. However some differences were observed in the temporal pattern of NO_3^- concentrations during the experiment due to disturbance of the soil profile when the cups and lysimeters were installed and the fact that in the soil core method, nitrate is extracted from all the soil pores whereas porous cups extract only mobile water. (Lord and Shepherd, 1993).

The choice of the sampling method for measuring nitrate leaching is dependent on the physical soil properties, soil water content, the available resources, and the aim of the sampling. Using a model simulation for drainage volume is often needed along with an appropriate sampling method for nitrate concentrations to estimate the amount of nitrate leaving the soil profile (Addiscott, 1990).

Table 2.8 Examples of studies comparisons between soil core, porous ceramic cups and lysimeters. N.S: no significant difference.

Soil type	Method used	Results	Location	Reference
loam	Suction cups & lysimeters	N.S	USA	Barbee and Brown (1986)
sandy loam	Suction cups & lysimeters	N.S	USA	Montgomery <i>et al.</i> , (1987)
sandy loam	Suction cups & lysimeters & soil core	N.S	UK	Webster <i>et al.</i> , (1993)
Silt loam	Suction cups & lysimeters	Cups significantly higher	New Zealand	Wang <i>et al.</i> , (2012)
Coarse sand	Suction cups & soil core	N.S	Denmark	Djurhuus & Jacobsen (1995)
Sand clay loam	Suction cups & soil core	N.S	Australia	Poss <i>et al.</i> , (1995)

2.6 Predicting nitrate losses

There are a number of methods that can be used to predict nitrate losses in the absence of direct field measurements of nitrate leaching, such as those described in section 2.5. The main advantages and limitations of these approaches (Table 2.9) are discussed in the following sections.

2.6.1 Nitrogen balance

Nitrogen balance approaches are most often used at the field, farm or national scale as a tool to estimate nitrate losses from agricultural land (Hatano *et al.*, 2002), to predict the likely impact of changed agricultural management practices (Stockdale, 1999; Watson and Atkinson, 1999), and to test the likely impact of policy scenarios to reduce the potential risk of nitrate losses (Yang *et al.*, 2007). A successful use of N balance has been reported in the Netherlands by (van Grinsven *et al.*, 2012). The N balance approach has been used to estimate nitrogen levels remaining in the soil at harvest which can be at risk of losses via leaching (residual soil nitrogen, N surplus). A number of authors have shown that estimated increases in N surplus are associated with increased inputs of N in applications of manure and fertiliser (Hatano *et al.*, 2002; Yang *et al.*, 2007) and

cultivation of legume crops (Drury *et al.*, 2007; Yang *et al.*, 2007), as well as reduction in N outputs i.e. through reductions in crop yield and N uptake due to drought (Drury *et al.*, 2007). Hatano *et al.* (2002) also used N balances to investigate the impacts of changing fertiliser inputs in Quibainong region in China under maize, sweet potato and soybean; they predicted that N application exceeding rate of 160 kg N ha⁻¹ will raise the N surplus to a level higher than crop uptake and if more than 185 kg N ha⁻¹ is applied this might raise the risk of nitrate leaching to ground water.

Table 2.9 *The benefits and limitations of a range of methods used to predict nitrate losses.*

Method	Benefits	Limitations
N balance	<ul style="list-style-type: none"> • Tool for agriculture management • Simple to calculate • Can be applied at a range of scales • Can consider all N processes 	<ul style="list-style-type: none"> • Potential losses not actual losses • Cannot predict timing of nitrate losses • May require measurement of N content in manure and feed inputs
Models	<ul style="list-style-type: none"> • Predicted N losses • Represent nitrate dynamics under different field situations • Possible to predict timing of nitrate losses • Possible to predict the long term trends • Can be used at both small (field) and large scale • Can be used as a tool for decision making • Can be used to support improve agricultural management practice. 	<ul style="list-style-type: none"> • Require expertise to use them • Input data uncertainty • Large number of input parameters • Validation required • Land use data required • Most of the evaluation done by the developer of the models • Depend on measurements to develop and validate them • Require knowledge about the input parameters and how to use them • Some models expensive
Using measurements to increase site specificity of models	<ul style="list-style-type: none"> • Applicable for farm scale • Models input 	<ul style="list-style-type: none"> • Time consuming • Expensive and difficult • Difficult for large scale • Long term monitoring required • Sampling error • Difficult to explain due to incomplete understanding • Require large sampling

The inputs and outputs needed for the estimation of the N balance clearly differ depending on the system defined i.e. farm, field or catchments (Schröder *et al.*, 2003). Defining the system boundary in space and time is not always easy, but should be done carefully (Watson *et al.*, 2002b).

Yang *et al.* (2007) estimated surplus N at harvest from the difference between the N inputs (applied mineral fertiliser, manure, biological fixation, N in crop residues) and the outputs (N content in the crops harvested). Hatano *et al.* (2002) and (Drury *et al.*, 2007) used a more complex N balance approach where biological fixation of N was also included as an N input and the N outputs included estimates of ammonia volatilisation and denitrification, i.e.

$$\text{Field N surplus} = (\text{fertiliser N} + \text{manure N} + \text{deposition N} + \text{N fixation}) \\ - (\text{ammonia volatilisation} + \text{denitrification} + \text{crop N uptake}).$$

Schröder *et al.* (2003) suggested that the simplest N balance can be estimated from a consideration of only the major inputs at field scale (particularly N in manure and mineral N fertilisers), together with removal N by crops as the major output.

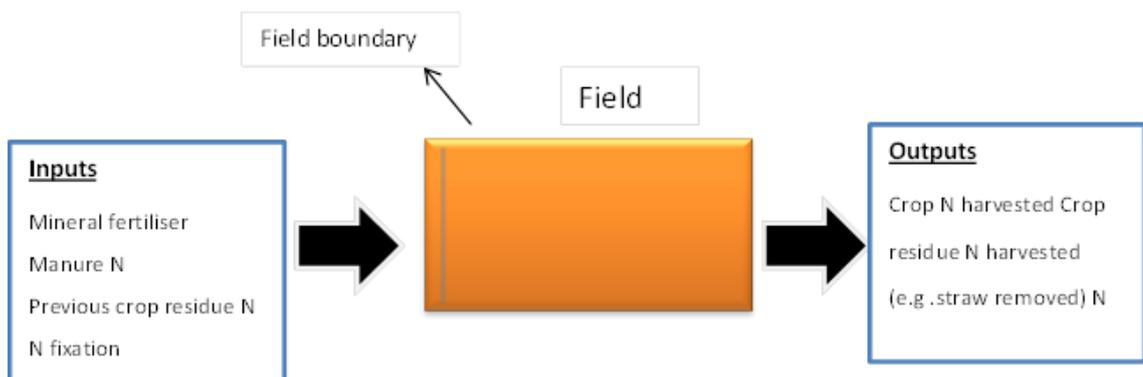


Figure 2.4 Diagram showing main inputs and outputs considered when calculating N balance at field scale to estimate N surplus/deficit.

Cherry *et al.* (2008) suggested that N losses could be estimated by calculating the inputs, outputs, and the internal N fluxes of the system over a given period of time. If the input and the output to the system are known, the N surplus can be estimated and, where any change in the amount of N stored in the soil is known, then the nitrogen losses can be predicted for the period of study (Wilson and Ball, 1999) i.e. N surplus can be partitioned between N remaining in the soil and N lost (by leaching). Hatano *et al.* (2002) also estimated the nitrate concentration in drainage by dividing the amount of field surplus N by the amount of drainage water after assuming that all the field surplus N in the field was leached (Hatano *et al.*, 2002). In general, there is a relationship between the estimated N surplus and the amount of nitrate in the soil that might be at risk of loss (Bechmann *et al.*, 1998; Aarts *et al.*, 2000; Power *et al.*, 2002). Therefore some farm management strategies have aimed to reduce nitrate leaching losses by estimating and minimising nitrogen balance at field and farm scale. Initial evaluation of field/farm data in terms of N balances can also help to improve understanding of all the other N processes such as chemical, physical and biological processes that contribute to nitrate losses (Wilson and Ball, 1999).

Goss and Goorahoo (1995) reported that in a third of cases the N balance approach lead to overestimation of the nitrate concentrations in the ground water. Bechmann *et al.* (1998) also showed that nitrogen surplus and nitrate leaching are not always closely related. They found high nitrate leaching when the nitrogen balance showed low N surplus in the soil in two sites; whereas in the third site, nitrate leaching was low when the nitrogen balance showed a high nitrogen surplus. There are many factors that determine whether the estimated N surplus actually is lost as nitrate, including soil properties, agricultural management and climate conditions, therefore N balance can only be used to predict the potential nitrogen losses to the environment (Cherry *et al.*, 2008). In addition, the N balance estimated only applies for the defined system (field/farm etc) and over the timescale for which it was calculated; it is not easy to extrapolate N budgets between scales. For example any results obtained from N balance at the farm system level cannot be simply multiplied by the catchment area to give values applicable for a whole catchment because of the variability in the inputs in different farms (Cherry *et al.*, 2008). Although nitrogen balance approaches are not a good tool to give a direct measure of nitrate leaching (Bechmann *et al.*, 1998), because they are relatively quick and simple to calculate, they can be used on farm to support

fertility management and improve N use efficiency through reduction in N surpluses (Hossain *et al.*, 2012).

2.6.2 Modelling

The advantages of applying models to estimate nitrate losses from agricultural systems are well known and recently have become the focus of much scientific research (Cherry *et al.*, 2008). These models can be used as tools to help understand the complexity of the agricultural system, the processes involved in nitrate leaching, and to predict the potential effect of changing land management practices (Addiscott and Wagenet, 1985; Addiscott, 1993; Lord and Anthony, 2000; Jégo *et al.*, 2012). In addition, models test scientific hypotheses and can be used to propose alternative scenarios to improve our agricultural management practices to minimise nitrate leaching (Cichota *et al.*, 2013). Economic models are connected to assess costs (Cherry *et al.*, 2008): Table 2.9 show some of the benefits and limitations of the models.

A number of nitrate leaching models have been developed and applied in agricultural soils, these models are usually applied to predict water and nitrate leaching from the root zone at field scale. In order to get a good estimation of nitrate leaching from arable soils, all N processes affecting the nitrogen balance and drainage should be part of the models (Wilson and Hinton, 1999). Addiscott and Wagenet (1985) described and classified leaching models in terms of their use in the field scale, complexity and flexibility. In addition they distinguished between models used as research tools for testing theoretical hypotheses and those that are used as guides for agricultural management.

In brief, some nitrate leaching models are simple empirical models based on field data, which target a specific part of nitrogen cycle in the root zone at the site, i.e. aiming to predict the available soil mineral nitrogen in spring to determine nitrogen fertiliser application; these models have been used in decision making of small scale (Simmelsgaard and Djurhuus, 1998). Other models are more sophisticated, mostly deterministic simulation models, and may consist of combinations of different models. They simulate water flow, nitrogen transformation, nitrate movement at large scale include saturated and unsaturated zone, surface water and the root zone. These models have been used for large scale i.e. suitable crop research and also their nitrogen application as well as predicting nitrate leaching (Simmelsgaard and Djurhuus, 1998).

One good example of using sophisticated models in large scale catchment of nitrate transport is presented by (Howden *et al.*, 2011), the authors used the model to predict losses of nitrate to surface water in Dorset UK using data from 1930 to 2007. The model combines all previous data of the nitrogen inputs (fertiliser input, animal manure, nitrogen deposition, biological fixation and grassland input) in the catchment. The model suggested that the increase in the mean amount of nitrate in river in the 1990s was the result of ploughing grassland and conversion to arable land tens of years before rather than from the current practice of applying fertilisers in arable land (Howden *et al.*, 2011).

Many models have been reported in the literature to predict nitrate leaching from agricultural soils, these models include: a mechanistic model to simulate nitrate leaching (Barraclough, 1989), a model to simulate change in soil mineral nitrogen (Addiscott and Whitmore, 1987), SOIL-SOILN model predict nitrate leaching from arable soil (Bergström and Jarvis, 1991), simulation model of solute leaching (Addiscott and Whitmore, 1991). Other models have been developed which link all the soil nitrogen transformations and uptake by crops, and also include predictions of nitrate leaching these models include SUNDIAL (Smith *et al.*, 1996), STICS model for prediction crop, water and nitrogen balance crops (Brisson *et al.*, 1998), LIXIM model (Mary *et al.*, 1999), NLEPL model (Shaffer *et al.*, 1991), DAISY Model (Hansen *et al.*, 1991), LEACHN model (Wagenet & Hutson, 1991).

Evaluation of models (i.e. comparison with independently measured data to test the predictions made) is an important part of the modelling process. For example (Ramos and Carbonell, 1991) used the first version of the LEACHN model (Wagenet and Hutson, 1991) model to estimate nitrate leaching and moisture content of the soil under arable crops. Jemison *et al.* (1994) applied and evaluated the model to predict water drainage, bromide leaching and also plant uptake of surface applied bromide. Xu *et al.* (2010) successfully evaluated and applied the model to estimate water drainage and nitrate leaching under different amount of rainfall in field conditions with good accuracy. Such evaluations help to identify limitations as well as strengths of the models; for example (Ersahin and Rüstü Karaman, 2001; Minshew *et al.*, 2002) showed that the influence of subsoil layers was not well addressed in the NLEPL model (Shaffer *et al.*, 1991).

2.6.2.1 NDICEA model (Nitrogen Dynamic in Crop rotations in Ecological Agriculture)

The NDICEA model has been developed by van der Burgt *et al.* (2006b) and is being developed for the UK by the Nafferton Ecological Farming Group. The model is a decision making tool able to describe soil water and soil mineral nitrogen dynamics in relation to crop demand and weather conditions in different crop rotations (Koopmans and Bokhorst, 2002). The model requires input data on soil water, applied fertiliser, manure and agronomic data. The calculation and estimation of the model is based on a weekly timestep (van der Burgt *et al.*, 2006b). The model combines four other models: N balance, water balance and organic matter balance and crop growth. The model divides the soil profile into two layers. The top layer from 0 to 30 cm depth usually contains the applied fertiliser and manure, whereas the subsoil layer (30-60 cm depth) stores water and any nutrients that have been transported from the upper layer with the assumption that any nitrate moved below the rooting zone is presumed to be lost via leaching (Van der Burgt *et al.*, 2006a). Measured soil mineral nitrogen can be used to calibrate or evaluate the model by comparing with the model prediction.

Validation of the NDICEA model on organic farms (Koopmans and Bokhorst, 2002) found that model estimation agreed with measured soil mineral nitrogen in the topsoil. van der Burgt and Timmermans (2009) also used the NDICEA Model to study the N dynamics in organic farming experiments and a good agreement was obtained between simulated and measured soil mineral nitrogen (RMSE = 12.5). In a more extensive validation study Van der Burgt *et al.* (2006a) found that for 60% of the field studied model performance was good (all the predicted values were within 20 kg N ha⁻¹ of the measured values). Nascimento *et al.* (2012) evaluated the performance of three models (NDICEA, APSIM and Century) in predicting the decomposition and N mineralisation of crop residues. They found that the NDICEA model gave predictions with the lowest RMSE values followed by Century and APSIM. However, Rayns *et al.* (2009) found that EU-Rotate-N model was better at predicting soil mineral nitrogen content in organically managed plots compared with to the NDICEA model. However, when local input data are used for calibration, model prediction by NDICEA improves (Van der Burgt *et al.*, 2006a) and in fact this is true for all models (Nascimento *et al.*, 2012). The strength of NDICEA is its built-in ability to use local input data e.g. soil mineral N, crop yield (Kersebaum *et al.*, 2007).

2.6.3 Combining limited field measurements with models

It has been demonstrated that direct measurements provide an indication of the nitrate concentrations in drainage (porous cups) or that might be at risk of leaching (soil cores) at both small and large scale (Cherry *et al.*, 2008). For example direct measurements of soil mineral nitrogen along with soil texture can give some estimate of the nitrogen that is likely to be at risk of loss (Wilson and Hinton, 1999). Measurements are a reliable tool for prediction of nitrate leaching especially at small scales and in research experiments, but at a large scale, models become more common. Nonetheless models always need measurements for calibration and validation. As discussed above, for NDICEA the strongest approach is where such data can be used for site specific calibration.

2.7 Using bromide tracers to help understand hydrological pathways

Knowledge of the hydrological pathways, variations in soil water movement and the effect of soil properties on the transport of water and nitrate, vertically and laterally, within the soil profile are important to understand and manage water availability for crops, drainage and nitrate leaching (Afyuni *et al.*, 1994; Addiscott, 1996b; Stockdale, 1999; Bullock *et al.*, 2008; Whetter *et al.*, 2008). The use of soluble tracers can help to study and monitor the transport of NO_3^- through soils and also help improve our understanding of the underlying hydrological processes (Bullock *et al.*, 2008; Thibodeau *et al.*, 2008; Whetter *et al.*, 2008).

In general, the tracer is applied to the soil surface either as a powder or as a solution at a certain rate, and then measurements are made of the amount and rate of transfer of the tracer as it is transported with the water through the soil profile. Tracers can be used either in the laboratory or in the field, but studying tracer transport in the lab may not represent the true transport in the field under natural conditions, therefore tracers are often used in the field under natural conditions (Iragavarapu *et al.*, 1998; Tilahun *et al.*, 2005). Labelled N compounds (^{15}N) have been used for studying nitrate transport in field soils; their main advantage is to provide a direct measurement of NO_3^- leaching losses from a particular source e.g. green manures, crop residues, and fertilisers (Kessavalou *et al.*, 1996; Stockdale, 1999; Addiscott, 2005). The use of such tracers is associated with high costs of the materials and their subsequent analysis (Addiscott,

2005). Interpretation of the data is also complex due to the number of transformations which N can undergo in soils (Jenkinson *et al.*, 1985; Kessavalou *et al.*, 1996).

Bromide is the most common tracer used for studying soil water and NO_3^- transport. Bromide behaves similarly to NO_3^- in terms of its low interaction with soil surfaces and also has a similar diffusion coefficient in soil. However, the Br^- ion is stable and not subject to microbial transformation and has very low background concentrations in the soil. It can be easily extracted from the soil and analysed; and is therefore a cheap tracer compared with the alternatives (Iragavarapu *et al.*, 1998; Thibodeau *et al.*, 2008; Wang *et al.*, 2010; Olatuyi *et al.*, 2012b).

Extraction of Br^- from soil samples can be easily performed using water. Bromide concentrations in either soil extractions or soil water samples obtained using porous ceramic cups can be measured using ion chromatography. Researchers have been concerned about the possible retention of bromide through adsorption to organic soils and as a result of electrostatic attraction to soil mineral surfaces (Evans *et al.*, 2008). However, even in peaty soils, the retention is low; Collins *et al.* (2000) found that about 10 % of the Br^- applied to organic soils was adsorbed. Although Br^- is not a required nutrient, uptake of Br^- by some plants has also been reported (Iragavarapu *et al.*, 1998).

Br^- is usually applied either as KBr (potassium bromide) or NaBr (sodium bromide) solution (Table 2.10). Br^- has been used widely with good results providing additional information to help interpret NO_3^- leaching studies by giving breakthrough curves, evidence of routes of water movement and mass balances (Kessavalou *et al.*, 1996; Iragavarapu *et al.*, 1998; Bullock *et al.*, 2008; Whetter *et al.*, 2008) (Table 2.10). Kessavalou *et al.* (1996) found that Br^- leaching losses were higher than NO_3^- leaching; this was explained by the losses of N by denitrification and microbial immobilisation. These differences are more likely to be large in surface soils, whereas in the subsoil the movement of NO_3^- and Br^- is more similar (Smith and Davis, 1974). In irrigated soils, Bandaranayake and Arshad (2006) found that applying 240 mm of irrigation water moved Br^- to depth of 40 cm within 10 days in a silty loam soil. Kessavalou *et al.* (1996) also reported large amounts of Br^- and NO_3^- leached from irrigated corn plots in a fine to medium textured soil.

Table 2.10 Examples of studies using bromide as a hydrological tracer in soil with details of methods used for application and extraction.

Reference	Extraction method	Amount	Tracer	Plot size
(Afyuni <i>et al.</i> , 1994)	1:5 soil/ water, shaken+ filter	300 kg ha ⁻¹	NaBr	5×2.7 m ²
(Bullock <i>et al.</i> , 2008)	1:5 soil/ water, shaken+ filter	600 g m ⁻²	NaBr	0. 3×3 m ²
(Kessavalou <i>et al.</i> , 1996)	1:5 soil/ water, shaken+ filter	200 kg ha ⁻¹	KBr	6.1×3.7 m ²
(Paramasivam <i>et al.</i> , 2002)	1:1 soil/ water, shaken + filter	80 kg ha ⁻¹	KBr	30.5×1.8 m ²
(Thibodeau <i>et al.</i> , 2008)	1:3 soil/ water, shaken + filter	555 g m ⁻²	NaBr	0. 3×3 m ²
(Tilahun <i>et al.</i> , 2005)	1:1 soil/ water, shaken + filter	135 kg ha ⁻¹	KBr	1×1 m ²
(Whetter <i>et al.</i> , 2008)	1:5 soil/ water, shaken+ filter	600 g m ⁻²	NaBr	0. 3×3 m ²
(Wang <i>et al.</i> , 2010)	1:10 soil/ water, shaken + filter	300 kg ha ⁻¹	KBr	5×15 m ²

Bromide has been used to study hydrological pathways in soil, both vertical and lateral movement of bromide have been shown. For example Afyuni *et al.* (1994) measured both lateral and vertical movement of Br⁻ in all positions in the landscape (foot slope, linear slope and interfluvium), they found that a maximum distance of lateral transport outside of the Br⁻ applied area was 150 cm with maximum concentrations found 45 cm downslope. Whetter *et al.* (2008) used bromide tracer in a loamy to clay loam soil in a hummocky landscape and found that different soil profile properties and topography (crest, midslope, depression) influenced on the amount of Br⁻ redistribution in both vertical and lateral directions; the author used lateral and vertical redistribution functions to determine the relative strength of lateral downslope and vertical downward movement of surface applied bromide tracer. Olatuyi *et al.* (2012a) also found evidence of lateral movement with 5-10% of the applied Br⁻ recovered outside the area in which it was applied; in this study Br⁻ seemed to have moved largely over the surface or in the surface soil with Br⁻ measured at distance of 100 cm away from the source but only in the top 20 cm. Afyuni *et al.* (1994) measured some lateral movement of Br⁻ in the

interfluvial where the slope gradient was small, hence it is important to consider lateral as well as vertical pathways for solute movement even in gently sloping sites.

CHAPTER

3

3 Site/trial description and methods for estimation of evapotranspiration and drainage

3.1 Site description

Field sampling and experiments were conducted between March 2010 and September 2012 at Newcastle University's Experimental Farm at Nafferton, Northumberland UK (54:59:09N; 1: 43:56 W) approximately 15 miles west of Newcastle (Figure 3.1). The farm is operated by Newcastle University's School of Agriculture Food and Rural Development. The total farm area is 294 hectares. The farming system is based on milk and beef production and arable rotation operated on a commercial basis. The standard farm rotation is winter and spring cereals such as wheat, barley and some vegetable with rye-grass leys (www.research.ncl.ac.uk/nefg).

The underlying geology of Nafferton farm is greyish till (derived from Carboniferous shale and sandstone) and the soils of the farm are mapped as part of the Brickfield Association dominated by stagnogleys (Payton and Palmer 1990). There is a weather station at Nafferton Farm which shows average rainfall of about 630 mm per year with no strong seasonal pattern; winters are cool (minimum winter temperature is about 5 °C) and summers warm but not hot (maximum summer temperature around 28 °C).

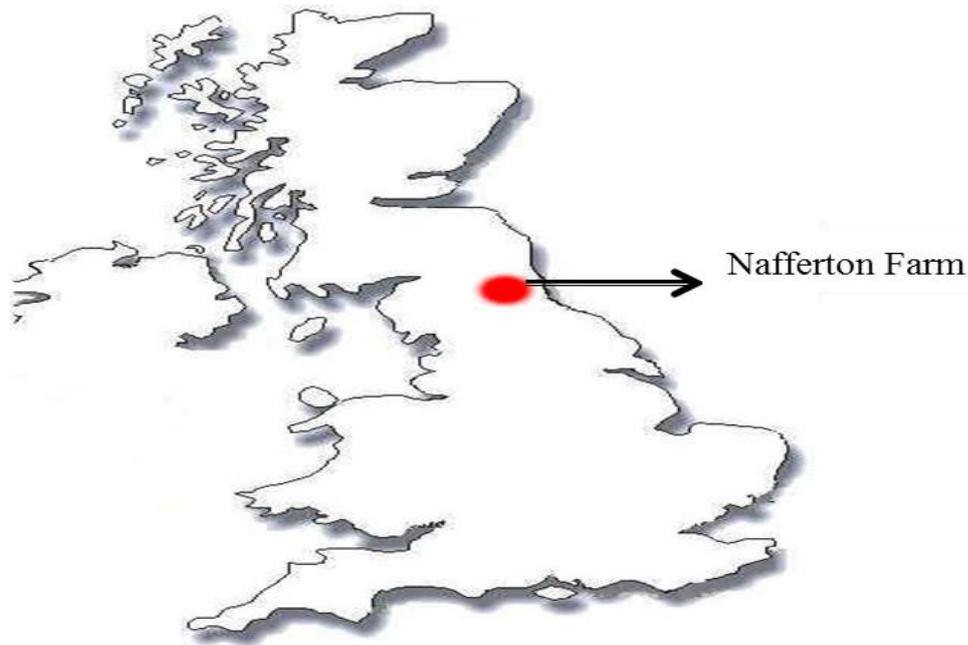


Figure 3.1 Location of the experimental site

3.2 Field trial design

Results reported in this thesis were obtained from two different field trials at Nafferton Farm.

The Nafferton Factorial Systems Comparison Trial (NFSC) was established in 2003. The overall aim of the trial is to provide data on the production and quality effects of a range of different crop production systems ranging from fully organic to fully conventional. The trial is therefore made up of a series of 4 field experiments established within 4 replicate blocks. These four experiments compare organic and conventional systems including studies of the impact of crop rotation, crop protection and fertility management using a split-split plot design. Two crop rotations form the main plot treatment: organic (a diverse rotation, rich in leguminous crops) and conventional (an arable crop dominated rotation, typical of conventional systems). The order of crops in each rotation is listed in (Table 3.1). The four experiments have the same overall rotation, however at the start of the trial each experiment was initiated at a different stage of the crop rotation, so that a diversity of crops can be studied in the trial each cropping year (Figure 3.2).

Each main plot (12 m × 96 m) is split into two crop protection subplots (12 m × 48 m): organic crop protection (ORG CP; with practices according to Soil Association organic farming standards) and conventional crop protection (CON CP with practices according to British farm assured practice). Each crop protection subplot is then sub-divided into two fertility management sub-subplots (12 m × 24 m): organic fertility management (ORG FM) in which composted dairy manure is applied to give the recommended rate of N for each crop and conventional fertility management (CON FM) in which inorganic fertiliser is applied as mineral NPK according to the recommended practice (Fertiliser Manual, RB209). The arrangement of crop protection subplots and fertilisation sub-plots within the main plots was randomised at the start of the trial. Separation strips of 10 metres have been created between crop protection subplots and 5 metres between fertilisation sub-subplots. As an example, the design of one of the blocks within the trial in 2010 and 2011 is shown in (Figure 3.3 and Figure 3.4).

A weather station (Delta-T Devices, Type M2-ENCL) is located about 15 metres from block 3 of the experiment. Weather data are recorded hourly (2 metres above the ground surface): maximum and minimum air and soil temperature, relative humidity, wind speed, rainfall and radiation. All data are downloaded regularly from the weather station and stored in an Excel spreadsheet. We have been told that the fields have some subsurface drainage installed a long time ago (> 20 years). However there is no written information available on drainage design and the depth and spacing of the drainage pipes are not known. During all the sampling described in the following chapters no evidence of drainage pipes were found.

The NUE-CROPS Trial 2010 was established to compare the response of different wheat varieties to contrasting fertility and crop protection treatments. The trial was established in 2009 within the standard farm rotation (Quarry field) on stagnogleyic soils. This trial was set up as a randomised complete block design with fertility treatment as the main plot (24 m x 24 m). Each fertility treatment main plot was split into two 12 m x 24 m crop protection subplots (Figure 3.4). One side was managed using conventional crop protection and the other side with organic crop protection. In autumn 2009, wheat variety sub-subplots were planted across the fertility management main plot so that each variety sub-subplot was 3 m x 12 m. These sub-sub plots within the trial were replicated four times (Figure 3.4).

Table 3.1 Sequence of crops in the organic (ORG) and conventional rotations (CON) in which potatoes were grown in 2010 and 2011 in the Nafferton Factorial Systems Comparison Trial

	rotation	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
expt 3	ORG	G/C ^a	G/C	potato	G/C	G/C	winter wheat	potato/veg winter wheat	beans winter barley	potato/veg	spring barley	G/C	G/C
	CON	G/C	G/C	potato/veg	grass	grass	wheat	wheat	barley	potato/veg	wheat	winter barley	G/C
expt 4	ORG	G/C	potato/veg	spring barley	G/C	G/C	G/C	winter wheat	potato/veg	beans winter	potato/veg	spring barley	G/C
	CON	G/C	potato	winter wheat	winter barley	G/C	G/C	wheat	winter wheat	barley	potato/veg	winter wheat	winter barley

^a GC= grass/clover. For cereals, beans, and grass/clover the whole area (12 m×24 m) of fertilisation sub-subplots was planted with the same crop. In years when potatoes/vegetable grown, half the area of fertilisation subplots (6 m×24 m) was planted with potatoes and the other half with four different vegetables (cabbages, onion, lettuce, and carrots) with each vegetable grown on a 6 m×6 m area.



Figure 3.2 Cropping sequence for the the four experiments of NFSC trial (2010-2012). Experiments 3 and 4 were the focus of he sampling for this PhD, especially the potato plots (2010, 2011) and the following cereals (2011, 2012).

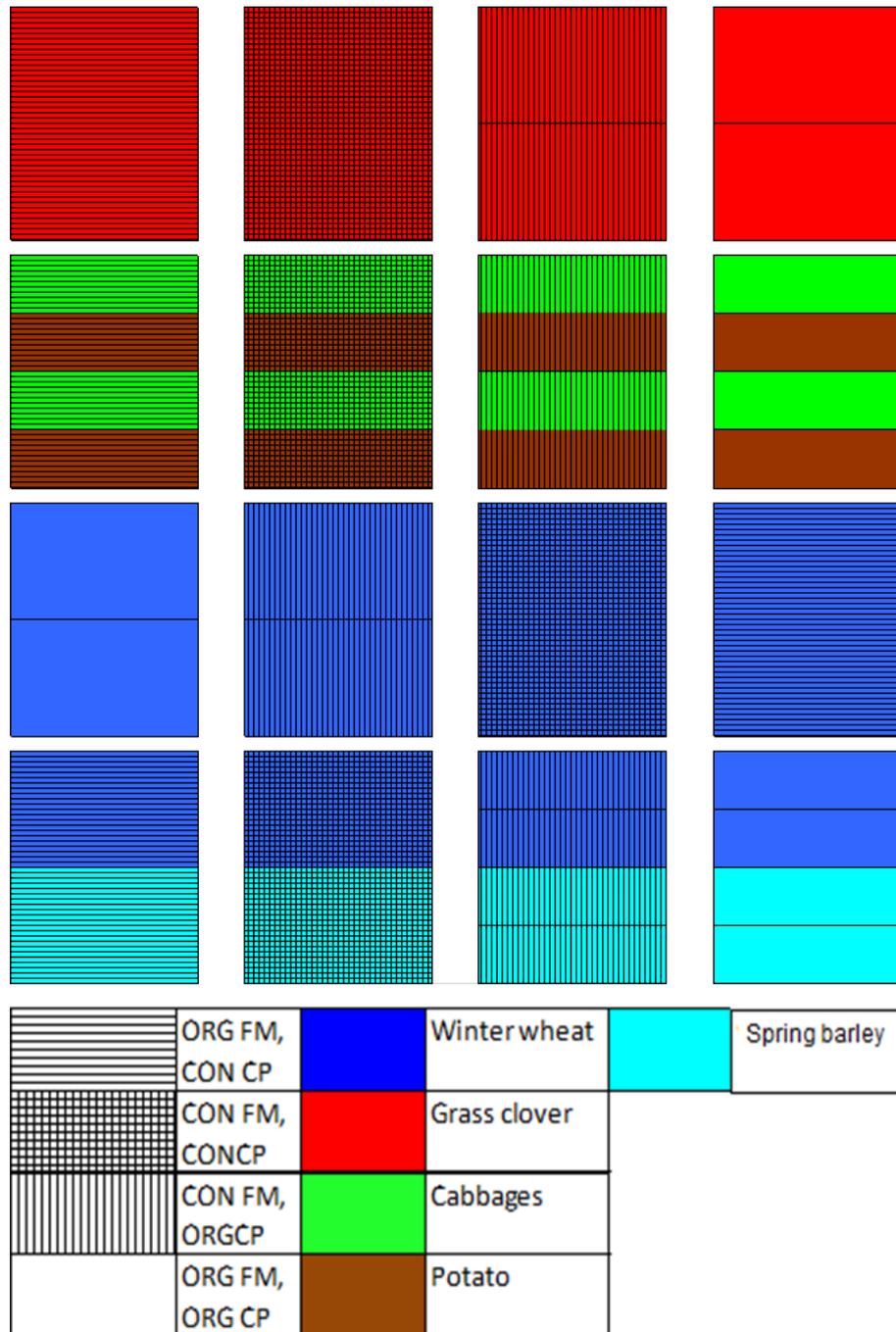


Figure 3.3 Organisation of the treatments within the blocks of the NFSC. As an example the figure shows Block 1 in 2011. Each crop rotation (main plot) is split vertically into two crop protection subplots (organic and conventional). Each crop protection subplot is then sub-divided into two fertility management sub-subplots. Management practices are shown by cell hatching; in both cases the ORG treatment has no hatching.

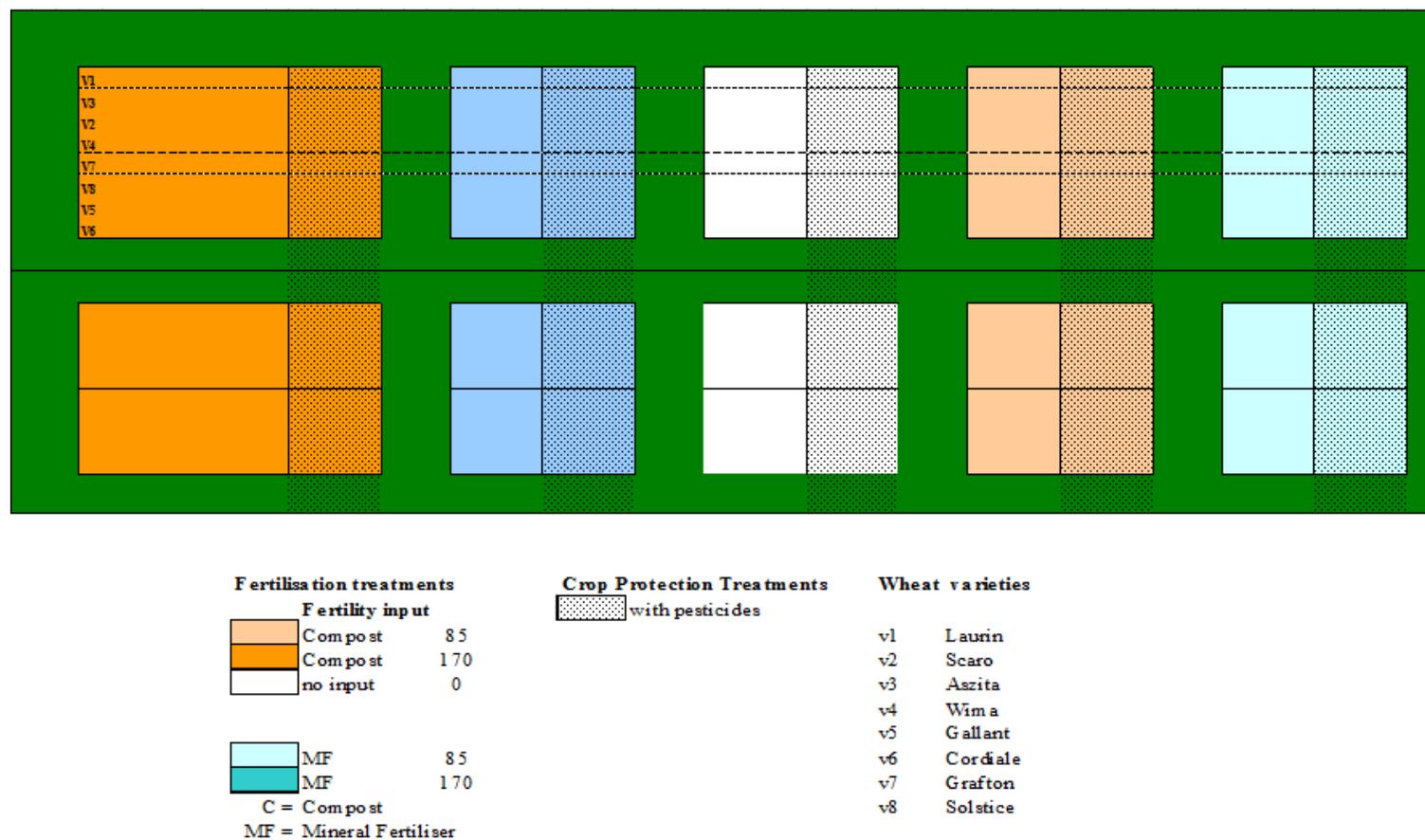


Figure 3.4 Organisation of treatments within the blocks of the NUE-CROPS Trial 2010. The area with green colour shows winter wheat grown as buffer strips between treatment plots. As an example, the figure shows details of Block 1. Fertility treatment is the main plot (shown by colours in the diagram). Each fertility treatment was split into two crop protection subplots, the subplots receiving pesticides are shown with stippling in the diagram. Wheat variety sub-subplots were planted across the fertility management and shown as numbers (v1) in the diagram.

3.3 Estimation of crop evapotranspiration

A step-by-step process for estimation of crop evapotranspiration has been widely proposed (Allen *et al.*, 1998; Temesgen *et al.*, 2005), which first calculates ET_0 (reference evapotranspiration) from the climate factors only, using standard crop and soil properties kept constant through time. Then crop coefficients (K_c) are used to modify ET_0 to calculate the actual ET (ET_c) for a certain crop / growth stage (Allen *et al.*, 1998). Reference evapotranspiration ET_0 was calculated on a daily basis using weather information and a reference grass crop type to deliver more accurate results for period 2010, 2011 and 2012 using method described by Allen *et al.* (1998). The unit is in mm day^{-1} which shows the amount of water lost by the soil. The most method used to estimate the reference evapotranspiration was the Penman-Monteith equation (Food and Agriculture Organisation 1990):

$$ET_0 = \frac{0.408\Delta(R_n - G) + \gamma \frac{900}{T + 273} u_2 (e_s - e_a)}{\Delta + \gamma(1 + 0.34 u_2)}$$

Where

ET_0 is reference evapotranspiration [mm day^{-1}],

R_n is net radiation at the crop surface [$\text{MJm}^{-2} \text{day}^{-1}$],

G is soil heat flux density [$\text{MJm}^{-2} \text{day}^{-1}$] the value was ignored for daily record therefore $G=0$,

T is average daily air temperature at two meters height [$^{\circ}\text{C}$],

u_2 is wind speed at two meter height [m s^{-1}],

e_s is saturation vapour pressure [kPa], e_a is actual vapour pressure deficit [kPa],

$e_s - e_a$ is saturation vapour pressure deficit [kPa],

Δ is slope of the vapour pressure curve [$\text{kPa}^{\circ}\text{C}^{-1}$],

γ is psychrometric constant [$\text{kPa}^{\circ}\text{C}^{-1}$].

All weather data was provided by the Nafferton Farm weather station. The input weather parameters are daily maximum and minimum temperature ($^{\circ}\text{C}$), mean daily wind speed (m s^{-1}), rainfall (mm day^{-1}), average daily humidity (%), solar radiation

(KW m⁻²) which was converted to MJ m⁻² day⁻¹ (KW m⁻² × 86.4 = MJm⁻² day⁻¹) (Allen et al., 1998). Due to problems with recoding at Nafferton Farm weather station, between 1/1/2012 and 15/1/2012 data recorded at Close House station (within 2 miles) were used.

The other input parameters were calculated according to (Allen et al., 1998) as follows:

- γ psychrometric constant; value was kept constant [0.067] during the calculation;
- Δ slope of the vapour pressure curve was calculated using the equation:

$$\Delta = \frac{4098[0.6108 \exp(\frac{17.27T}{T + 237.3})]}{(T + 237.3)^2}$$

where T is air temperature

- e_s is saturation vapour pressure was calculated using the following equation:

$$e_s = \frac{e^0(Tmax) + e^0(Tmin)}{2}$$

Where e^0 is saturation vapour pressure at the air temperature T [kPa]

- potential evapotranspiration (ET_c) was calculated as follows

$$ET_c = K_c \times ET_o$$

We were unable to adjust the value of K_c for British conditions because the mean potato height during each growth stage was not measured at the farm therefore the values of were derived from FAO-56 which apply for Europe conditions, 0.5 for initial growth stage, 1.15 for mid growth stage and 0.75 for end growth stage. For grass 0.95 for initial growth stage, 1.05 and 1.0 for mid and end growth stage respectively. For cereal 0.4 for initial growth stage, 1.15 mid growth stage and 0.25 for end growth stage (Allen et al., 1998).

3.4 Methods of estimating drainage

Cumulative drainage for 2010, 2011 and 2012 was calculated using daily meteorological data together with estimated evapotranspiration (Section 3.3) and measured soil field capacity ($\text{cm}^3 \text{ cm}^{-3}$ Section 6.2.8). Briefly daily rainfall was measured by the weather station at Nafferton farm, daily evapotranspiration was estimated using Penman equation and field capacity was measured for three horizon depths. The average field capacity values obtained from the pressure plate (0.05 bar) for the three depths 0-30 cm and 30-60 cm and 60-90 cm depth were taken and used as the field capacity values to initiate the drainage model. The average soil water content in the 0-90 cm profile at field capacity was 279 mm.

Vertical drainage was computed using a simple water balance method using data for inputs (rainfall and irrigation; mm) and output (evapotranspiration; mm) and Θ_v volumetric water content ($\text{cm}^3 \text{ cm}^{-3}$) at the start of the drainage estimation period. Soil samples collected for soil mineral nitrogen (Section 5.2.4) were used to confirm that the soil was at field capacity when the drainage calculations started.

We used the calculation functions within Excel to estimate daily values of Θ_v and drainage volume out of the soil profile (beyond 90 cm):

For Θ_v If $(\Theta_v + (P - ET) > 279, (279), (\Theta_v + (P - ET))$

For drainage If $(\Theta_v + (P-ET) > 279, (P-ET), (0))$

The predicted Θ_v values were compared with the Θ_v values measured in soil samples collected for soil mineral nitrogen (Section 5.3.2) to establish a site specific calibration which gave a close match between the predicted and measured values. Cumulative drainage for each experimental period was also calculated. Drainage data are presented in each chapter as appropriate.

Table 3.2 *A comparison of the measured soil water content Θ_v (mm) in soil samples collected for soil mineral nitrogen with predicted values based on water balance Θ_v (mm.)*

Date	Measured soil water Θ_v (mm)	Predicted soil water Θ_v (mm)
17.7.2010	246	245.3
27.10.2010	261	288
30.3.2011	297	280.3
2.8.2011	270	259.9
20.10.2011	285	274.7
1.3.2012	273	282.2
14.9.2012	291	283.2

4 Effects of winter wheat variety and autumn-applied composted cattle manure on overwinter leaching

4.1 Introduction

Cover crops grown after harvest have been shown to reduce nitrate (NO_3^- -N) leaching losses from soils (Shepherd and Webb, 1999; Moreau *et al.*, 2012; Premrov *et al.*, 2012). The success of cover crops is related to the combination of N uptake by the crops and a reduction in drainage volume resulting from the presence of a growing crop (Beckwith *et al.*, 1998; Sapkota *et al.*, 2012). Several different crops have been grown as cover crops these include winter wheat, legumes, winter rye and brassica (Shepherd *et al.*, 1996; Beckwith *et al.*, 1998; Thorup-Kristensen *et al.*, 2009; Campiglia *et al.*, 2011). The N uptake by winter wheat grown over winter may reduce the potential of NO_3^- -N leaching losses (Webster *et al.*, 2003). However N uptake by winter wheat depends on several factors including wheat varieties, weather conditions, soil mineral N, and others. Some researchers have reported that long-straw wheat varieties have more vigorous, larger root systems compared with modern short-straw varieties (Siddique *et al.*, 1990; Dawson *et al.*, 2011) and therefore may take up more mineral N from the soil profile during the winter season.

Where solid livestock manures are applied the amount of NO_3^- -N leaching losses depend on the amount of readily available N in the manure, the timing of the application and the rate of the application (Cameron *et al.*, 2013; Shepherd and Newell-Price, 2013). Larger amount of NO_3^- -N leaching losses were reported from poultry manure or slurry than from composted cattle manure due to higher amounts of N present in readily mineralisable forms (Beckwith *et al.*, 1998; Cameron *et al.*, 2013).

Timing of FYM application also affects NO_3^- -N leaching with the greatest leaching occurring when the manure is applied in late summer or early autumn; warm soil in

early autumn allows more mineralisation releasing NO_3^- -N, which is then subject to leaching over winter (Beckwith *et al.*, 1998; Shepherd and Newell-Price, 2013). Excessive application rates of FYM can also increase the mineral N in the soil which is then subject to leaching (Beckwith *et al.*, 1998; Shepherd and Newell-Price, 2013). Therefore, the aim of the study is to determine the effect of winter wheat variety with and without autumn-applied composted cattle manure on overwinter leaching of nitrate by measuring the amount of mineral N in the soil profile in early spring.

4.2 Methods

4.2.1 Trial design

The trial was established as a randomised complete block design in Quarry field (NUE crops trial) at Nafferton Farm to study whether there was a differential response of winter wheat varieties (yield, N use efficiency) to fertility and crop protection treatment; the results of this main study are not part of this PhD study. However, the opportunity was taken to use the existing plots to measure whether there was any effect of winter wheat variety and/or autumn-applied composted cattle manure on the overwinter leaching of nitrate. This trial replicated some of the treatments of the main NFSC trial, (Section 3.2.1) but did not form part of that trial.

Within the trial, fertility treatment is the main plot (24 m x 24 m) with one plot maintained as a control (no additional N applied) and plots with either composted cattle manure or fertiliser N applied at two rates (85 or 170 kg N ha⁻¹, Table 4.1). The composted cattle manure had a total N content of 3.4 % on a dry matter basis with 2-7 % in the mineral nitrogen form. Hence in application of 170 kg N ha⁻¹ there would have been 3-12 kg N ha⁻¹ of readily available N. Each main plot is split into two 12 m x 24 m crop protection subplots where one was managed using conventional crop protection and the other with organic crop protection approaches. This study focussed only on organic crop protection plots where no pesticides were applied during crop growth. Wheat variety sub-subplots were planted across the fertility management main plot so that each variety sub-subplot was 3 m x 12 m. The eight varieties of wheat selected represented four commonly grown UK short-straw varieties (Cordiale, Grafton, Gallant, Solstice) and four organically bred long-straw varieties from Switzerland (Sativa Seeds; www.sativa-rheinau.ch; Aszita, Scaro, Laurin, Wiwa). The trial had 4 replicate blocks (Figure 3.4).

Table 4.1 *Management of winter wheat (2009-2010) during the study of management and variety interactions on yield and N use efficiency*

Previous Crop	Winter Barley
Winter wheat varieties used	Laurin, Scaro, Aszita, Wima, Gallant, Solstice, Grafton, Cordiale
Planting date	13 October 2010
Seeding rate	400 seeds m ⁻²
Harvest date	1 September 2010
Fertility Input	
Composted cattle manure	8 October 2009; total application supplying equivalent of 170 (high) and 85 kg (low) total N ha ⁻¹
Ammonium nitrate	6 April 2010 - Application of 85 kg N ha ⁻¹ (high); 42 kg N ha ⁻¹ (low) 22 April 2010 - Application of 85 kg N ha ⁻¹ (high); 43 kg N ha ⁻¹ (low)

4.2.2 Soil core sampling

On 18 March 2010, 160 (8×5×4) wheat plots were selected for soil sampling representing 8 wheat varieties at 5 fertility input levels under organic crop protection only. In each plot three replicates soil cores were collected with 2 metres distance between each soil core inside the plot. The replicate cores were collected and mixed to ensure that each sample was as good representation of the soil mineral nitrogen in each plot.

Soil core samples were collected using a hydraulic soil sampler bought from Atlas Copco company (www.atlascopco.com; Figure 4.1). The aluminium soil core tube used was 100 cm in length and had 3 cm inner diameter. The core tube was attached to a tractor-driven hydraulic pump which was used to push the core into and then to pull it out of the soil. To collect soil core samples, the tube was pushed vertically into the soil to 90 cm depth; the sampler was then withdrawn from the hole bringing with it an intact soil core (0-90 cm). In general 2 to 3 minutes was spent collecting each soil core. This sampling approach was used: 1) to reduce physical effort needed to collect soil core samples; 2) to reduce the time needed to take all hundreds of soil cores reducing within sampling variation due to weather, and; 3) to minimise the disturbance of soil cores during sampling. However, there were some problems during sampling. For example, some soil core samples stick inside the sampler tube during the operation, especially if the soil is very wet, which increased sampling time and increased soil disturbance. In

these stony soils, some pieces of rock also became stuck inside the sampler tube. However, similar problems would occur with a manual auger.

Once the core had been withdrawn, each soil core sample was separated by hand into three portions: 0-30, 30-60 and 60-90 cm with a clean knife. Due to the variable nature of the soil in the field, three replicate soil samples from the same depth in each plot were mixed together to provide a more representative sample for each plot. For each plot a single composite sample for each layer was placed into plastic bag. All the soil sample bags were numbered in reference to the plot, date and depth.



Figure 4.1 *Hydraulic soil sampler in use in the field to collect soil cores*

After collection all samples were transported quickly to Newcastle University main campus and kept frozen (-20°C) before analysis to slow down any possible microbial activities which could cause change in mineral nitrogen content.

4.2.3 Sample preparation and determination of soil water content and bulk density

Soil samples were taken out of the freezer and stored at 4°C overnight before analysis. After thawing all soil samples were mixed carefully within the bag.

One soil core was chosen from each sample and depth to measure the bulk density. For each core, a 5 cm section was selected and cut carefully from the main core. For the 0-30 cm soil core the top 14 cm was discarded and the depth between 15 cm to 20 cm was always used to calculate the bulk density to avoid the disturbed soil surface. The section of field moist core was then weighed and then dried at 105°C for 24 hours in a fan oven, and then reweighed. Soil bulk density was determined for each sample as the mass of oven dried soil per unit volume (Martin, 1993).

All soil samples were then sieved (< 4 mm) and homogenised. This mixing is essential because soil properties can be variable even over a small distance in the field. The water content of each soil sample was determined gravimetrically. Between 60 and 100 g of moist soil was weighed into container of known weight, dried at 105°C for 24 hours in a fan oven, and then reweighed. Soil water content was then calculated as a percentage of the mass of oven dry soil.

4.2.4 Extraction of mineral N (ammonium and nitrate)

Soil mineral nitrogen was extracted using the method described by Sparks *et al.* (1996). In brief, 5 to 6 g of moist soil was placed in a 125 ml acid-washed plastic bottle, and then 50 ml of 2M KCl was added. 2M KCl has the ability to extract both exchangeable ammonium, and also nitrate which is soluble in water (Sparks *et al.*, 1996; Griffin *et al.*, 2010). The bottles were placed in a shaker (type IKA KS 260B) for one hour at 300 rpm. The samples were then centrifuged at 4000 rpm for 10 minutes at temperature of 20°C. The soil extract was then filtered (Whatman 42) into plastic vials. The possible contamination of filter paper or the extraction method was taken into account by using a blank extraction in each batch. The blank extraction was determined in the same way as the samples. Any measured ammonium or nitrate concentration in the blank sample was subtracted from the nitrate and ammonium concentrations obtained. We noted that the extracts had no colour which is suitable for colorimetric determinations of nitrate and ammonium. The extracts were frozen at -20 °C until the time of analysis.

4.2.5 Determination of nitrate and ammonium concentrations using an Auto analyser

A Technicon Auto Analyser III was used to measure the concentration of nitrate and ammonium in the soil extraction samples. The analysis of nitrate and ammonium content required around 5 ml of the sample solution. The working concentration range for the auto analyser is (0- 8 mg N l⁻¹ for ammonium, and 0-40 mg N l⁻¹ for nitrate. The machine uses a continuous flow system which automatically withdraws samples from a tray of sample containers and separates them within the continuous flow system with air bubbles to prevent any cross-contamination. Colour is developed in the sample after addition of reagents during the process and the absorbance is displayed on a chart recorder as a peak; using the standards included in the sample run the nitrate and ammonium concentration is then presented automatically as mg l⁻¹.

Nitrate concentrations in the soil solution extract were determined using the method described by (Carter, 1993; Sparks *et al.*, 1996). In this method nitrate is reduced to nitrite using hydrazine in alkaline solution with a copper catalyst at 37 °C, at pH 9.5 and then the sample reacted with sulphanilamide and N-1-Naphthylethylenediamine to form a pink compound (an azo Chromophore) which can be determined colorimetrically at 550 nm. The detection limit is 0.006 mg l⁻¹.

The concentration of ammonium in the soil extracts was determined using the method described by (Carter, 1993; Sparks *et al.*, 1996). In this method the sample is treated with salicylate and hypochlorite to form a green colour (indophenol dye) which can be measured colorimetrically at 667 nm. The detection limit is 0.003 mg l⁻¹. All the reagents were prepared on the same day as the analysis was carried out.

The preparation of the reagents for the Auto analyser is shown in Table 4.2. We noticed that mixing fresh preparing reagents with old reagents during the run of the analysis had negative effect on the baseline causing it to drift down. Therefore freshly prepared reagents should be used for each day of the analysis. This was particularly important for the phosphoric acid and buffer reagents. NO₃⁻-N and NH₄⁺-N concentrations were converted to mg kg⁻¹ dry soil and the total amount of N in the soil was also calculated as kg N ha⁻¹ after conversion using bulk density values.

Table 4.2 *Reagent preparation for Nitrate-N and Ammonium-N analysis using the Auto analyser*

Reagent	Concentration
Nitrate –N	
Colour reagent	5 g sulphanilamide, 0.25 g N-1Naphthylethylenediamine di – HCL (NEDD), 50 ml of Ortho-phosphoric acid in 500 ml of de-ionised water.
Sodium Hydroxide	20g of sodium hydroxide, 0.5 ml of diluted Brig-35 solution in 500 ml of de-ionised water.
Phosphoric acid	2 g of tetra-sodium-diphosphate X10H ₂ O, 0.5 ml of diluted Brig-35 solution, 1.5ml Ortho-phosphoric acid in 500 ml of de-ionised water.
Hydrazine sulphate	7 ml of the stock Copper solution (made by dissolving 0.5 g cupric sulphate in 500 ml of de-ionised) , 5 ml of the stock Zinc solution (made by dissolving 5 g of zinc sulphate in 500 ml of de-ionised water), 3 g of hydrazine sulphate in 500 ml of de-ionised water.
Nitrate standards	Stock solution was made by dissolving 7.218 g of potassium nitrate in 1000 ml of de-ionised water. Standards were made by diluting the stock solution using 2.0 M KCl. Standards used were 0, 0.5, 1, 2, 4, 5, 6, 8, 10 ppm.
Ammonium –N	
Buffer	20 of tri-sodium citrate, 0.5 ml of diluted Brig-35 solution in 500 ml of de-ionised water.
Sodium salicylate	20 g of sodium salicylate, 0.5 g of sodium nitroprusside in 500 ml of de-ionised water.
DCL solution	10 g of sodium hydroxide and 1.5 g of dichloro-isocyanuric acid sodium salt.
Ammonium standards	Stock solution was made by dissolving 4.717 g of ammonium sulphate in 1000 ml of de-ionised water. Standards were made by diluting the stock solution using 2.0 M KCl. Standards used were 0, 0.5, 1, 2, 3, 4, 5 ppm.

4.2.6 Quality Control tests carried out to verify methods used for mineral N determination

Verification of auto analyser during sample determination

In each autoanalyser batch, 5 samples of known concentrations (1, 2, 3, 4, 5 ppm for NH_4^+ -N and 2, 4, 6, 8, 10 ppm for NO_3^- -N) were measured after 40 samples had been analysed to observe whether there was any drift in measuring the concentrations. No correction for NO_3^- -N and NH_4^+ -N concentrations was needed using these known samples as no drift occurred. However on some occasions, the baseline of the ammonium channel drifted down before the start of the sample run. Therefore it was necessary to change the channel membrane and run the autoanalyser with deionised water for 15-20 minutes before starting the run again. When this occurred, 5 ammonium known standards were run as samples to check the baseline (Figure 4.2) each time the membrane was changed in the ammonium channel.

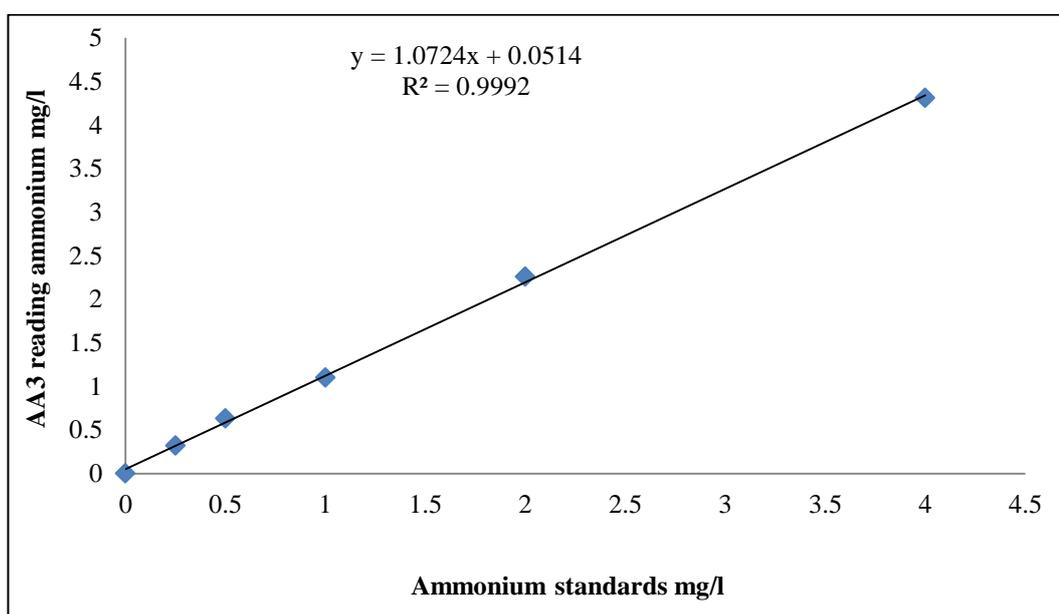


Figure 4.2 *Sample of known ammonium concentration used for check the base line and the reading of the AA3*

Determination of the spike recovery (spike control)

The accuracy of the methods for determining NH_4^+ and NO_3^- concentrations was evaluated by determining the recovery efficiency of the amount of NH_4^+ and NO_3^- added in a known “spike”. To determine recovery efficiency, 5 samples of known concentration were added to the blank (2 M KCl). The concentration of each sample was measured 3 times. The average of the three measured concentrations of nitrate and ammonium were calculated for each sample. The spike recovery was calculated by comparing the average measured concentration with the known concentration (Table 4.3). These tests confirmed that the method of determination of nitrate and ammonium using the auto analyser were reliable.

Table 4.3 *Recovery of ammonium and nitrate for spikes of known concentrations determined on the auto analyser.*

Known spike concentration	Measured concentration			% spike recovery
	1	2	3	
NH_4^+ mg L⁻¹				
5	4.95	4.95	5.11	100.06
4	3.97	3.96	4.04	99.75
3	3.02	3.01	3.05	100.88
2	2.14	2.15	2.17	107.66
1	1.02	1.02	0.97	100.33
NO_3^- mg L⁻¹				
10	9.67	9.74	10.00	98.03
8	8.15	8.14	8.29	102.41
6	6.27	6.13	6.28	103.77
4	4.08	4.13	4.14	102.91
2	1.93	2.00	2.03	99.33

Analytical control

A known soil standard was also used to give an accuracy and performance check of the extraction and analysis method. 3 kg of soil collected from the field was sieved (< 4 mm), homogenised, air-dried and stored. In each extraction batch, between 5-6 g of the standard soil was extracted in the same way as the samples. The results for 10 extraction batches are shown in (Table 4.4); this confirms that the extraction method and methods of determination are robust and reliable.

Table 4.4 *Concentrations of NH₄⁺ -N and NO₃⁻ -N in soil standard replicates*

Date of extraction batch	NH ₄ ⁺ mg kg	NO ₃ ⁻ mg kg
July 2010	2.36	21.73
July 2010	2.14	21.61
October 2010	2.21	23.75
October 2010	2.02	21.40
September 2011	1.98	21.72
September 2011	2.55	23.21
September 2011	2.59	22.23
September 2012	2.13	23.06
September 2012	2.12	23.75
September 2012	2.54	21.32
Mean	2.26	22.37
SE Mean	0.07	0.30

4.2.7 Statistical analysis

For soil NH₄⁺ -N and NO₃⁻ -N the main effects of fertility management, depth of soil sampling and crop varieties, and the interactions among these factors on response variables were analysed using 3-way ANOVA. When the interactions between factors occurred the dataset was subset and the effects at each level of interacting factor was analysed by 2-way ANOVA. Differences among interaction means were tested using Tukey contrasts in the general linear hypothesis testing (glht) function of the multcomp package in R. A liner mixed effects model was used for the Tukey contrasts containing a treatment main effects representing each level of the two-way interaction and the random error term specified as described below.

The hierarchical nature of the split plot design was reflected in the random error structures that were specified as block/fertility management/variety/sampling depth. Where analysis at a given level of a factor was carried out, that factor was removed from the random error term. The normality of the residuals of all models was tested and the data had normal distribution.

4.3 Results

4.3.1 Weather patterns

The main experimental period studied in this experiment ran from late autumn 2009 to early spring 2010 (Table 4.5). In general, air and soil temperatures were low during these 6 months overwinter; the highest air and soil temperatures were 10 °C and 7 °C in October 2009 respectively. There was higher rainfall in October and November than other months, the highest amount of rainfall 59 mm was recorded in November 2009 with highest level of humidity in December 2009. The cumulative rainfall during the 6 months from October 2009 to March 2010 was 198 mm.

Table 4.5 *Weather variables measured over winter 2009-2010 at Nafferton Farm*

Parameter	Oct-09	Nov-09	Dec-09	Jan-10	Feb-10	Mar-10
Precipitation (mm)	41	59	26	18	34	20
Mean relative humidity (%)	80	84	87	60	54	70
Mean Air Temperature (°C)	10	6	2	3	4	5
Mean Soil Temperature (°C)	7	6	3	2	3	5

4.3.2 Soil water content and bulk density

Volumetric water content was always higher in the top soil 0-30 cm (ranging from 0.23 to 0.44 cm cm⁻³) than at 30-60 cm (0.21 to 0.41 cm cm⁻³) and 60-90 cm (0.21 to 0.40 cm cm⁻³). Bulk density was lower for the 0-30 cm layer (1.30 g cm⁻³) and for 30-60 cm (1.43 g cm⁻³) and 60-90 cm (1.50 g cm⁻³).

4.3.3 Soil mineral N

Mean soil NH_4^+ -N content in the plots measured on 18 March 2010 ranged from 5 to 15 kg N ha^{-1} ; soil NO_3^- -N content from 5 to 9 kg N ha^{-1} ; total soil mineral N ranged from 11 to 22 kg N ha^{-1} in the soil profile when all 5 fertility treatments, depths and wheat varieties were considered (Table 4.6).

Table 4.6 *Main effect means \pm SE and ANOVA P-values for the effects of fertiliser input levels, depths and wheat varieties on the NH_4^+ -N, NO_3^- -N and total mineral-N as kg N ha^{-1} content in soil.*

Factors		NH_4^+ -N	NO_3^- -N	Total mineral-N
Fertility treatment				
High compost	(1)	15.02 \pm 0.94	7.96 \pm 0.33	22.98 \pm 1.08
Low compost	(2)	8.67 \pm 0.70	7.80 \pm 0.54	16.48 \pm 0.82
No input (high NPK)	(3)	6.41 \pm 0.69	7.63 \pm 0.31	14.04 \pm 0.89
No input (low NPK)	(4)	5.91 \pm 0.50	5.20 \pm 0.31	11.12 \pm 0.69
No input	(5)	4.89 \pm 0.70	9.03 \pm 0.53	13.92 \pm 1.00
Depth				
0-30cm		14.11 \pm 0.58	8.69 \pm 0.30	22.81 \pm 0.75
30-60cm		5.66 \pm 0.49	6.57 \pm 0.28	12.24 \pm 0.61
60-90cm		4.78 \pm 0.51	7.30 \pm 0.39	12.08 \pm 0.63
Variety V				
Laurin	(1)	8.31 \pm 0.95	7.46 \pm 0.52	15.78 \pm 1.23
Scaro	(2)	8.76 \pm 1.18	6.49 \pm 0.40	15.25 \pm 1.33
Aszita	(3)	8.73 \pm 1.08	7.35 \pm 0.54	15.72 \pm 1.39
Wima	(4)	8.30 \pm 1.16	7.36 \pm 0.49	15.66 \pm 1.35
Gallant	(5)	7.45 \pm 0.83	7.32 \pm 0.42	14.77 \pm 0.97
Cordiale	(6)	8.34 \pm 0.94	7.16 \pm 0.57	15.51 \pm 1.15
Grafton	(7)	7.64 \pm 1.08	8.53 \pm 0.59	16.18 \pm 1.32
Solstice	(8)	8.29 \pm 0.97	8.52 \pm 0.75	16.82 \pm 1.31
ANOVA (P-values)				
Fertility treatment (FR)		0.2922	0.2848	0.1501
Depth (Dep)		00000	0.0011	0.0000
Variety (V)		0.3267	0.0824	0.9627
FR \times Dep		0.5820	0.9734	0.9157
FR \times V		0.1265	0.2948	0.1035
Dep \times V		0.0054	0.7185	0.4452
FR \times Dep \times V		0.4584	0.9996	0.9898

There was a highly significant difference ($p=0.000$, $p=0.001$ and $p=0.000$; Figure 4.3) between NH_4^+ -N, NO_3^- -N and total soil mineral N content with soil depth. The amount of NH_4^+ -N, NO_3^- -N and total soil mineral N content in the top 0-30 cm was significantly higher than the amount at 30-60 and 60-90 cm depth. There was no significant difference between the amount measured at 30-60 and 60-90 cm depth of the soil profile.

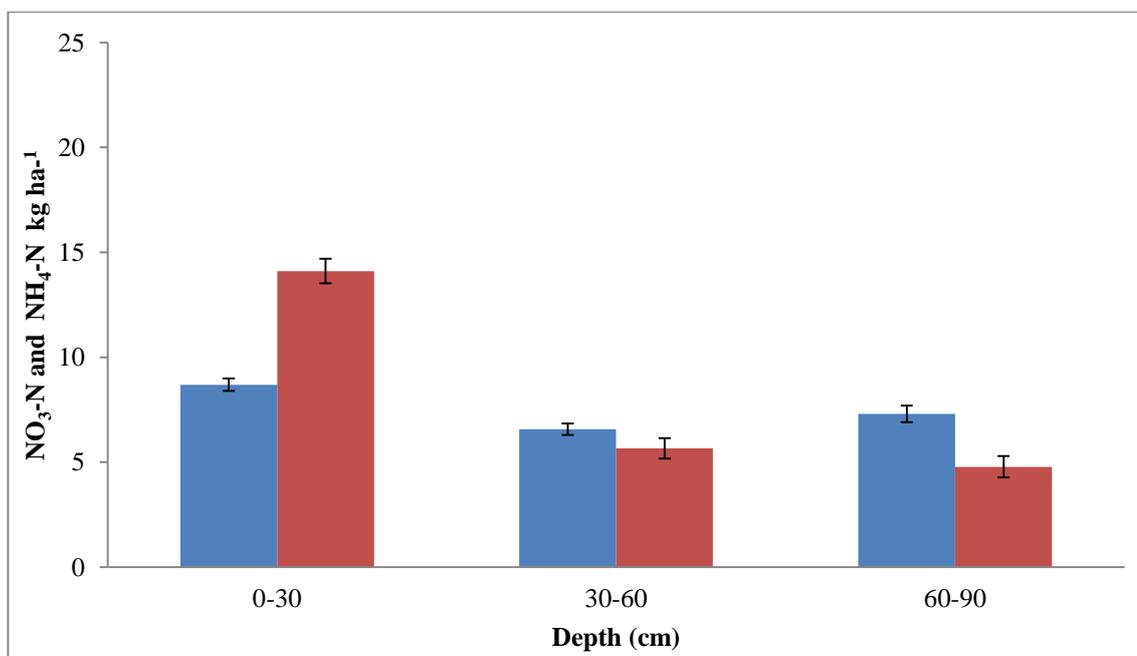


Figure 4.3 Significantly higher mean soil NO_3^- -N and NH_4^+ -N (kg ha⁻¹) was measured at 0-30, than at 30-60, and 60-90 cm depths in March 2010 under 8 wheat varieties sown in the previous autumn. Blue bars: NO_3^- -N (kg ha⁻¹); Red bars: NH_4^+ -N (kg ha⁻¹).

There were no significant differences between NO_3^- -N and total soil mineral N content (at any soil depth or considered for the whole profile) where either the high (23.97, 68.61 kg NO_3^- -N ha⁻¹, kg SMN ha⁻¹ for 0-90 cm) or low rate (24.20, 50.26 kg NO_3^- -N ha⁻¹, kg SMN ha⁻¹ for 0-90 cm) of composted cattle manure had been applied in autumn compared with the plots receiving no inputs (22.79, 42.62 kg NO_3^- -N ha⁻¹, kg SMN ha⁻¹ for 0-90 cm) before the soil sampling took place. However, there was some indication that NH_4^+ -N content (0-90 cm) was slightly higher ($p= 0.0898$) where composted cattle manure had been applied (44.65, 26.07, 19.83 kg NH_4^+ -N ha⁻¹ in the low rate , high rate and no compost plots respectively).

There were no significant differences between NH_4^+ -N and total soil mineral N content where different wheat varieties were grown overwinter. However, the effect of wheat varieties on the amount of NO_3^- -N content was almost significant ($p= 0.0824$); Scaro had slightly lower nitrate content in spring than Solstice and Grafton (Table 4.6). For soil NH_4^+ -N content there was a significant 2-way interaction found between depth and wheat varieties with small differences between varieties in the NH_4^+ -N content in the topsoil ($p=0.0054$; Figure 4.4), but this showed no clear patterns with varieties and depth interactions. All other 2-way and 3-way interactions were not significant.

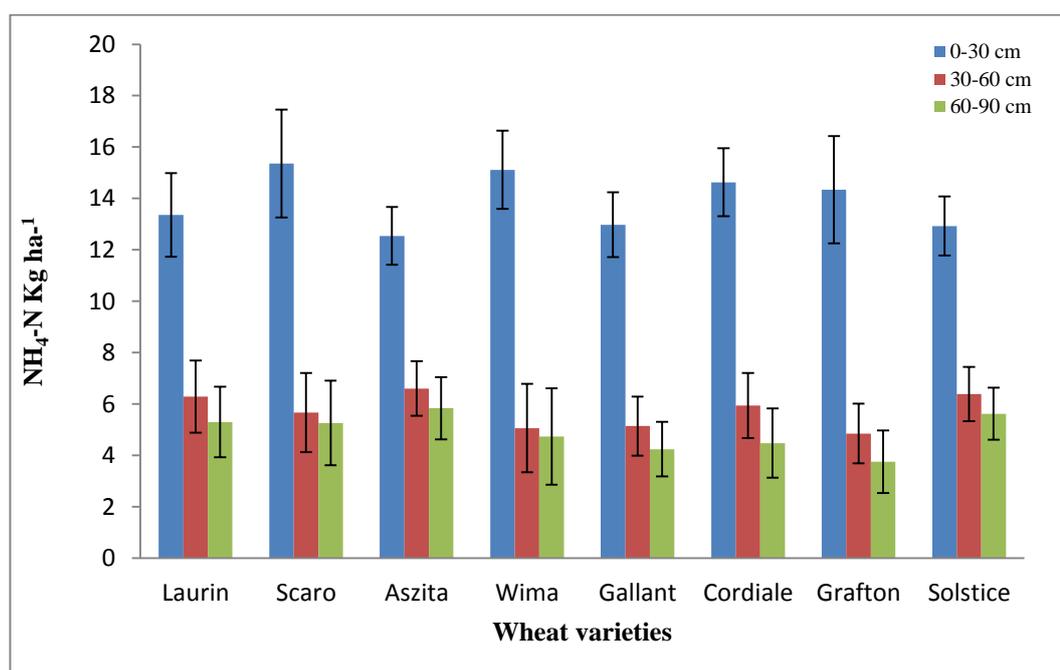


Figure 4.4 Soil NH_4^+ -N content (mean with SE shown) measured in soil (0-30, 30-60 and 60-90 cm depth) in March 2010 where 8 winter wheat varieties were growing

4.4 Discussion

In the UK, drainage and associated NO_3^- -N leaching are known to occur over winter (Webster *et al.*, 1993; Webster *et al.*, 2003; Addiscott, 2005). March is often considered as the end of any leaching period as the rate of evapotranspiration (*Etc*) begins to increase and hence drainage reduces (Burt *et al.*, 1993; Addiscott, 2005). March is also recognised as being before soil mineralisation rates start to increase (Addiscott, 2005; Cameron *et al.*, 2013). The higher amount of NO_3^- -N content in the topsoil than subsoil under all treatments is probably because of higher biological activity and organic matter in the topsoil and the fact that the topsoil was beginning to warm up when the soil samples were taken (Table 4.5) and therefore more soil mineral N was being released by soil microbial activity through mineralisation of soil organic N from both soil and applied manure (Addiscott, 2005).

It is well known that the amount of N provided to a following crop after manure is applied depends on many processes including mineralisation, nitrification, immobilisation and leaching (Shepherd, 1993a). The amount of soil mineral N to a depth of 90 cm measured in the early spring of 2010 (ranging from 33-69 kg N ha⁻¹) was similar to the range reported by Jackson and Smith (1997) when they applied manure at rate of 170- 240 kg N ha⁻¹ to winter wheat grown on different soil types (30-90 kg N ha⁻¹), and similar to the range of 19 to 91 kg N ha⁻¹ measured by Grylls *et al.* (1997). The amount of mineral N measured was lower than that reported by (Shepherd, 1993a); 86 to 137 kg N ha⁻¹). Shepherd *et al.* (1993) was reporting measurements made from soils which had received frequent and large application of manures and this is probably the reason for the higher amount of mineral N measured compare to the amount measured in our study (Shepherd, 1993a). The amount of soil mineral N measured in early spring also differs between years and sites as a result of the amount and pattern of overwinter rainfall (Grylls *et al.*, 1997). In 2009/10 the overwinter rainfall of (198 mm) was lower of that measured at Nafferton 2010 /11 (293 mm) and higher than 2011/12 (168 mm).

It is not possible to give any absolute values of NO_3^- -N leaching for the measurements made in this experiment as neither autumn SMN nor drainage was measured. However relative differences between treatments in the amounts of mineral N and its distribution within the profile can be used to consider relative differences in leaching between the

treatments. All plots were managed uniformly in the previous crop of winter barley and hence no differences in SMN content between the plots are expected before the compost application or the sowing of the winter wheat varieties. There were no significant differences between the fertility treatments (170 kg and 85 kg total N ha⁻¹ rates as composted cattle manure) on the amount of NH₄⁺-N, NO₃⁻-N and total soil mineral N content measured in the soil profile at any depth. Given the low % of available N in the compost (2-7%) it is not surprising that no differences were seen. Applying the piston flow model of drainage (Rose *et al.*, 1982; Wierenga *et al.*, 1991), any nitrate at the soil surface in autumn would be moved by leaching to a depth of c. 44 cm, which could be detected in the soil samples collected in March. Therefore we assume there was no significant difference in the NO₃⁻-N moved by leaching over winter resulting from the application of composts or the different wheat varieties.

Chambers *et al.* (2000) also found that the differences in the amount of NO₃⁻-N leached from plots receiving manure at a rate of 250 kg total N ha⁻¹ and plots receiving no manure were very small. In contrast Sorensen and Rubaek (2012) applied different rates of composted manure (76, 95, 118 kg N ha⁻¹) to winter wheat grown in lysimeters in loamy sand and sandy loam soil in Denmark found that nitrate leaching was ranged from 19-34 kg N ha⁻¹. The level of leaching in their experiment may be due to high amount of drainage (336 mm) recorded from the lysimeters. NO₃⁻-N leaching from applied manure is dependent on several factors including the time of application and manure type, especially the proportion of the manure N which is readily available, for example there is a larger readily available N content in poultry manures than in cattle manure (Chambers *et al.*, 2000). Beckwith *et al.* (1998) did not find an increase in the amount of soil mineral N following application of manure in autumn (200 kg N ha⁻¹) to winter rye used as cover crop, and hence the leaching of NO₃⁻-N was low c. 10 kg N ha⁻¹; larger amounts of leaching losses occurred when the manure was applied in late summer when soils were still warm. In our experiment manure was applied in late autumn when the temperature is usually cool (Table 4.5) therefore it is likely that mineralisation processes of N content in both soil and applied manure were slow. Shepherd and Newell-Price (2013) found no significant difference in the amount of NO₃⁻-N leaching from cereal plots on loamy sand receiving 210 kg N ha⁻¹ of manure applied in autumn and control plots receiving no manure for 4 years. However after 4 years of manure application, the leaching of NO₃⁻-N increased significantly on manured

plots due to the mineralisation of soil N that accumulated from applied manure (Shepherd and Newell-Price, 2013). Goulding *et al.* (2000) also reported leaching of NO_3^- -N equivalent to 25 % of the applied autumn manure to winter wheat grown in the Broadbalk Wheat Experiment where manures had been applied for over 100 years, and attributed the large amount of N that was at risk of leaching to the higher amount of organic matter in plots where manure had been applied manure for many years.

Different cover crops have been used to reduce the NO_3^- -N leaching over winter with marked differences observed between crop species (Thorup-Kristensen, 2006; Thorup-Kristensen *et al.*, 2009; Sapkota *et al.*, 2012; Fraser *et al.*, 2013). However Chambers *et al.* (2000) found that catch crops planted in autumn had little influence in reducing NO_3^- -N leaching over winter. In our experiment we did not find significant difference between the effects of 8 wheat varieties on reducing NO_3^- -N leaching. During the main growing period it is suggested that long-straw wheat varieties have more vigorous, larger root systems compared with modern short-straw varieties (Siddique *et al.*, 1990). However, in general there is little winter wheat root development during the autumn and winter compared with other cover crops. For example in comparison between cover crop roots sown in August, the depth of the roots by November was 100 cm for oats, 180 cm for winter rye and 200 cm for brassica while only 50 cm recorded for winter wheat (Thorup-Kristensen *et al.*, 2009). Thorup-Kristensen *et al.* (2009) also found that winter wheat planted in August showed deeper root growth by November compared with that planted in September. Vincent and Gregory (1989) compared the root systems of winter wheat sown in early and late autumn and found that early sown wheat had a root system that was about 7 times larger compared with that of a late autumn crop. Where a root system is not well developed, its ability to recover soil mineral N before leaching occurs can be low (Thorup-Kristensen *et al.*, 2009). In this experiment, winter wheat was planted in the middle of October, when soil temperatures were cool, therefore it is not expected that the wheat roots would have occupied a large part of the soil, and there would have been little growing time for differences in rooting between varieties to be demonstrated. Webster *et al.* (2003) compared the effectiveness of winter wheat in reducing NO_3^- -N leaching with that of other cover crops and found that winter wheat was less effective in reducing the NO_3^- -N leaching largely due to earlier sowing of the other cover crops compared with winter wheat which generally take places in October. Shepherd and Lord (1996) found that leaving the soil fallow and undisturbed

during the winter time (with a weed cover regenerating) was more effective than autumn sown winter wheat in reducing nitrate losses. However if winter wheat is planted in early autumn then the wheat may become more effective at reducing NO_3^- -N leaching through increased N uptake (Webster *et al.*, 2003). Francis *et al.* (1998) reported that in general all cover crops are more effective if they are planted in early autumn so that drainage occurs after the crops have had the opportunity to take up a large amount of soil mineral N. However this will also depend on the volume and the start time of soil drainage.

4.5 Conclusion

There was no evidence from soil mineral N measurements made in early spring that application of composted manures with low proportion of available N (at 170 or 85 kg total N ha^{-1}) in autumn increased nitrate leaching losses compared to no input in this experiment. These data are derived from only one season of study with one manure type and hence should not be widely extrapolated for management. However, both the timing of application and manure type are important in determining N availability and nitrate leaching risk from manures (Shepherd, 1993b; Chambers *et al.*, 2000; Shepherd and Newell-Price, 2013).

Late autumn sown winter wheat also had no effect on NO_3^- -N leaching after autumn applications of composted cattle manure with no difference between the 8 winter wheat varieties sown in October in this experiment. However for winter wheat to be most effective at reducing NO_3^- -N leaching over winter, (Widdowson *et al.*, 1987; Addiscott *et al.*, 1991) suggested that winter wheat should be planted as early as possible in autumn and therefore the impact of crop variety (as well as crop) on nitrate leaching may also be affected by sowing date.

5 Effects of crop management practices on nitrate leaching risk in crop rotations with potatoes and cereals

5.1 Introduction

Meeting the nitrogen (N) requirement for crop growth through N fertilisation (whether with mineral or organic sources) to obtain maximum yield while minimising, at the same time, the soil NO_3^- -N that is at risk of leaching remains a major challenge for agricultural management. N fertiliser management has often been associated with over-application of N fertilisers or application at a time not well matched to crop demand, thus leading to excessive plant available soil N and thereby increasing the potential risk of NO_3^- -N leaching (Cameron *et al.*, 2013; Shepherd and Newell-Price, 2013). Where both the rate and timing of N application whether mineral or organic fertiliser are correct then the risk of leaching of NO_3^- -N after crop harvest is minimised (Goulding *et al.*, 2000). However the risk of leaching is the result of a combination of manageable factors, including crop rotation, crop/variety selection, crop protection and other environmental factors including soil conditions, hydrology and weather patterns (Macdonald and Gutteridge, 2012; Cameron *et al.*, 2013). Therefore one of the main aims of this study is to examine how changes in agricultural management practices (rotation management, crop protection and crop variety) affect NO_3^- -N leaching risk when combined with N fertiliser applied at a rate close to the recommended rate (whether as ammonium nitrate or composted cattle manure).

The objectives of this study were therefore to:

- Determine the effect of rotation, fertility management, potato variety and crop protection practices on the risk of nitrate leaching following potato and cereal crops in rotation (measured by the amount of mineral N in the soil after harvest).

- Study the temporal (sampling date) and spatial (depth) relationships of mineral N in the soil profile in contrasting rotations with potatoes and the effects of N source (ammonium nitrate or composted cattle manure).

5.2 Methods

5.2.1 Detailed management information for plots selected for study

Plots in experiments 3 and 4 of the main Nafferton Factorial Systems Comparison trial (NFSC; see Section 3.2.1 detailed description) were selected for detailed monitoring as part of this PhD study in 2014. There were slight differences between the experiments in the cropping plan in both rotations before 2005 (Table 3.1). Of particular importance, in Experiment 3 in both rotations potatoes were grown in 2004, whereas in the same rotational position in Experiment 4 (2005) cereals were grown in the conventional rotation and a grass/clover ley was grown in the organic rotation. There was an additional year of the fertility building grass-clover ley in the organic rotation Experiment 4 (3 years, 2005-2007) compared with Experiment 3 (2 years, 2005-2006). In 2010 potatoes were growing in the organic and conventional rotations of experiment 3, followed in 2011 by spring wheat in the conventional rotation and spring barley in the organic rotation. Initially the cropping plan had been to grow winter wheat, but the ground conditions in autumn prevented sowing. In 2011 potatoes were growing in both rotations of experiment 4, followed in 2012 by winter wheat in the conventional rotation and spring barley in the organic rotation. In both experiments, the additional factor of variety was added for the potato plots, so that two varieties of potatoes (Sante and Sarpo Mira) were compared. Each fertility management sub-subplot was divided into two variety sub-sub-subplots (6 x 6 m). In the conventional rotation in the year following potatoes, wheat variety was introduced as a factor. The potato portion of the rotation main plot was therefore divided into two 3 m x 96 m plots for each of the spring wheat (Paragon and Tybalt) or winter wheat (Cordiale and Scaro) varieties. The resulting size of the wheat variety sub-sub-subplot was therefore 3 x 6 m.

5.2.2 Agronomic practices for potato production (Experiments 3 and 4)

Non chitted potato seeds of both varieties (Sante and Sarpo Mira) were planted on 29/4/2010 and 6/5/2011 using a semi-automatic two-row potato planter. Potato seed tubers planted in conventional crop protection subplots were produced under

conventional seed potato production conditions whereas seed tubers for organic crop protection subplots were produced to organic seed potato production standards.

In organic fertilisation sub-subplots, composted cattle manure was applied at rate equivalent to 175 kg total N ha⁻¹ per year (based on standard recommended rates in England taken from RB209) in a single application on either 8/4/2010 or 10/3/2011, the composted cattle manure had a total N content of 3% on a dry matter basis with 1.5 % in the mineral nitrogen form. Hence in application of 175 kg N ha⁻¹ there would have been 2.6 kg N ha⁻¹ of readily available N. After defoliation, tubers were left in the ground for four weeks to allow skin maturation, after that period both varieties were harvested using a single-row potato harvester on 7 October 2010 and 20 September 2011. Potato yield was assessed by weighing the tubers from the two middle rows of each plot. A sub-sample of chopped potato was dried in an oven at 80°C to determine tuber moisture content. In contrast mineral fertilisers were applied 4 weeks prior to planting of tubers with ammonium-nitrate (Nitram) equivalent to 180 kg N ha⁻¹ and superphosphate and KCl as compound fertiliser (0:20:30) equivalent to 134 kg P₂O₅ ha⁻¹ and 200 kg K₂O ha⁻¹ were applied on 21/4/2010 and 28/4/2011 respectively. No irrigation was applied throughout the growing season. Further details of the crop protection regime are given in (Table 5.1). Potatoes growing in the NFSC trial at Nafferton farm are shown in (Figure 5.1).



Figure 5.1 *Potatoes growing on Nafferton farm in experiment 3, 2010-2011; organic fertility sub-sub plot in the foreground.*

Table 5.1 Potato management during the two years of the study including organic (ORG) and conventional (CON) fertility management (FM) practices and organic and conventional crop protection (CP) practices.

	2010 (experiment 3)	2011 (experiment 4)
Previous Crop		
for ORG	2 years Peas/Beans; Potato /Brassica	Peas/Beans; Potato/Brassica
for CON	winter barley; winter wheat	winter barley; winter wheat
Planting date	29/04/2010	06/05/2011
Seeding density	35cm spacing	35cm spacing
Harvest date	07/10/2010	20/09/2011
Fertility Input		
ORG FM	Composted cattle manure to the equivalent of 175 kg total N ha ⁻¹ per year on 8/4/2010 and 10/3/2011	
CON FM	Ammonium- nitrate (Nitram) to the equivalent to 180 kg N ha ⁻¹ and superphosphate and KCL as compound fertiliser (0:20:30) equivalent to 134kg P ₂ O ₅ ha ⁻¹ and 200 kg K ₂ O ha ⁻¹ on 21/4/2010 and 28/4/2011.	
Crop protection		
ORG CP		
Fungal Control	Copper Oxychloride five times	
Weed control	Potatoes mechanically weeded with ridger 3 times in June.	
CON CP		
Herbicides	Pendimethalin 1.8l/ha Linuron 1.2l/ha 18/5/2010 Reglone 2l/ha 15/9/10	
Insecticides	Oxamyl 50 kg ha ⁻¹ 23/4/2010	
Fungicides	Fubol Gold 1.9 kg ha ⁻¹ 30/6/10, 9/7/10, 27/7/10 Shirlan 300 ml/ha 22/6/10, 5/7/10, 21/7/10, 3/8/10, 12/8/2010, 20/8/10	

5.2.3 Agronomic practices for wheat and barley following potatoes (Exp 3 and 4)

Weather conditions after potato harvest in 2010 meant that it was not possible to establish winter wheat, hence spring wheat (varieties Paragon and Tybalt) were sown in spring 2011 (Figure 5.2) in the conventional rotation plots of Experiment 3. In contrast, winter wheat (varieties Scaro and Cordiale) were established successfully in October 2011 in the conventional rotation plots of Experiment 4. As part of the planned rotation in the NFSC experiment, spring barley (variety Westminster) was established in the organic rotation plots in Experiment 3 (2011) and Experiment 4 (2012) (Table 5.2). In organic fertility sub-subplots cattle manure was incorporated on 9/3/2011, 7/10/2011 and 30/3/2012 for spring wheat, winter wheat and spring barley respectively. The composted cattle manure applied to spring wheat and spring barley had a total N content of 2 % on a dry matter basis with 2.5 % in the mineral nitrogen form. Whereas for winter wheat had a total N content of 3.6 % on a dry matter basis with 10 % in the mineral nitrogen form. In conventional fertility sub subplots, mineral fertiliser was applied on 5/4/2011 for spring wheat, 22/3/2012 and 16/4/2012 for winter wheat and 17/4/2012 and 9/5/2012 for spring barley. Full agronomic information is given in (Table 5.2). Wheat and barley crops were harvested using a plot combine harvester (Claas Dominator 38, Claas U.K Ltd, Bury St. Edmunds, UK) allowing yield to be determined in the central strip of each plot.

5.2.4 Soil sampling for determination of soil mineral N

The procedures used for soil sampling and determination of soil water content and soil mineral N (nitrate and ammonium concentrations) in these experiments were the same procedures used in the NUE-CROPS trial (Sections 4.2.2 – 4.2.5).

Soil core samples were collected from Experiment 3 (2010-11) and 4 (2011-12; Table 5.3). In Experiment 3, 64 potato plots were sampled in July 2010 when the both varieties of potato were well developed and then again in October 2010 after potato harvest. The following year soil core samples were taken from the spring wheat (variety Tybalt) in only the conventional crop protection plots following the Sante variety of potatoes (total of 16 plots) so that the only treatment factor was fertility management.



Figure 5.2 *Spring wheat during growth (above) and immediately before harvesting (below) in Experiment 3, 2011.*

Table 5.2 Agronomic management in spring wheat, spring barley and winter wheat during the two years of the study including organic fertility management (ORG FM) and conventional fertility management (CON FM) practices and organic crop protection (ORG CP) and conventional crop protection (CON CP) practices.

	2011 Spring wheat	2011 Spring barley	2012 Winter wheat	2012 Spring barley
	Following potato, Exp 3	Following potato, Exp 3	Following potato, Exp 4	Following potato, Exp 4
	Conventional rotation	Organic rotation	Conventional rotation	Organic rotation
Planting date	8/4/2011	7/4/2011	14/10/2011	31/3/2011
Seeding rate	Tybalt Con 184 kg ha ⁻¹ Tybalt Org 204 kg ha ⁻¹ Paragon Con 196 kg ha ⁻¹ Paragon Org 200 kg ha ⁻¹	Westminster Con 216 kg ha ⁻¹ Westminster Org 212 kg ha ⁻¹	Scaro Con/Org 168 kg ha ⁻¹ Cordiale Con 212 kg ha ⁻¹ Cordiale Org 210 kg ha ⁻¹	Westminster Con 192 kg ha ⁻¹ Westminster Org 184 kg ha ⁻¹
Harvest date	14/9/2011	9/9/2011	3/9/2012	7/9/2012
fertility Input				
ORG FM	250 kg N ha ⁻¹ cattle manure on 9/3/2011	170 kg N ha ⁻¹ cattle manure	250 kg ha ⁻¹ cattle manure on 7/10/2011	170kg N ha ⁻¹ cattle manure on 30/3/2012
CON FM	180 kg N ha ⁻¹ Ammonium-Nitrate on 5/4/2011	120 kg N ha ⁻¹ Ammonium Nitrate on 7/5/2011 and 31/5/2011	210kg N ha ⁻¹ Ammonium Nitrate on 22/3/2012 and 16/4/2012	120kg N ha ⁻¹ Ammonium Nitrate on 17/4/2012 and 9/5/2012
Crop protection				
ORG CP				
Insect Control				
Weed control CON CP				
Herbicides	Finish 70ml/ha 14/6/2011	Finish 70ml/ha 14/6/2011	Liberator 0.6L/ha 24/10/11 Axial 0.25L/ha on 15/4/2012 chimera 0.8g/ha Minstrel 6/5/2012	Alistel 3.5L/ha 14/6/12
Insecticides				
Fungicides	Prosaro 0.5L/ha 14/6/2011 Comet 0.5L/ha 14/6/2011 Prairie 1.5L/ha 12/7/2011	Comet 0.5L/ha 14/6/2011 Prosaro 0.5L/ha 14/6/2011 Prairie 1.5L/ha 12/7/2011	Capalo 0.5L/ha 7/4/12 Kestrel 0.7L/ha 6/5/2012	Alto-Elite 1L/ha 28/7/12

In Experiment 4, soil core samples were taken in early March 2011 from 32 plots before potatoes were planted (at this point variety subplots had not been allocated to the two separate varieties) Soil core sampling in potato crops is shown in (Figure 5.3). In early August 2011, 64 potato plots were sampled when the potato was already well grown and then plots were sampled again after potatoes had been harvested. The same 64 plots were sampled winter wheat (variety Cordiale) in the conventional rotation and spring barley (variety Westminster) in the organic rotation in spring and after harvest (Table 5.3).

Table 5.3 *Soil core samples collected for mineral N measurement in experiments 3 and 4 of the NFSC trial, 2010-2012.*

Crop	Season	Experiment	Date of sampling	Plots	Total no. of samples
Potato	2010	3	01/07/2010	64	192
Potato	2010	3	29/10/2010	64	192
Potato	2011	4	01/03/2011	32	96
Potato	2011	4	02/08/2011	64	192
Potato	2011	4	20/10/2011	64	192
Spring wheat	2011	3	01/03/2011	16	48
Spring wheat	2011	3	14/09/2011	16	48
Winter wheat spring barley	2012	4	31/03/2012	64	192
Winter wheat spring barley	2012	4	14/09/2012	64	192



Figure 5.3 *Soil core sampling in potato crops*

5.2.5 Statistical Analyses

For soil mineral N data following the potato harvest in 2010 (Experiment 3) and 2011 (Experiment 4), the main effects of year, crop rotation, crop protection, fertilisation, and variety and the interactions among these factors on response variables were analysed using a 5-way ANOVA. When interactions between year and other factors occurred the dataset was subset (by year) and the effects of rotation, fertility, crop protection and variety and their interactions within each year were analysed by 4-way ANOVA. Data in 2012 following winter wheat or spring barley (Experiment 4) were also analysed using this 4-way model. If rotation interacted with any of the other factors, the data was further subset by rotation and a 3-way ANOVA (CP x FM x VAR) was conducted at each level of rotation. This model was also used for analysis of the data for soils sampled in 2011 following spring wheat (Experiment 3). Where variety was involved in an interaction, the data was subset by variety and the effects of crop protection and fertility management studied as a 2-way ANOVA. Differences among interaction means were tested using Tukey contrasts in the general linear hypothesis testing (glht) function of the multcomp package in R (Pinheiro *et al.*, 2011). For two-way interactions a linear mixed effects model was used for the Tukey contrasts containing a treatment main effect with four levels with the random error term specified as described above.

In all cases linear mixed-effects models (Pinheiro and Bates, 2000) were used to analyse the data to produce ANOVA *P*-values for main effects and all interactions using (nlme package) R software (R development core team 2009). The maximal model (including all main effect and interaction terms) was fit initially and then simplified according to the model simplification procedure described in Crawley (Crawley 2007) where non-significant terms are dropped from the model. The simpler model was used for further analysis where there was no significant difference ($P > 0.05$) in Akaike's information criterion (AIC) between the two models. Terms not included in the model are shown as ns (not significant) in the results tables.

The hierarchical nature of the split plot design was reflected in the random error structures that were specified as block/year/rotation/crop protection/fertility management. Where analysis at a given level of a factor was carried out, that factor was removed from the random error term. The normality of the residuals of all models was

tested and data were transformed using square-root or log where necessary to meet the criteria of normal data distribution.

For mineral N results following potato harvest in 2010 and 2011 an additional analysis to investigate the interaction between potato variety and sampling depth was conducted. For this analysis the 2-way model VAR x DEP was used with the random error term specified as block/rotation/crop protection/fertility management/variety. *P*-values were used to assess differences between the two potato varieties ($P < 0.05$). Differences between the three sampling depths were assessed using Tukey contrasts as described above.

The temporal soil moisture and mineral N data patterns (Section 5.3.2 and 5.3.5) were plotted with the mean of each showing the standard error bars. Where the standard error bars did not overlap (for any sampling date between soil depths or for each depth between sampling dates), we considered that the means were significantly different.

5.3 Results

5.3.1 Weather patterns 2010 – 2012

In both years when potatoes were grown (2010, 2011) the growing season started with cool temperatures in April and then became warmer for the remainder of the season (Table 5.4). The air and soil temperatures followed the same pattern with the highest temperatures reached in July. Estimated cumulative ET_c for the growing season was higher in 2010 (241 mm; 76 % of the annual total) than in 2011 (174 mm; 63% of the annual total) for the period of potato planting until the haulms were killed (Table 5.4) with a daily maximum of 5.69 mm at full coverage. The cumulative rainfall during the growing seasons (April-September) was 233 mm in 2010 and 206 mm in 2011. Due to high ET_c in the growing season there was little to no drainage (Figure 5.4). The highest monthly rainfall recorded during the potato growing season was 82 mm in August in 2011 and this was the only month in either growing season when any drainage was estimated from the water balance (Table 5.4).

For growing cereals conditions in 2012, the highest air and soil temperatures were recorded in July. 2012 was a markedly different growing season with very high rainfall

from April to the end of the year (Figure 5.4) and drainage throughout the summer; in contrast to the more typical growing seasons in 2010 and 2011. The cumulative rainfall during winter wheat growing seasons (Oct 2011-Sep 2012) was 721 mm and 573 mm for spring barley. Estimated cumulative ETc for the cereal growing season was lower than potato grown seasons (Figure 5.4).

Table 5.4 *Climatic conditions during the growing seasons for potato in 2010 (Experiment 3) and 2011 (Experiment 4).*

	April	May	June	July	Aug.	Sept.	Oct.
Precipitation (mm)							
2010	8.40	19.16	24.80	42.00	36.20	62.60	39.40
2011	4.40	31.00	8.20	37.60	81.60	15.80	28.20
Mean relative humidity (%)							
2010	74.25	76.48	77.62	79.78	82.58	84.95	84.33
2011	75.48	72.87	81.01	82.09	86.68	81.30	85.70
Mean air temperature (°C)							
2010	7.56	8.78	13.64	15.04	13.31	12.50	9.05
2011	9.76	10.48	12.38	13.44	13.41	12.85	10.69
Mean soil temperature (°C)							
2010	8.06	11.36	15.94	16.89	14.73	12.92	9.09
2011	11.01	12.48	14.94	15.33	14.33	12.52	11.27

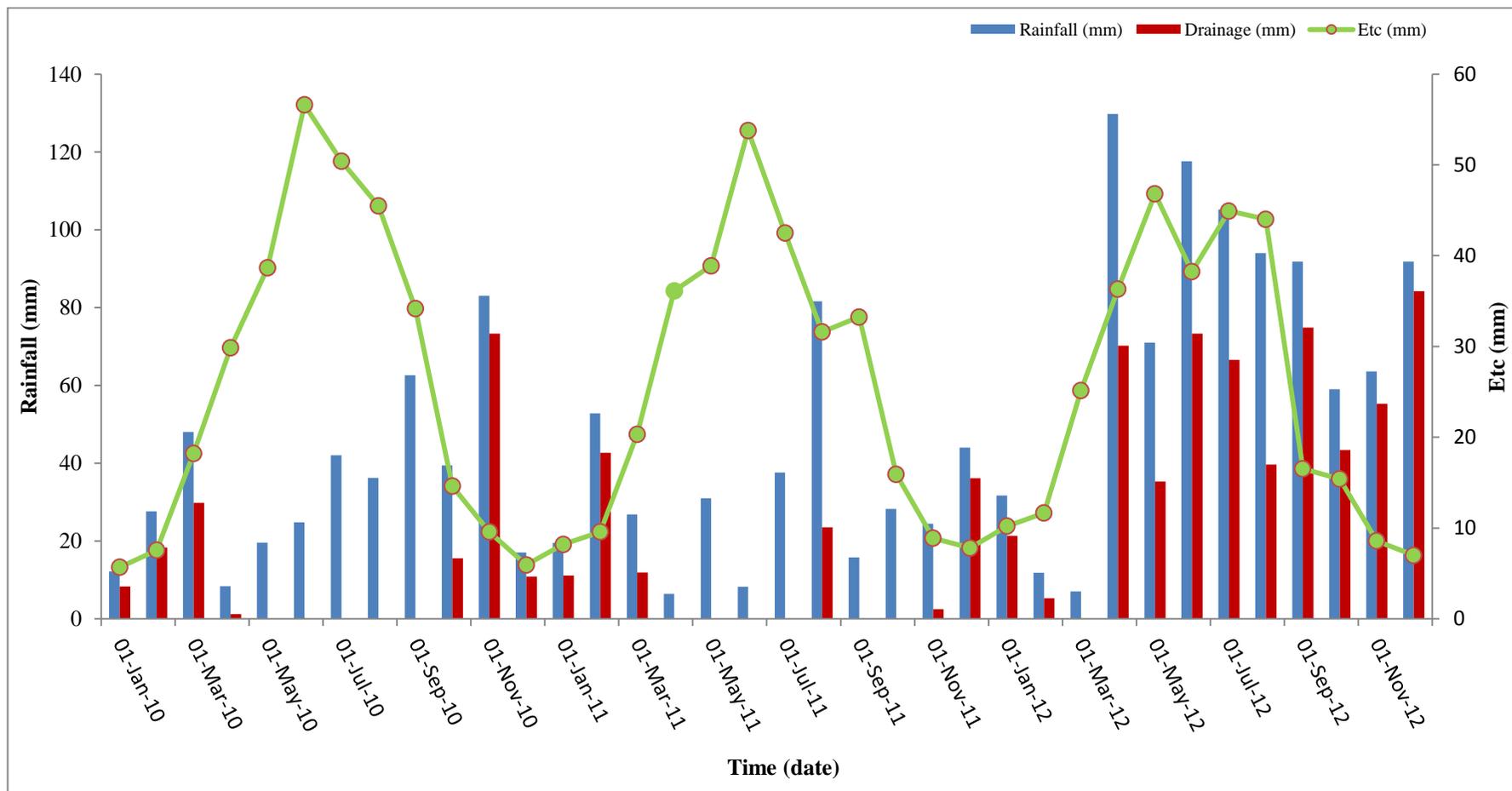


Figure 5.4 Total monthly rainfall and evapotranspiration data, 2010-12. Rainfall data was obtained from weather station at Nafferton farm, evapotranspiration was estimated using Penman-Monteith equation, for the whole period April to September 2010 and 2011. Drainage was estimated from the water balance.

5.3.2 Soil water content

In both experiments, volumetric water content showed similar patterns, volumetric water content was always higher in the top soil (0-30 cm, ranging from 0.20 to 0.45 cm cm⁻³) than subsoil (0.18 to 0.42 cm cm⁻³; Figure 5.5). No differences in the volumetric water content were usually found between the 30-60 cm and 60-90 cm layer. However, there was a difference in both March 2011 and September 2012 when the volumetric water content was significantly higher in the 30-60 cm layer than in the 60-90 cm layer.

5.3.3 Amount of mineral N remaining in the soil after potato harvest

Total soil mineral N (SMN) content found after potato harvest (0-90 cm) was 50 kg N ha⁻¹ on average across both years. Most of the SMN was found in the topsoil (0-30 cm depth) with 66 % and 85 % of SMN in the topsoil in 2010 and 2011 respectively. NO₃⁻-N always made up more than half of the SMN in the soil profile.

Soil NO₃⁻-N in the plots measured after potato harvest in both years ranged from 1 kg N ha⁻¹ to 96 kg N ha⁻¹ in topsoil (0-30 cm) and 1 to 116 kg N ha⁻¹ in the whole profile (0-90 cm) when all rotations, N fertility, crop variety and crop protection treatments were considered. Soil NO₃⁻-N in the plots measured after potato harvest had mean values of 19 and 29 kg N ha⁻¹ at 0-30 cm depth, and 24 and 33 kg N ha⁻¹ at 0-90 cm depth in 2010 and 2011 respectively. Although the soil NO₃⁻-N concentration was slightly higher in 2011 than 2010, this difference was not significant (p= 0.054 at 0-30 cm depth; p= 0.063 at 0-90 cm depth).

Soil NH₄⁺-N in the plots measured after potato harvest in both years ranged from 0 kg N ha⁻¹ to 49 kg N ha⁻¹ in topsoil (0-30 cm) and 0 to 64 kg N ha⁻¹ in (0-90 cm) when all rotations, N fertility, crop variety and crop protection treatments were considered. Soil NH₄⁺-N in the plots measured after potato harvest had mean values of 15 and 12 kg N ha⁻¹ at 0-30 cm depth and 29 and 15 kg N ha⁻¹ at 0-90 cm depth for 2010 and 2011 respectively. Although soil NH₄⁺-N contents were greater in 2010 than 2011, especially in the subsoil, they were not significantly so (p=0.0501).

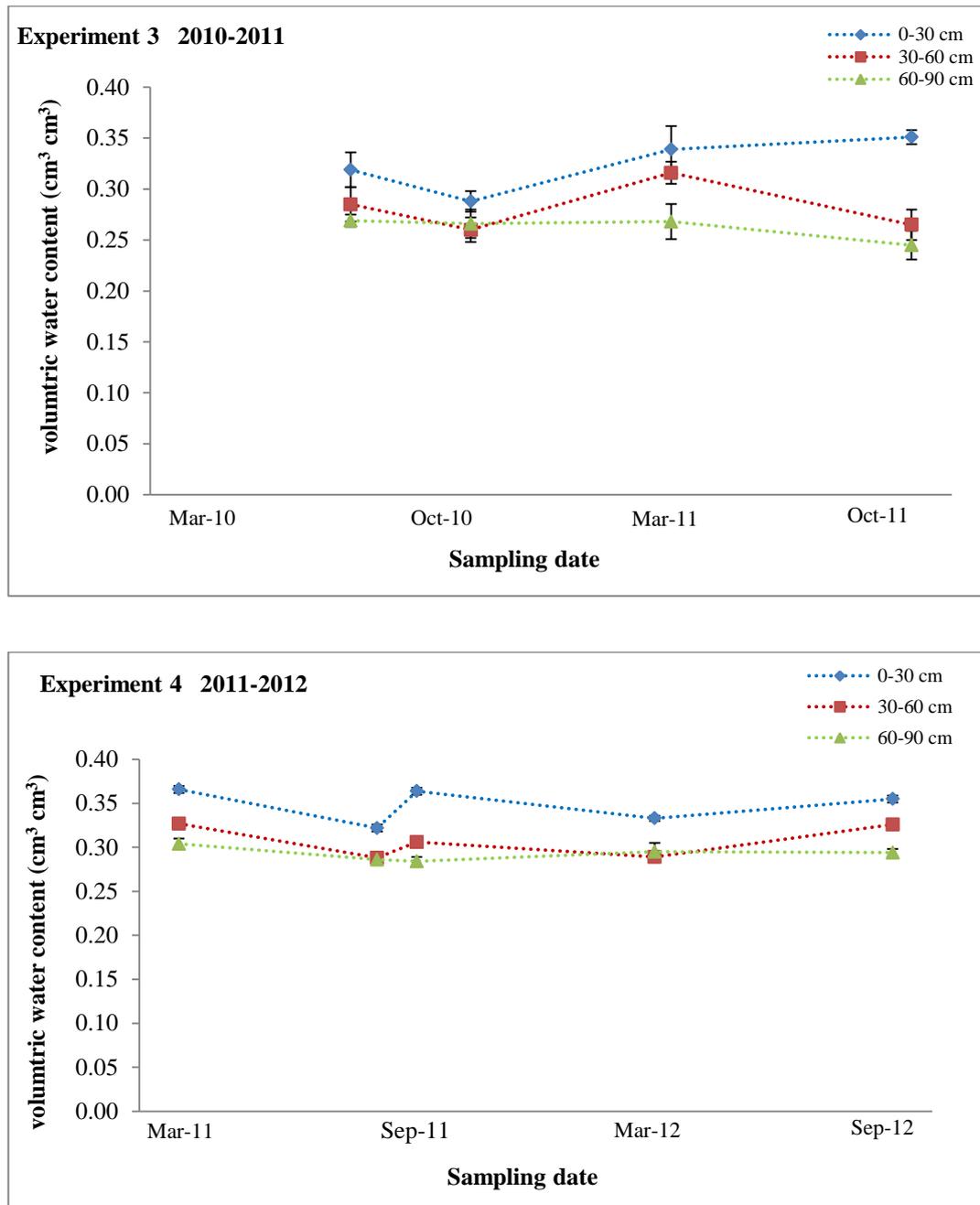


Figure 5.5 Mean volumetric water content (with SE) for the three soil layers (0-30, 30-60 and 60-90 cm) of the soil profile under all treatments during the growing seasons 2010-2011 in experiment 3 and 2011-2012 experiment 4.

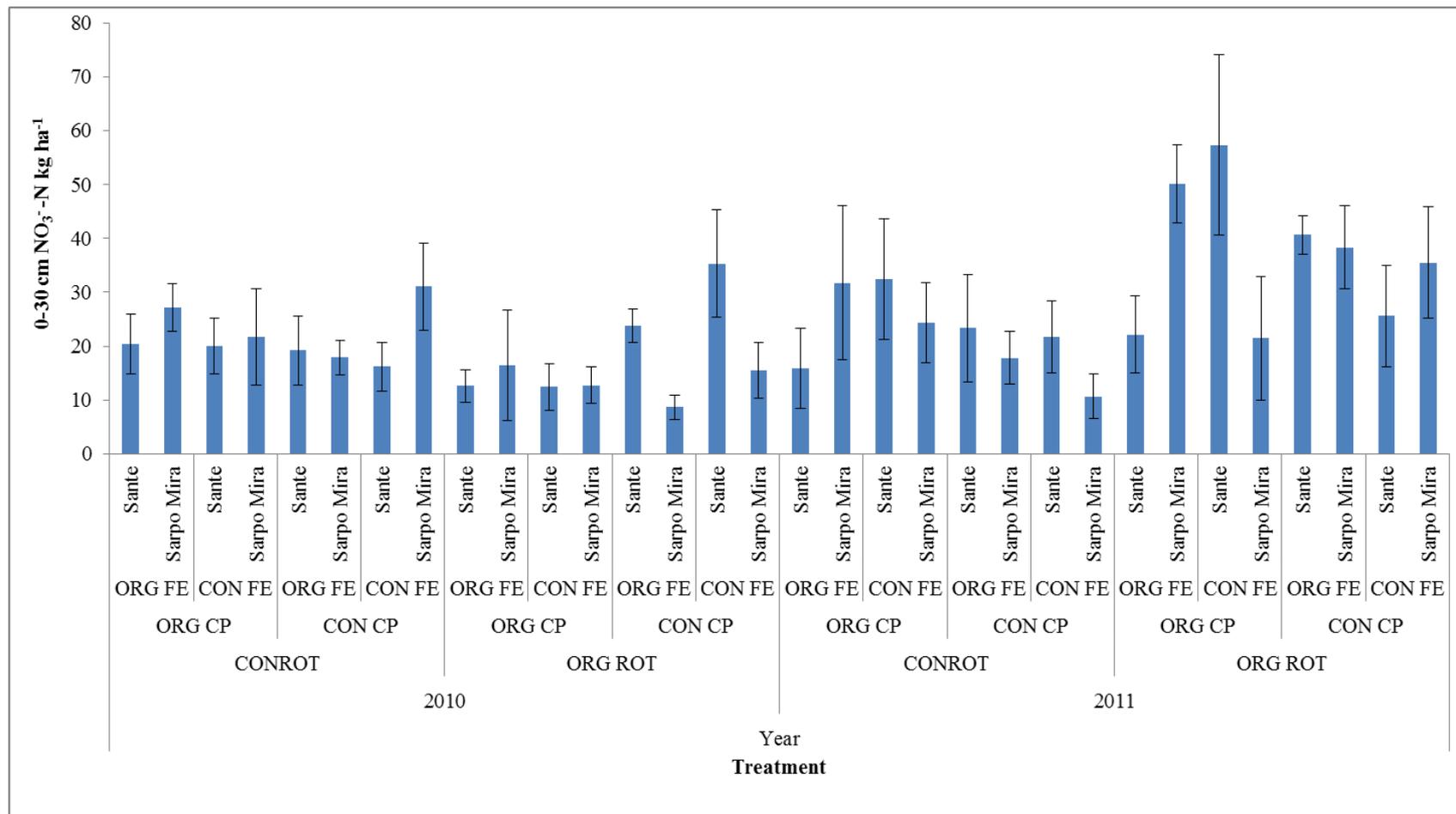


Figure 5.6 Effect of year, rotation, crop protection, fertility and potato variety on the amount of soil NO₃⁻-N content measured at 0-30 cm depth after potato harvest in 2010 and 2011. Five-way interaction ($p=0.024$).

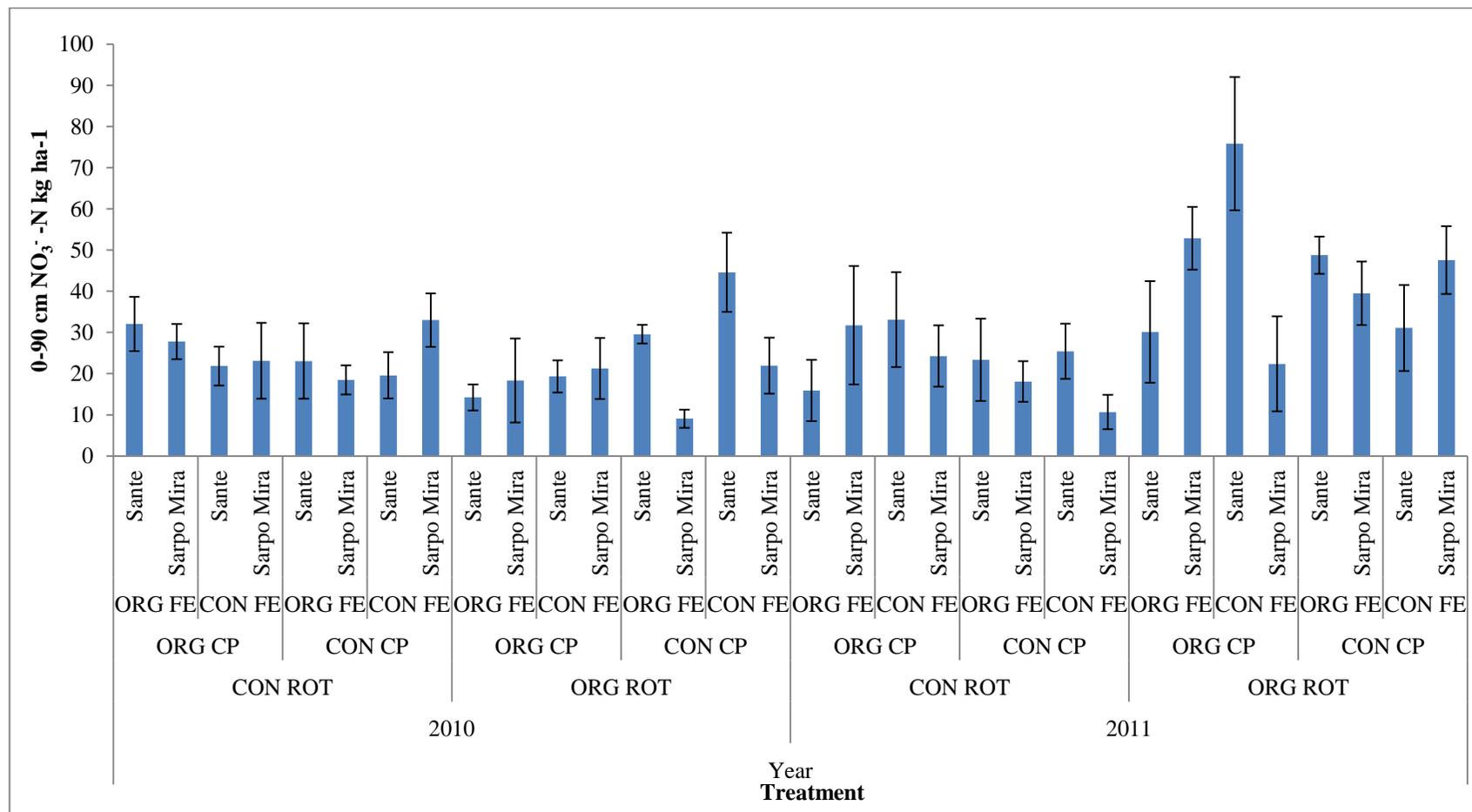


Figure 5.7 Effect of year, rotation, crop protection, fertility and potato variety on the amount of soil NO₃⁻-N content measured at 0-90 cm depth after potato harvest in 2010 and 2011 in experiment 3 and 4. Five –way interaction $p= 0.0007$).

5.3.3.1 2010 (Experiment 3)

Main effect of Rotation

Soil NO_3^- -N in the plots measured after potato harvest had mean values of 22 and 17 kg N ha^{-1} for 0-30 cm depth and 25 and 22 kg N ha^{-1} for 0-90 cm depth in the CON and ORG ROT respectively, when all N fertility, crop variety and crop protection treatments were considered. There was no significant difference between NO_3^- -N levels for either 0-30 cm or 0-90 cm between both rotation treatments.

Soil NH_4^+ -N in the plots measured after potato harvest had mean values of 14 and 16 kg N ha^{-1} for 0-30 cm depth and 28 and 30 kg N ha^{-1} for 0-90 cm depth in the CON and ORG ROT respectively, when all N fertility, crop variety and crop protection treatments were considered. There was no significant difference between NH_4^+ -N levels for either 0-30 cm or 0-90 cm between both rotation treatments.

Main effect of Fertility management

Soil NO_3^- -N in the plots measured after potato harvest had mean values of 21 and 18 kg N ha^{-1} for 0-30 cm depth and 26 and 22 kg N ha^{-1} for 0-90 cm depth in the CON and ORG FE respectively, when all rotation, crop variety and crop protection treatments were considered. There was no significant difference between NO_3^- -N levels for either 0-30 cm or 0-90 cm between both fertility treatments.

Soil NH_4^+ -N in the plots measured after potato harvest had mean values of 14 and 16 kg N ha^{-1} for 0-30 cm depth and 27 and 30 kg N ha^{-1} for 0-90 cm depth in the CON and ORG FE respectively, when all rotation, crop variety and crop protection treatments were considered. There was no significant difference between NH_4^+ -N levels for either 0-30 cm or 0-90 cm between both fertility treatments.

Main effect of crop protection

Soil NO_3^- -N in the plots measured after potato harvest had mean values of 21 and 18 kg N ha^{-1} for 0-30 cm depth and 26 and 21 kg N ha^{-1} for 0-90 cm depth in the CON and ORG CP respectively, when all rotation, N fertility, crop variety and were considered. There was no significant difference between NO_3^- -N levels for either 0-30 cm or 0-90 cm in both crop protection treatments.

Soil NH_4^+ -N in the plots measured after potato harvest had mean values of 17 and 14 kg N ha^{-1} for 0-30 cm depth and 31 and 26 kg N ha^{-1} for 0-90 cm depth in the CON and ORG CP respectively, when all rotation, N fertility, and crop variety were considered. There was no significant difference between NH_4^+ -N levels for either 0-30 cm or 0-90 cm between both crop protection treatments.

Main effect of crop variety

Soil NO_3^- -N in the plots measured after potato harvest had mean values of 18 and 20 kg N ha^{-1} for 0-30 cm depth and 25 and 22 kg N ha^{-1} for 0-90 cm depth for the Sante and Sarpo Mira varieties when all rotation, N fertility, and crop protection treatments were considered. There was no significant difference between soil NO_3^- -N levels for either 0-30 cm or 0-90 cm depth where the different potato varieties were grown.

Soil NH_4^+ -N in the plots measured after potato harvest had mean values of 16 and 14 kg N ha^{-1} for 0-30 cm depth and 30 and 27 kg N ha^{-1} for 0-90 cm depth for the Sante and Sarpo Mira varieties respectively when all rotation, N fertility, and crop variety were considered. There was no significant difference between NH_4^+ -N levels for either 0-30 cm or 0-90 cm depth where the different potato varieties were grown.

Interactions between factors

For soil NO_3^- at 0-30 cm depth, the 2-way interaction between rotation and crop protection was almost significant ($p=0.0846$), but a highly significant 3-way interaction was detected between rotation, crop protection and potato variety ($p=0.0087$). For 0-90 cm there was a similar highly significant 3-way interaction detected between rotation, crop protection and potato variety treatments ($p=0.0019$).

When the 3-way interaction was examined (Figure 5.6; 2010 only), in the CON CP under ORG ROT, soil NO_3^- -N content at 0-30 cm depth was markedly higher under Sante (22.7 kg N ha^{-1}) in contrast with other all treatments (16 kg N ha^{-1}) where soil NO_3^- -N content at 0-30 cm depth was generally slightly or significantly higher where Sarpo Mira was grown (20 kg N ha^{-1} on average). The amount of soil NO_3^- -N content in the whole profile (0-90 cm; Figure 5.7; 2010 only) was also significantly higher where Sante was grown than Sarpo Mira when CON CP was combined with organic rotation (34 kg N ha^{-1} and 13 kg N ha^{-1} for Sante and Sarpo Mira respectively).

At 0-90 cm depth, there was also a significant 3-way interaction detected between rotations, fertility and potato varieties ($p = 0.0327$; Figure 5.7 2010 only). When the 3-way interaction was examined NO_3^- -N content was significantly higher where Sante was grown than Sarpo Mira when CONFЕ combined with ORGROT (Figure 5.7, 33.15 and 20.42 kg N ha⁻¹ for Sante and Sarpo Mira respectively). In contrast, soil NO_3^- -N level was higher where Sarpo Mira was grown than Sante when CONFЕ was combined with CONROT (Figure 5.7, 28 and 21 kg N ha⁻¹ for Sarpo Mira and Sante). All other 2-way and 3-way interactions were not significant.

5.3.3.2 2011 (Experiment 4)

Main effect of Rotation

Soil NO_3^- -N in the plots measured after potato harvest had mean values of 22 and 36 kg N ha⁻¹ for 0-30 cm depth, and 23 and 44 kg N ha⁻¹ for 0-90 cm depth in the CON and ORG ROT respectively, when all N fertility, crop variety and crop protection treatments were considered. The main effect of rotation on the amount of soil NO_3^- -N at 0-30 cm depth was almost significant ($p=0.0788$; Figure 5.6). There was a significant main effect ($p=0.0332$; Figure 5.7) of rotation on the level of soil NO_3^- -N measured at 0-90 cm, with soil NO_3^- -N content significantly higher in the ORG ROT than CON ROT.

Soil NH_4^+ -N in the plots measured after potato harvest had mean values of 12 and 11 kg N ha⁻¹ for 0-30 cm depth and 15 and 15 kg N ha⁻¹ for 0-90 cm depth in the CON and ORG ROT respectively, when all N fertility, crop variety and crop protection treatments were considered. There was no significant difference between NH_4^+ -N levels for either 0-30 cm or 0-90 cm between both rotation treatments.

Main effect of Fertility management

Soil NO_3^- -N in the plots measured after potato harvest had mean values of 29 and 30 kg N ha⁻¹ for 0-30 cm depth and 34 and 33 kg N ha⁻¹ for 0-90 cm depth in the CON FE and ORG FE respectively where rotation, crop variety and crop protection treatments were considered. There was no significant difference between NO_3^- -N levels for either 0-30 cm or 0-90 cm between fertility treatments.

Soil NH_4^+ -N in the plots measured after potato harvest had mean values of 12 and 11 kg N ha^{-1} for 0-30 cm depth and 15 and 15 kg N ha^{-1} for 0-90 cm depth in the CON FE and ORG FE respectively where all rotation, crop variety and crop protection treatments were considered. There was no significant difference between NH_4^+ -N levels for either 0-30 cm or 0-90 cm between fertility treatments.

Main effect of crop protection

Soil NO_3^- -N in the plots measured after potato harvest had mean values of 27 and 32 kg N ha^{-1} for 0-30 cm depth and 31 and 36 kg N ha^{-1} for 0-90 cm depth in the CON CP and ORG CP respectively where rotation, fertility and crop variety treatments were considered. There was no significant difference between NO_3^- -N level for either 0-30 cm or 0-90 cm between crop protection treatments.

Soil NH_4^+ -N in the plots measured after potato harvest had mean values of 11 and 12 kg N ha^{-1} for 0-30 cm depth, 15 and 15 kg N ha^{-1} for 0-90 cm depth in the CON CP and ORG CP respectively where rotation, N fertility, and crop variety were considered. There was no significant difference between NH_4^+ -N levels for either 0-30 cm or 0-90 cm between both crop protection treatments.

Main effect of crop variety

Soil NO_3^- -N in the plots measured after potato harvest had mean values of 30 and 29 kg N ha^{-1} for 0-30 cm depth and 35 and 31 kg N ha^{-1} for 0-90 cm depth for the Sante and Sarpo Mira varieties respectively, where all rotation, N fertility, and crop protection treatments were considered. There was no significant difference between soil NO_3^- -N levels for either 0-30 cm or 0-90 cm between potato varieties.

Soil NH_4^+ -N in the plots measured after potato harvest had mean values of 12 and 12 kg N ha^{-1} for 0-30 cm depth and 14 and 16 kg N ha^{-1} for 0-90 cm depth for the Sante and Sarpo Mira varieties respectively where rotation, N fertility, and crop protection treatments were considered. There was no significant difference between soil NH_4^+ -N level for either 0-30 cm or 0-90 cm between potato varieties.

Interactions

At 0-30 cm depth, the 4-way interaction between rotation, crop protection, fertility and potato variety was almost significant ($p= 0.0761$; 2011 in Figure 5.6); the interaction was significant when the whole profile (0-90 cm) was considered ($p= 0.013$; Figure 5.7). There was a significant 2-way interaction between fertility and potato variety ($p= 0.0151$) and a highly significant 3-way interaction between crop protection, fertility and potato variety ($p =0.0056$). All other 2-way and 3-way interactions were not significant. When the 3-way interaction was examined (Figure 5.6, 2011 only), the soil NO_3^- -N content was significantly higher where Sante (45 kg N ha^{-1}) was grown than Sarpo Mira (23 kg N ha^{-1}) when CON FE was combined with ORG CP. In contrast, the soil under Sarpo Mira (41 kg N ha^{-1}) had significantly higher NO_3^- -N content than Sante (19 kg N ha^{-1}) when ORG FE was combined with ORG CP. There was no significant difference in the amount of soil NO_3^- -N content for other treatments. The same patterns were seen for the whole soil profile (0-90 cm, Figure 5.7, 2011 only). For 0-90 cm, the soil NO_3^- -N concentration in the ORG ROT was significantly higher where Sante (76 kg N ha^{-1}) was grown than Sarpo Mira (22 kg N ha^{-1}) when CON FE combined with ORG CP. However the soil concentrations become significantly higher where the Sarpo Mira (48 kg N ha^{-1}) was grown than Sante (31 kg N ha^{-1}) when the ORG FE is combined with ORG CP. This difference is not apparent in the CON ROT.

Some interactions were found when soil NH_4^+ -N content at 0-30 cm depth was investigated. The 3-way interaction between (rotation, crop protection and potato variety) and (crop protection, fertility and potato variety) were almost significant ($p=0.0981$; $p=0.0570$) respectively. A significant 2-way interaction ($p=0.0249$; Figure 5.8) was observed between fertility and potato variety, with higher NH_4^+ -N content in the 0-30 cm depth in the organic fertility where Sarpo Mira was grown compared to Sante. However, there was higher NH_4^+ -N content in the conventional fertility where Sante was grown compare to the Sarpo Mira. All the other 2-way and 3-way interactions were not significant.

For NH_4^+ -N content at 0-90 cm depth, the 3-way interaction between crop protection, fertility and potato variety was almost significant ($p=0.081$). All other 2-way and the 3-way interactions were not significant.

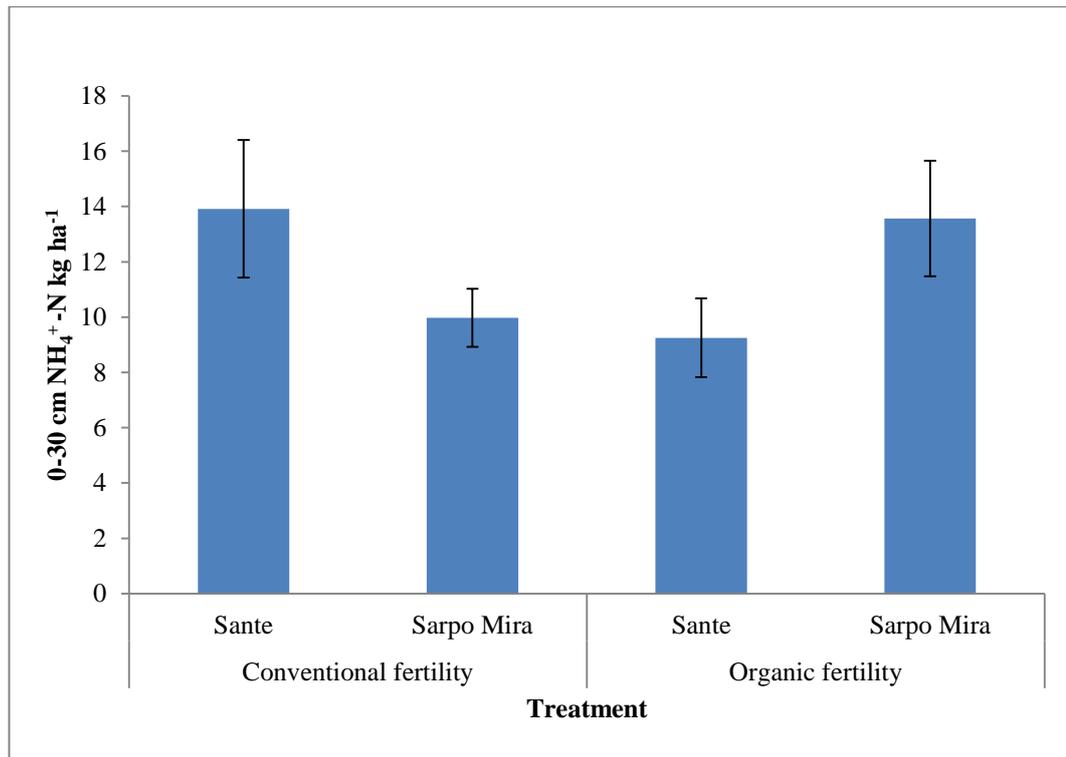


Figure 5.8 Effect of fertility and potato variety on the amount of NH_4^+ -N in soil measured at 0-30 cm depth after potato harvest in 2011. Two-way interaction, $p = 0.0249$

5.3.3.3 Common patterns in both seasons

When the results of both growing seasons (2010 and 2011) are considered together, interactions between factors (rotation, fertility, crop protection, crop variety) are found. However, there are no clear consistent effects of any factors (or their interactions) on soil NO_3^- -N content (Figure 5.6 and Figure 5.7), soil NH_4^+ -N or the SMN content remaining in the soil profile after potato harvest. A summary of main effect of and interaction between factors on soil NO_3^- -N content for both growing seasons 2010 and 2011 is presented on (Table 5.5).

There was a significant 2-way interaction found between year and rotation at both 0-30 cm ($p=0.0274$) and 0-90 cm ($p=0.0129$), in 2011 the amount of soil NO_3^- -N content was significantly higher in ORG ROT (mean of 36.39 and 43.52 kg N ha⁻¹ for 0-30 and 0-90) than in CON ROT (mean of 22.25 and 23 kg N ha⁻¹ for 0-30 and 0-90), this difference was not observed in 2010; there was no significant difference between soil NO_3^- -N content in CON ROT measured in 2010 and 2011. In the whole profile (0-90

cm) there was also a significant 2-way interaction between fertility and potato variety ($p=0.0493$), we found no significant difference between the potato varieties in the ORG FE treatment (mean of 27.13 and 27.0 kg N ha⁻¹ for Sante and Sarpo), but in the CON FE the soil NO₃⁻-N content was higher where Sante was grown (mean of 34 kg N ha⁻¹, 0-90 mean) than Sarpo Mira (mean of 26 kg N ha⁻¹, 0-90 mean).

Higher level interactions were also found showing the high variability of post-harvest nitrate concentrations and the limited impact of each of the treatment factors studied.

- A significant 3-way interaction between year, fertility and potato variety (0-30 cm $p=0.016$; 0-90 cm $p=0.019$)
- A significant 3-way interaction between crop protection, fertility and potato variety (0-30 cm $p=0.002$; 0-90 cm $p=0.001$)
- A significant 4-way interaction between year, rotation, crop protection and potato variety (0-30 cm $p=0.011$; 0-90 cm $p=0.0009$)
- A significant 5-way interaction between year, rotation, crop protection, fertility and potato variety (0-30 cm $p=0.024$ Figure 5.6; 0-90 cm $p=0.007$ Figure 5.7).

For soil NH₄⁺-N levels, only the 3-way interaction between crop protection, fertility and potato variety was significant ($p= 0.0112$; Figure 5.9). All other 2-way and 3-way interactions were not significant. When the 3-way interaction was examined (Figure 5.9) the NH₄⁺-N content was significantly higher where Sarpo Mira was grown compared with Sante when ORG CP was used with the CON FE treatment. But when ORG CP was used with CON FE the NH₄⁺-N content was significantly higher where Sante was grown compared with Sarpo Mira. This difference was not found with the CON CP.

Table 5.5 *Main effect of, and interaction between rotations, crop protection, fertility management and potato variety on concentrations of nitrate-N, as kg/ha in soil (Experiments 3, and 4, 2010/ 2011).*

Main effect	2010 0-30 cm	2010 0-90 cm	2011 0-30 cm	2011 0-90 cm
ROT	NS	NS	T	*
CP	NS	NS	NS	NS
FE	NS	NS	NS	NS
VAR	NS	NS	NS	NS
Interactions				
ROT × CP	T	NS	NS	NS
ROT × FE	NS	NS	NS	NS
CP × FE	NS	NS	NS	NS
ROT × VR	NS	NS	NS	NS
CP × VR	NS	T	NS	NS
FE × VR	NS	NS	*	*
ROT × CP × FE	NS	NS	NS	NS
ROT × CP × VR	*	*	NS	T
ROT × FE × VR	NS	*	NS	NS
CP × FE × VR	NS	NS	*	*
ROT × CP × FE × VR	NS	NS	T	*

In the table, NS= Non Significant, *= Significant (P<0.05), T= Trend.

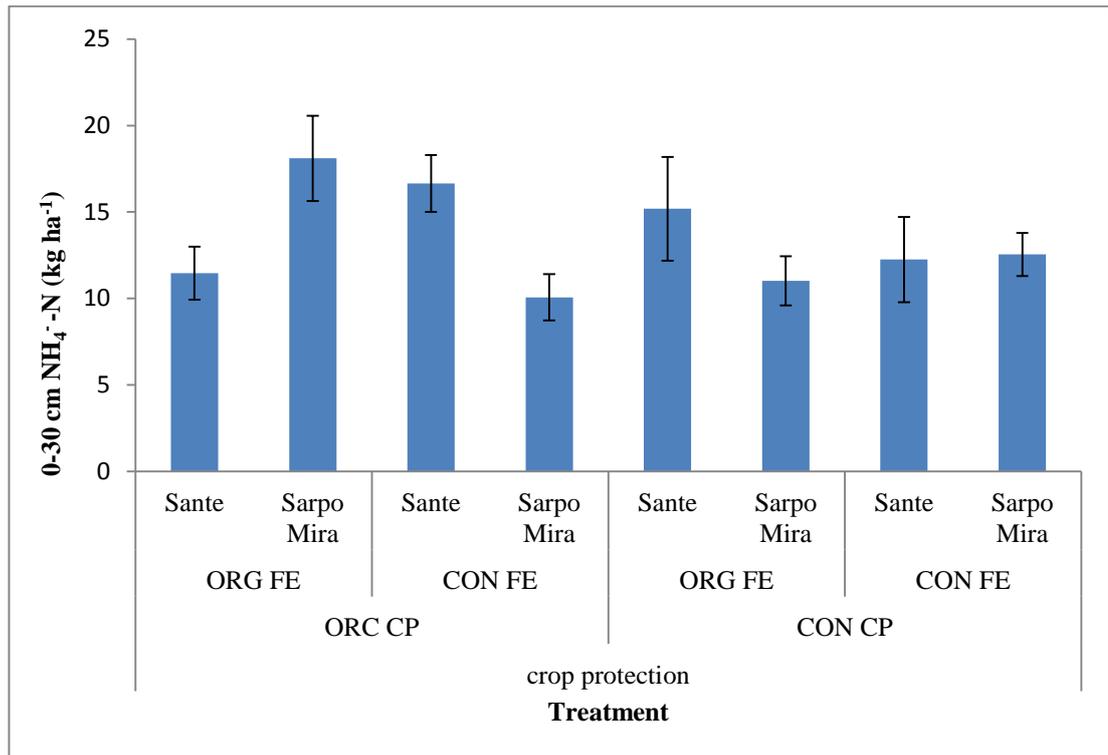


Figure 5.9 *Three -way interaction; effect of crop protection, fertility and potato variety on the soil NH₄⁺-N concentration measured at 0-30 cm depth after potato harvest in 2010 and 2011 in experiment 3 and 4.*

5.3.3.4 The effect of potato variety on the amount of soil mineral N measured at different depths in the soil profile after potato harvest

In both years, the NO₃⁻-N content measured in the top 0-30 cm was significantly higher than in subsoil 30-90 cm depth (p=0.000; Figure 5.10). In 2010, soil NO₃⁻-N content measured after potato harvest had mean values of 19 kg N ha⁻¹ for 0-30 cm and 4 kg N ha⁻¹ for 30-90 cm depth. In 2011, soil NO₃⁻-N content in the plots measured after potato harvest had mean value of 29 kg N ha⁻¹ for 0-30 cm and 4 kg N ha⁻¹ for 30-90 cm depth. Although the soil NO₃⁻-N concentration was slightly higher in 2011 than 2010, this difference was not significant (Section 5.3.3.3).

There was no significant difference between soil NH₄⁺-N content for either 0-30 cm (15 kg N ha⁻¹) or 30-90 cm (14 kg N ha⁻¹) depths in 2010, but in 2011 significantly lower soil NH₄⁺-N contents were measured at 30-90 cm (3 kg N ha⁻¹) than at 0-30 cm (12 kg

N ha⁻¹). There was no significant difference between soil NH₄⁺-N levels for either 0-30 cm or 30-90 cm where Sante is compared with Sarpo Mira in either 2010 or 2011.

In both years there was no significant difference in the soil NO₃⁻-N content (0-30 cm) after potato harvest between varieties (Figure 5.10). However in 2010, the soil NO₃⁻-N content at 30-90 cm depth was significantly higher where Sante was grown (7 kg N ha⁻¹) compared with Sarpo Mira (1 kg N ha⁻¹; 2 way interaction p=0.001). In 2011, at 30-90 cm the amount of soil NO₃⁻-N content was higher (though not significantly) where Sante (6 kg N ha⁻¹) is grown than Sarpo Mira (2 kg N ha⁻¹; Figure 5.10b).

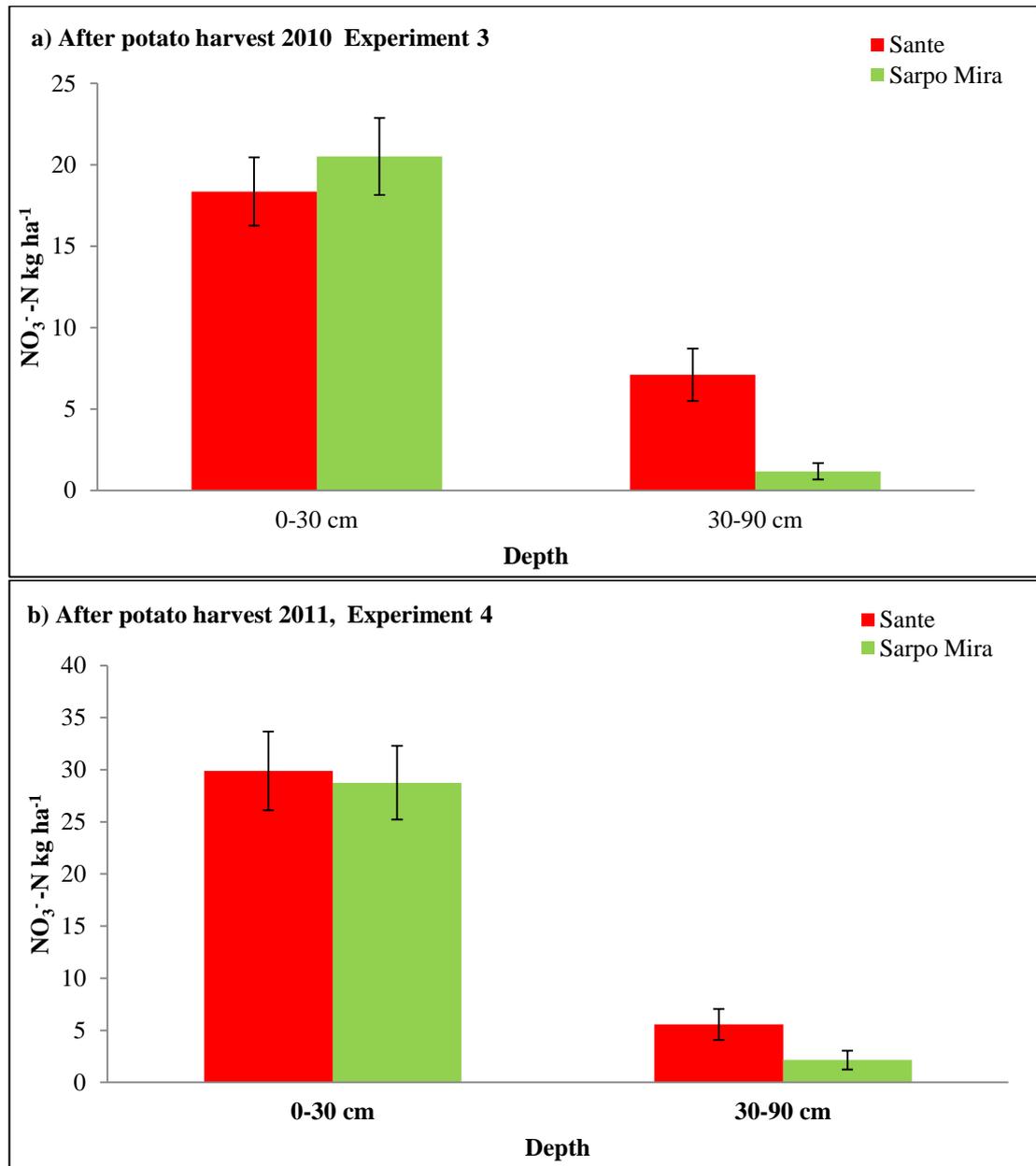


Figure 5.10 Effect of depth (0-30 cm and 30-90 cm) and potato variety on the soil NO_3^- -N content measured after potato harvest. Two-way interaction 2010 $p = 0.001$; 2011 $p > 0.0$.

5.3.4 Amount of mineral N remaining in the soil after cereal harvest

5.3.4.1 Soil mineral N measured following Spring Wheat (Experiment 3; 2011)

In 2011 in Experiment 3, only plots in the conventional rotation under conventional crop protection were sampled so that the only treatment factor was fertility management.

Soil mineral N measured after the harvest of spring wheat was 82 kg N ha⁻¹ on average at 0-90 cm depth and soil NO₃⁻-N made up about 21 % of the SMN. Soil NO₃⁻-N ranged from 4 kg N ha⁻¹ to 27 kg N ha⁻¹ in topsoil (0-30 cm) and 5 to 28 kg N ha⁻¹ in the whole profile (0-90 cm). Soil NH₄⁺-N ranged from 27 kg N ha⁻¹ to 65 kg N ha⁻¹ in topsoil 0-30 cm and 45 to 101 kg N ha⁻¹ in the whole profile.

There was no significant effect of fertility treatment on soil NO₃⁻-N or NH₄⁺-N content for either 0-30 cm or 0-90 cm depths. Mean values of soil NO₃⁻-N were 13 and 11 kg N ha⁻¹ for 0-30 cm depth, and 14 and 19 kg N ha⁻¹ for 0-90 cm depth, in the CON FE and ORG FE respectively. Mean values of soil NH₄⁺-N content in the plots measured after spring wheat harvest were 47 and 46 kg N ha⁻¹ for 0-30 cm depth, and 61 and 71 kg N ha⁻¹ for 0-90 cm depth in the CON FE and ORG FE respectively.

5.3.4.2 Soil mineral N measured following cereals in Experiment 4, 2012 (Conventional rotation - Winter Wheat; Organic rotation - Spring Barley)

Soil mineral N content in the plots measured after winter wheat and spring barley harvest had mean values of 52 and 71 kg N ha⁻¹ for the soil profile (0-90 cm) respectively, soil NO₃⁻-N content represented 47 % and 58 % of the total SMN content of the soil profile respectively.

Soil NO₃⁻-N content in the plots measured after winter wheat and spring barley harvest ranged from 1 to 47 kg N ha⁻¹ in topsoil (0-30 cm) and 5 to 63 kg N ha⁻¹ for 0-90 cm when all rotations, fertility treatment, crop variety and crop protection treatments were considered. Soil NH₄⁺-N content in the plots measured after winter wheat and spring barley harvest ranged from 0 to 91 kg N ha⁻¹ in topsoil 0-30 cm and 0 to 117 kg N ha⁻¹ for 0-90 cm when all rotations, fertility treatment, crop variety and crop protection treatments were considered. A summary of main effect of and interaction between factors on soil NO₃⁻-N content for growing season 2012 is presented on (Table 5.6).

Table 5.6 Main effect of, and interaction between rotations, crop protection, fertility management and cereal on concentrations of nitrate-N, as kg/ha in soil (Experiment 4, 2012).

Main effect	0-30 cm	0-90 cm
ROT	*	*
CP	NS	
FE	NS	NS
Previous crop VAR (potato)	NS	NS
Interactions		
ROT × CP	*	NS
ROT × FE	NS	NS
CP × FE	NS	NS
ROT × VR	NS	NS
CP × VR	*	NS
FE × VR	NS	NS
ROT × CP × FE	NS	NS
ROT × CP × VR	NS	NS
ROT × FE × VR	NS	NS
CP × FE × VR	NS	NS
ROT × CP × FE × VR	*	T

In the table, NS= Non Significant, *= Significant (P<0.05), T= Trend.

Main effect of rotation (confounded with crop in 2012)

Soil NO₃⁻-N content in the plots measured after winter wheat (CON ROT) and spring barley (ORG ROT) harvest had mean values of 13 and 22 kg N ha⁻¹ for 0-30 cm depth, and 21 and 35 kg N ha⁻¹ for 0-90 cm depth in the CON ROT and ORG ROT treatments respectively, when all fertility treatments, crop variety and crop protection treatments were considered. There was a significant difference between soil NO₃⁻-N levels for both 0-30 cm and 0-90 cm depths in both rotations treatments (p= 0.0249 and p= 0.0191; Figure 5.11), the soil NO₃⁻-N content was significantly higher in ORG ROT than in CON ROT for both 0-30 cm and 0-90 cm depths. Cereal yields were higher (3.7 t ha) where spring barley was grown in the organic rotation compare with yield of (2.641 t ha) where winter wheat grown in the conventional rotation.

Soil NH₄⁺-N content in the plots measured after winter wheat and spring barley harvest had mean values of 26 and 28 kg N ha⁻¹ for 0- 30 cm depth, and 31 and 36 kg N ha⁻¹ for 0-90 cm depth in the CON ROT and ORG ROT respectively, when all N fertility, crop

variety and crop protection treatments were considered. There was no significant difference between soil NH_4^+ -N levels for either 0-30 cm or 0-90 cm between both rotations.

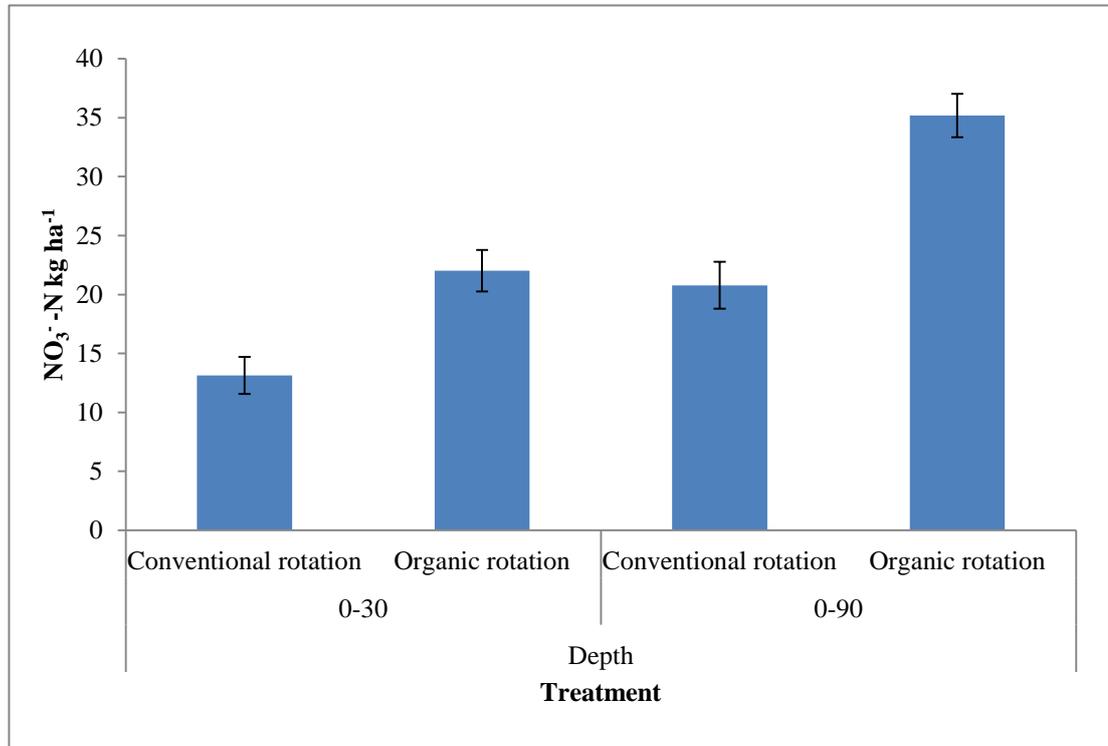


Figure 5.11 *The main effect of rotation on the amount of soil NO_3^- -N measured after winter wheat and spring barley harvest at 0-30 cm and 0-90 cm depths in 2012.*

Main effect of fertility management

Soil NO_3^- -N content in the plots measured after winter wheat and spring barley harvest had mean values of 17 and 19 kg N ha^{-1} for 0-30 cm depth, and 26 and 30 kg N ha^{-1} for 0-90 cm depth in the CON FE and ORG FE respectively, when all rotation, crop variety and crop protection treatments were considered. There was no significant difference in soil NO_3^- -N content when comparing fertility treatments for either 0-30 cm or 0-90 cm.

Soil NH_4^+ -N content in the plots measured after winter wheat and spring barley harvest had mean values of 26 and 29 kg N ha^{-1} for 0-30 cm depth, and 30 and 36 kg N ha^{-1} for 0-90 cm depth in the CON FE and ORG FE respectively, when all rotation, crop variety and crop protection treatments were considered. There was no significant difference in soil NH_4^+ -N content when comparing fertility treatments for either 0-30 cm or 0-90 cm.

Main effect of crop protection

Soil NO_3^- -N content in the plots measured after winter wheat and spring barley harvest had mean values of 16 and 19 kg N ha⁻¹ for 0- 30 cm depth, and 27 and 29 kg N ha⁻¹ for 0-90 cm depth in the CON CP and ORG CP respectively, when all rotation, fertility and previous potato variety treatments and were considered. There was no significant difference in soil NO_3^- -N content when comparing crop protection treatments for either 0-30 cm or 0-90 cm.

Soil NH_4^+ -N content in the plots measured after winter wheat and spring barley harvest had mean values of 28 and 27 kg N ha⁻¹ for 0- 30 cm depth, and 32 and 36 kg N ha⁻¹ for 0-90 cm depth in the CON CP and ORG CP respectively, when all rotation, fertility, and previous potato variety treatments were considered. There was no significant difference in soil NH_4^+ -N content when comparing crop protection treatments for either 0-30 cm or 0-90 cm.

Main effect of previous crop variety (potato).

Soil NO_3^- -N content in the plots measured after winter wheat and spring barley harvest had mean values of 17 and 19 kg N ha⁻¹ for 0-30 cm depth, and 26 and 30 kg N ha⁻¹ for 0-90 cm depth following the potato varieties Sante and Sarpo Mira respectively, when all rotation, N fertility, and crop protection treatments were considered. There was no significant difference in soil NO_3^- -N content when comparing previous potato variety for either 0-30 cm or 0-90 cm.

Soil NH_4^+ -N content in the plots measured after winter wheat and spring barley harvest had mean values of 30 and 24 kg N ha⁻¹ for 0- 30 cm depth, and 37 and 30 kg N ha⁻¹ for 0-90 cm depth following the potato varieties Sante and Sarpo Mira respectively, when all rotation, N fertility, and crop variety were considered. There was no significant difference in soil NH_4^+ -N content when comparing previous potato variety for either 0-30 cm or 0-90 cm.

Interactions between factors

For soil NO_3^- -N content at 0-30 cm depth, there was **(a)** a significant 2-way interaction found between rotation and crop protection treatments ($p=0.0485$), **(b)** a significant 2-way interaction between crop protection and previous potato variety ($p =0.0130$) and **(c)** a significant 4-way interaction found between rotation, crop protection, fertility and

previous potato variety ($p=0.0384$; figure (Figure 5.12). At 0-90 cm depth, only the 4-way interaction between rotation, crop protection, fertility and previous potato variety was almost significant ($p= 0.0762$). All other 2-way and 3-way interactions were not significant.

When interactions were examined (Figure 5.12) **a**) there was no significant difference found in the CON ROT between the CP treatments (12 and 14 kg N ha⁻¹ for ORG CP and CONCP or overall). But in the ORG ROT the NO₃⁻-N concentration was significantly higher under the ORG CP (26 kg N ha⁻¹) than CON CP (18 kg N ha⁻¹). When the other two way interaction **b**) is examined, in the ORG CP the amount of soil NO₃⁻-N after harvest was significantly higher following Sarpo Mira (23 kg N ha⁻¹) compared with Sante (16 kg N ha⁻¹). This difference was not apparent in the CON CP (mean of 17 and 14 kg N ha⁻¹ for Sante and Sarpo Mira). Where the 4-way interaction **c**) was examined, in the CON ROT where the CON FE and CON CP treatment are combined, there was significantly higher soil NO₃⁻-N content following Sante (19 kg N ha⁻¹) than Sarpo Mira (11 kg N ha⁻¹). However when the ORG FE was combined with CON CP the soil NO₃⁻-N content was higher following Sarpo Mira (16 kg N ha⁻¹) compared with Sante (10 kg N ha⁻¹). This trend was not apparent in the ORG ROT. When the data of the soil NH₄⁺-N content at 0-30 cm and 0-90 cm depths investigated, all 2-way, 3-way and 4-way interactions were not significant.

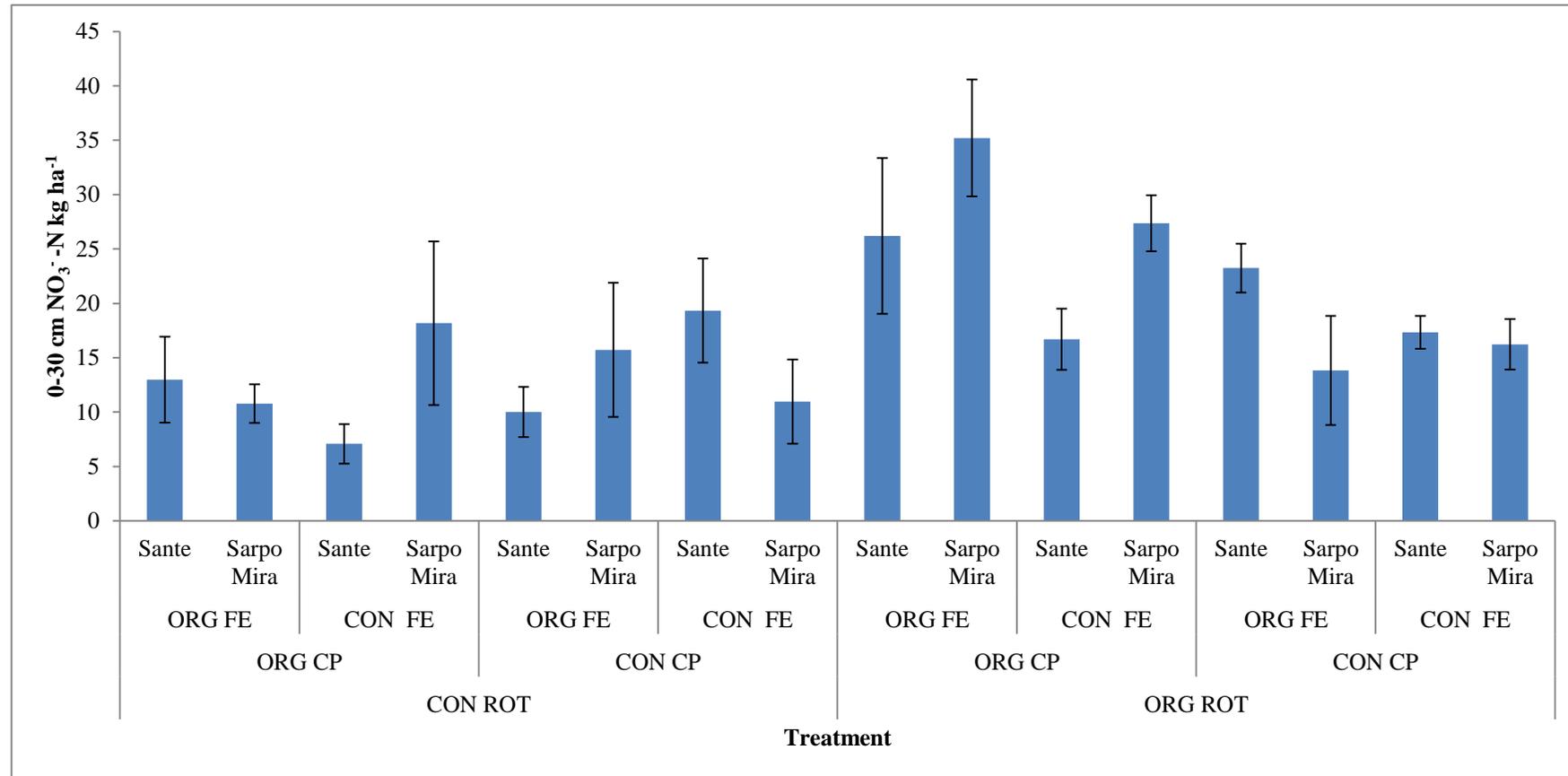


Figure 5.12 Effect of rotation, crop protection, fertility and previous potato variety on the amount of soil NO₃⁻-N content measured at 0-30 cm depth after winter wheat (CON ROT) and spring barley (ORG ROT). Four-way interaction, $p=0.0384$.

5.3.5 Temporal and spatial patterns in mineral N concentrations

5.3.5.1 Experiment 3 (2010-11)

Because of the limited sampling in 2011, only the CON ROT, CON CP plots can be followed throughout the experiment. In general, the soil NO_3^- -N content showed similar patterns with sampling time under both CON and ORG FE treatments (Figure 5.13 and Figure 5.14) for the growing seasons 2010 (potato) and 2011 (spring wheat). Soil NO_3^- -N content was significantly higher in the topsoil (0-30 cm depth) than in the subsoil (30-60 and 60-90 cm depths), except in March and October 2011 under ORG FE treatment. At most sampling times there was no significant difference in the amount of soil NO_3^- -N measured at either 30-60 cm or 60-90 cm depths.

The highest concentration of soil NO_3^- -N was measured in March 2011 at all depths; this was immediately before the planting of spring wheat. Low concentrations of soil NO_3^- -N content were measured after spring wheat harvest (October 2011) followed by potato harvest (October 2010). There was no significant difference between the soil NO_3^- -N concentrations measured in samples taken after potato harvest and the July sampling, except for the ORG FE treatment in the top 30 cm which was significantly higher in October 2010 compared to July 2010.

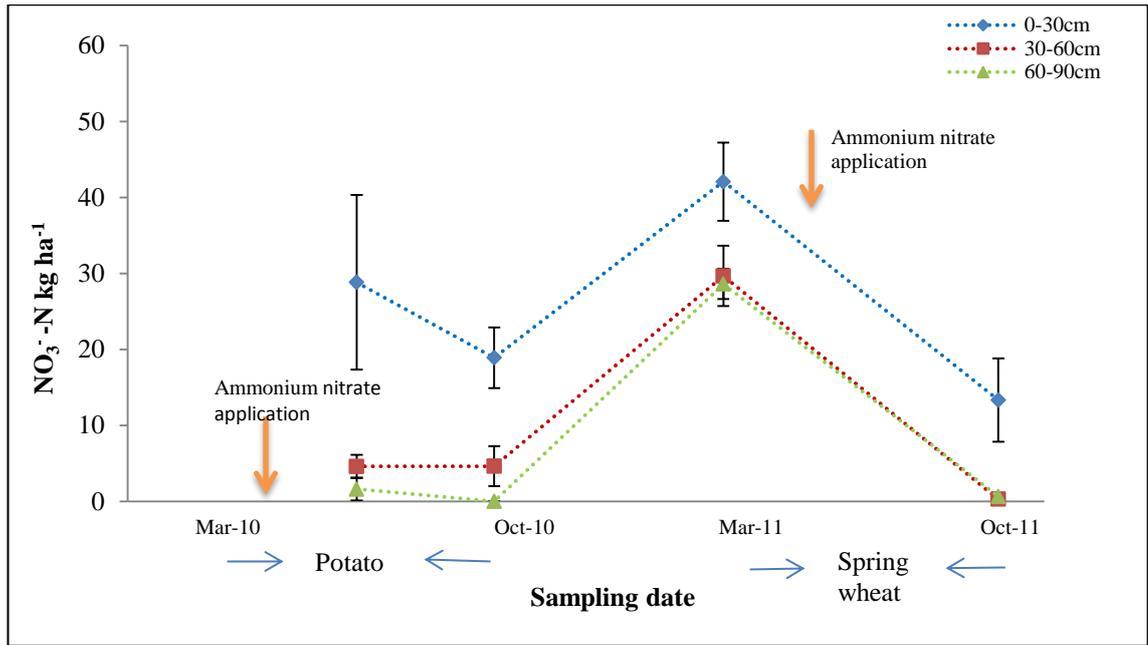


Figure 5.13 Soil NO_3^- -N content (mean with SE) for CON ROT, CON FE treatments measured at depths 0-30, 30-60 and 60-90 cm during the growing seasons 2010 and 2011 for experiment 3.

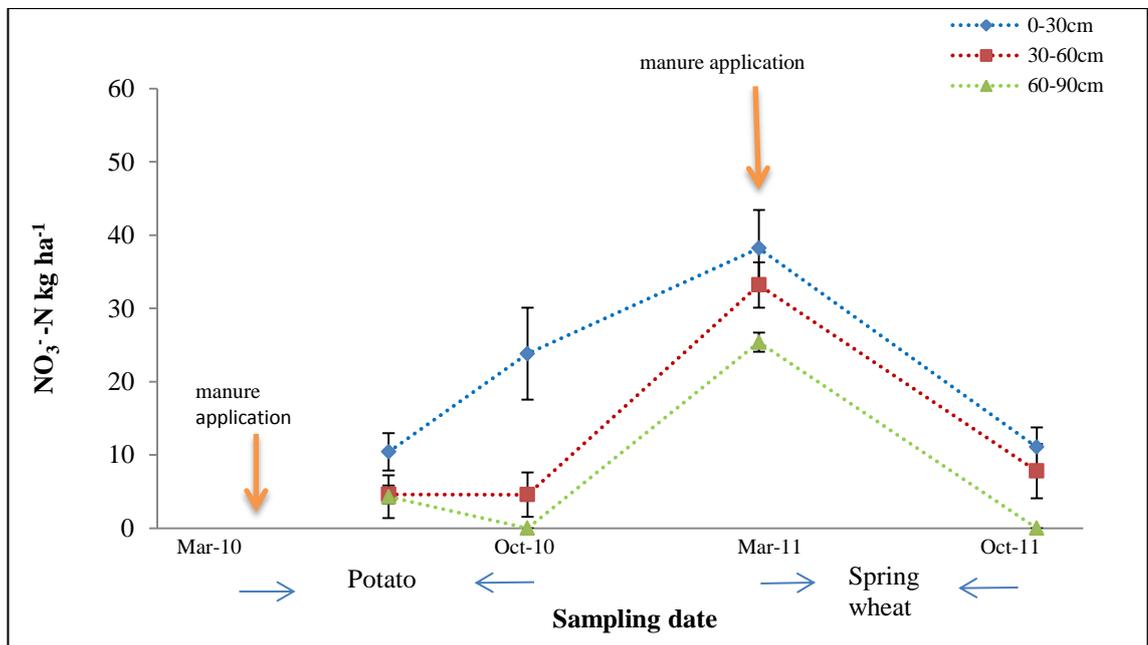


Figure 5.14 Soil NO_3^- -N content (mean with SE) for CON ROT, ORG FE treatments measured at depths 0-30, 30-60 and 60-90 cm during the growing seasons 2010 and 2011 for experiment 3.

In general soil NH_4^+ -N concentrations showed a similar pattern with sampling time for the growing seasons 2010 and 2011 in the topsoil (0-30 cm depth) under both fertility treatments, but no clear common pattern for the amount measured in the subsoil (Figure 5.15 and Figure 5.16). The highest soil NH_4^+ -N content was measured after spring wheat harvest in the top 0-30 cm of the soil profile and this was significantly higher than the amount measured after potato harvest, subsoil (30-60 and 60-90 cm depth) at the same sampling time (Figure 5.15 and Figure 5.16).

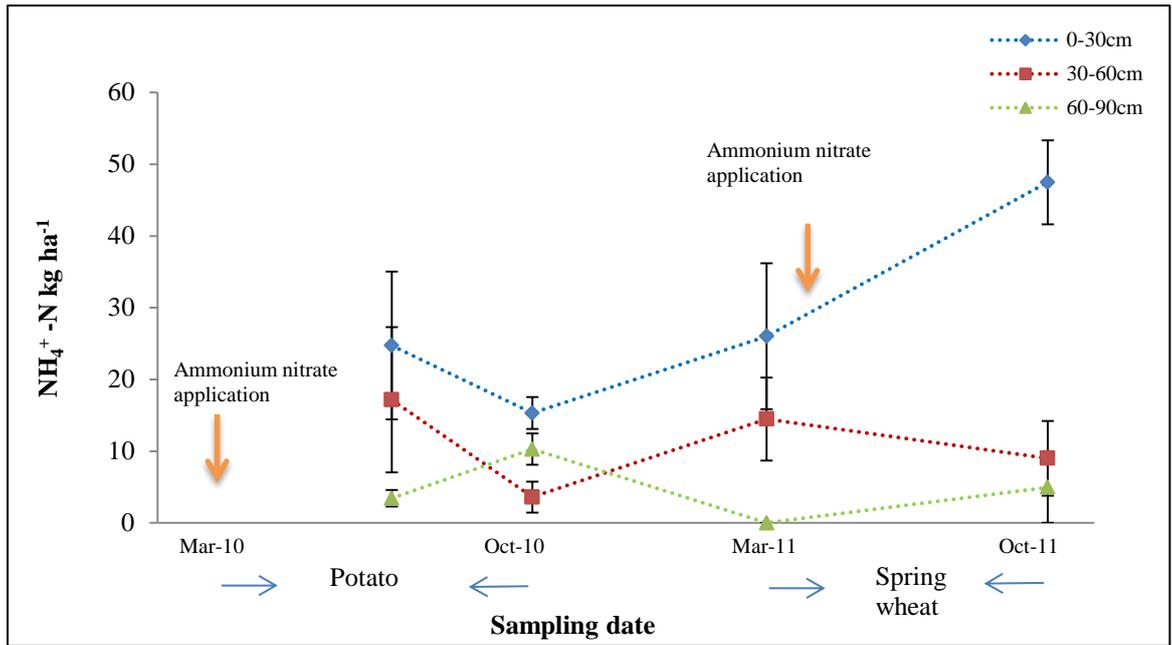


Figure 5.15 Soil NH_4^+ -N content (mean with SE) measured on different sampling time at depths 0-30, 30-60 and 60-90 cm for CON ROT, CON FE treatments during growing seasons 2010 and 2011 for experiment 3.

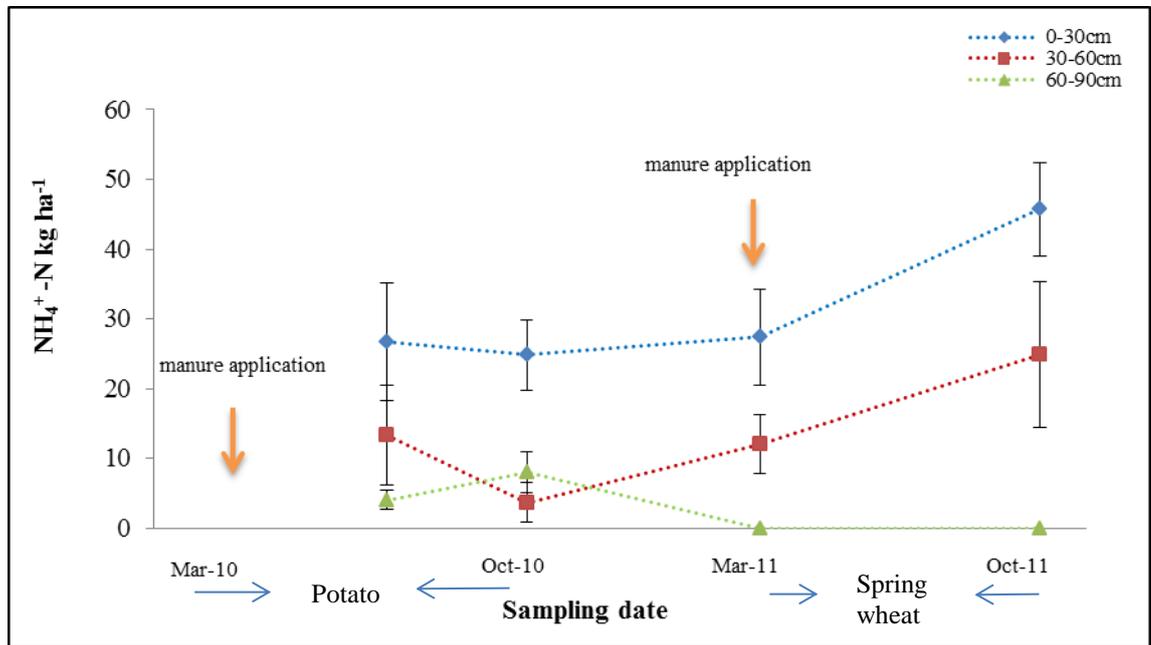


Figure 5.16 Soil NH_4^+ -N content (mean with SE) measured on different sampling time at depths 0-30, 30-60 and 60-90 cm for CON ROT, ORG FE treatments during growing seasons 2010 and 2011 for experiment 3.

5.3.5.2 Experiment 4 (2011-12)

The soil NO_3^- -N content measured on different sampling times at 0-30 cm depth showed a similar pattern for the growing seasons 2011 (potato) and 2012 (winter wheat and spring barley) under (ORG ROT-ORG FE; Figure 5.17 ORG ROT- CON FE; Figure 5.18) and (CON ROT- ORG FE; Figure 5.19, CON ROT- CON FE; Figure 5.20). In most sampling times soil NO_3^- -N content at 0-30 cm depth was significantly higher than the level at subsoil 30-60 cm and 60-90 cm depths of the soil profile, especially after harvest on both seasons. There were no significant differences between the 30-60 cm and 60-90 cm depth during both study years 2011 and 2012 under all treatments.

Soil NO_3^- -N content peaked in September 2011 after potato harvest and peaked again in September 2012 after spring barley in the organic rotation and to a lesser extent after winter wheat in the conventional rotation. The lowest NO_3^- -N content at all depths was observed in March 2011 before potato planting. Soil NO_3^- -N concentrations measured at 0-30 cm depth under ORG ROT were higher than the amount measured in the CON ROT at each sampling time. The increase in the amount of soil mineral N in March 2012 (CON ROT CONFE) at all depths reflects the application of ammonium nitrate fertiliser not long before the sampling.

In general soil NH_4^+ -N content showed a similar pattern with sampling time for the growing seasons 2011 and 2012 at all three depths and under (ORG ROT-ORG FE; Figure 5.21, ORG ROT- CON FE; Figure 5.22) and (CON ROT- ORG FE; Figure 5.23, CON ROT- CON FE; Figure 5.24) treatments. More soil NH_4^+ -N content accumulated after both winter wheat and spring barley harvest on September 2012 in the top 0-30 cm depth, and it was significantly higher than the amount accumulated after potato harvest on September 2011 under all treatments at the same depth. The soil NH_4^+ -N content measured in the top 0-30 cm depth was significantly higher than the amount measured in the subsoil 30-60 and 60-90 cm depth for all sampling times, except in March 2011 under CON ROT-ORG FE treatment. There were no big differences between 30-60 cm and 60-90 cm depth during 2011 and 2012 under all treatments. There was a lower NH_4^+ -N content in the top soil 0-30 cm in March 2011 than in March 2012.

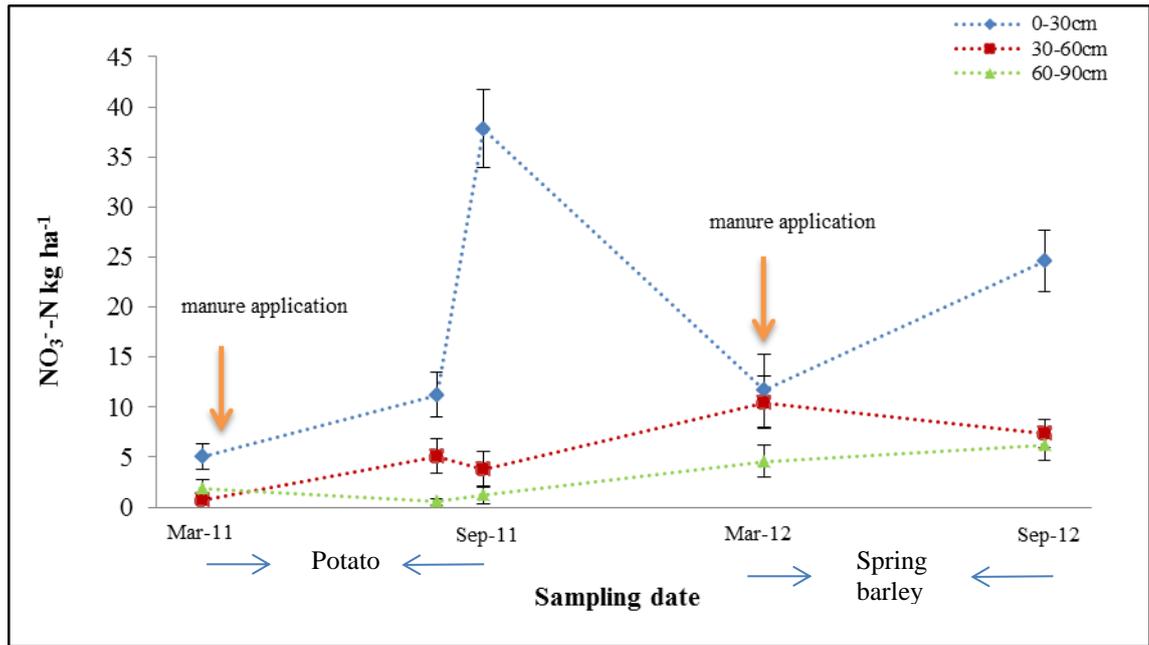


Figure 5.17 Soil NO_3^- -N content (mean with SE) measured on different sampling time at depths 0-30, 30-60 and 60-90 cm for ORG ROT, ORG FE treatment during growing seasons 2011 and 2012

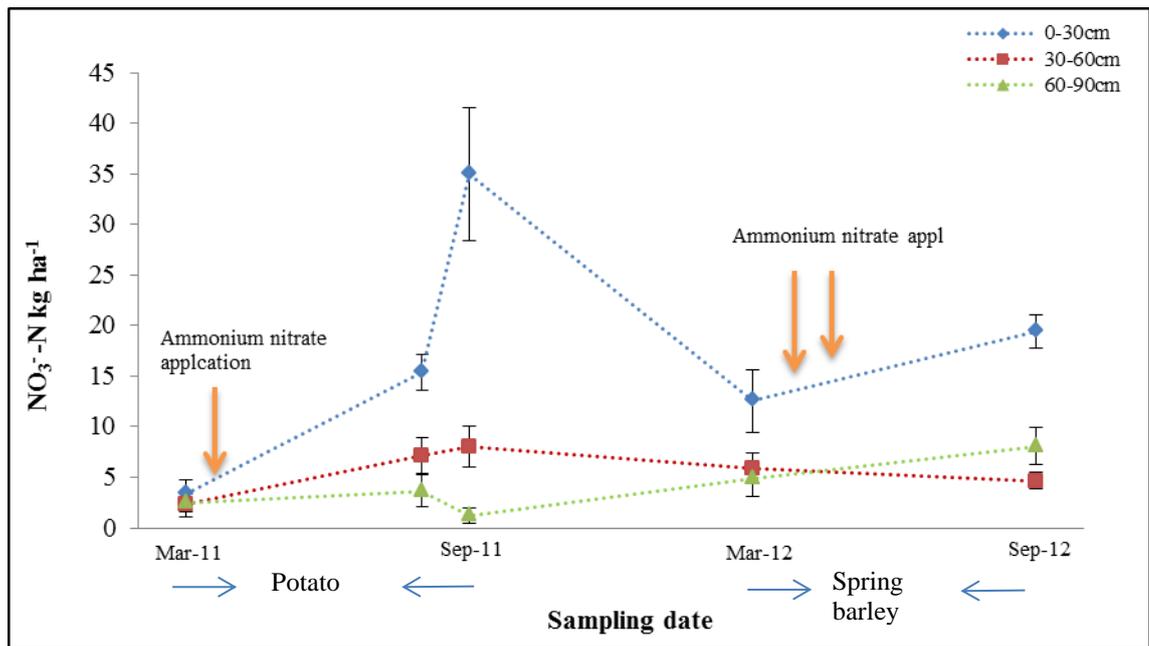


Figure 5.18 Soil NO_3^- -N content (mean with SE) measured on different sampling time at depths 0-30, 30-60 and 60-90 cm for ORG ROT, CON FE treatment during growing seasons 2011 and 2012.

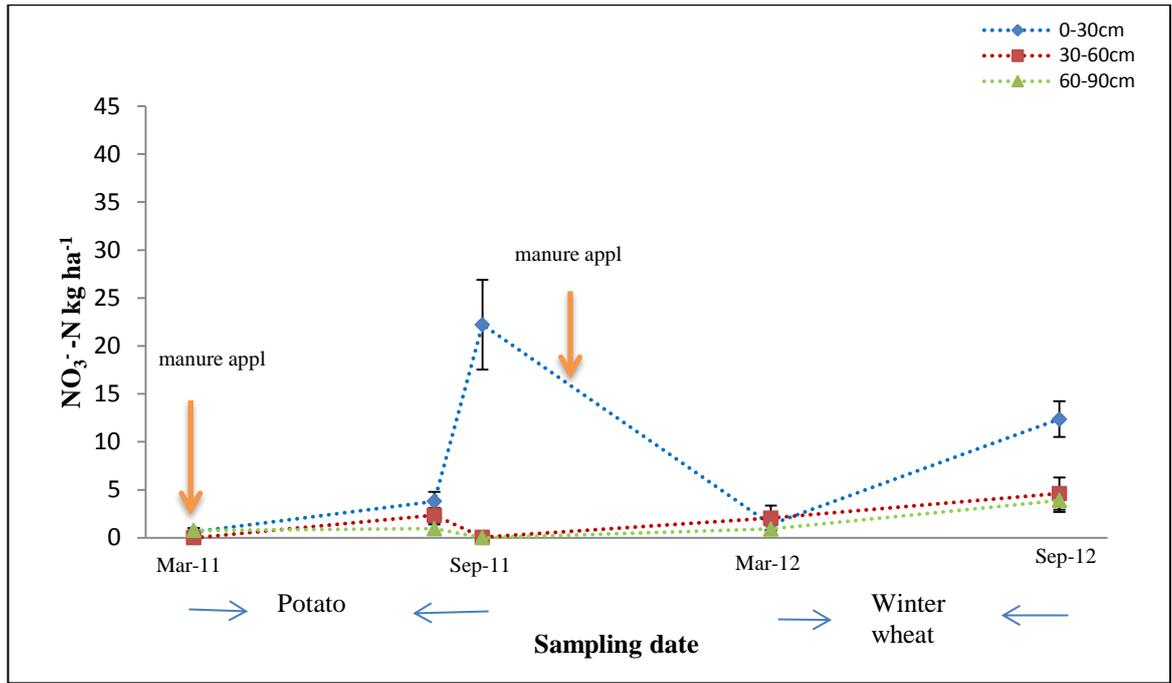


Figure 5.19 Soil NO_3^- -N content (mean with SE) measured on different sampling time at depths 0-30, 30-60 and 60-90 cm for CON ROT, ORG FE treatment during growing seasons 2011 and 2012.

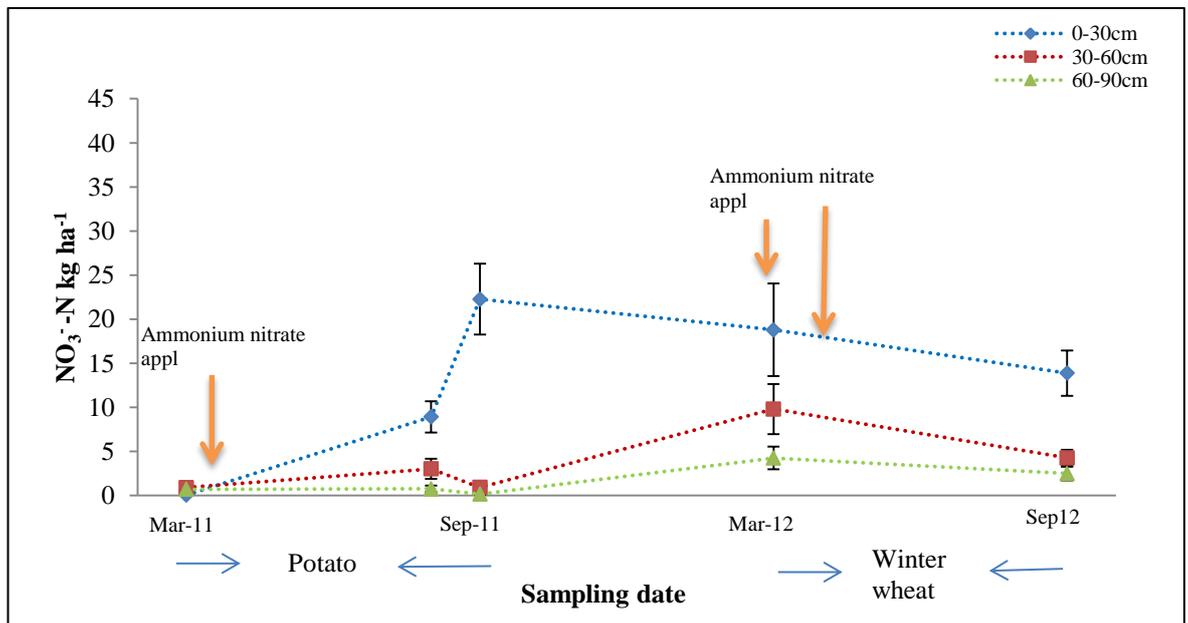


Figure 5.20 Soil NO_3^- -N content (mean with SE) measured on different sampling time at depths 0-30, 30-60 and 60-90 cm for CON ROT, CON FE treatment during growing seasons 2011 and 2012.

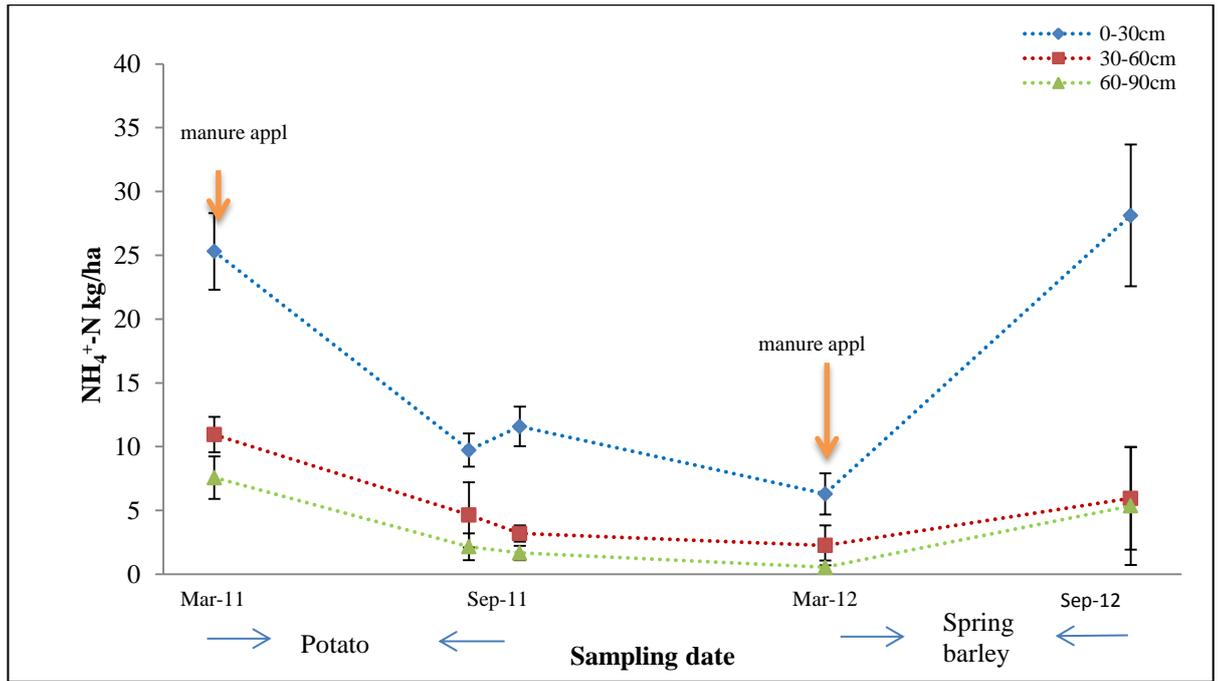


Figure 5.21 Soil NH₄⁺-N content (mean with SE) measured on different sampling time at depths 0-30, 30-60 and 60-90 cm for ORG ROT, ORG FE treatment during growing seasons 2011 and 2012.

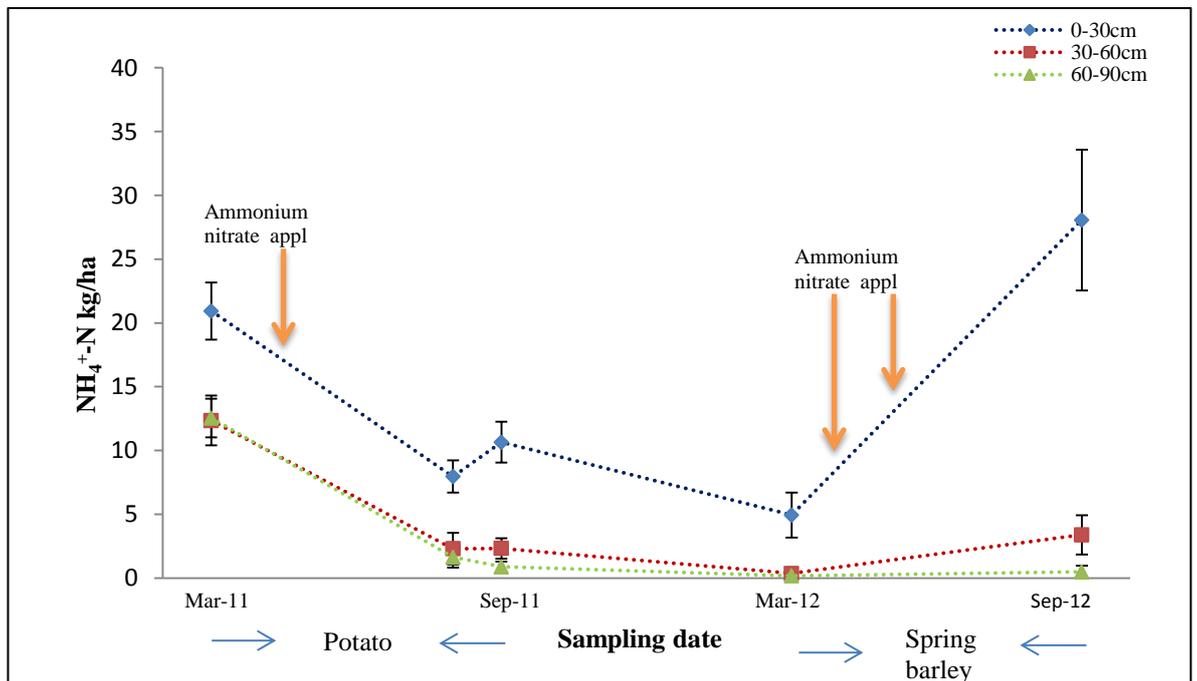


Figure 5.22 Soil NH₄⁺-N content (mean with SE) measured on different sampling time at depths 0-30, 30-60 and 60-90 cm for ORG ROT, CON FE treatment during growing seasons 2011 and 2012.

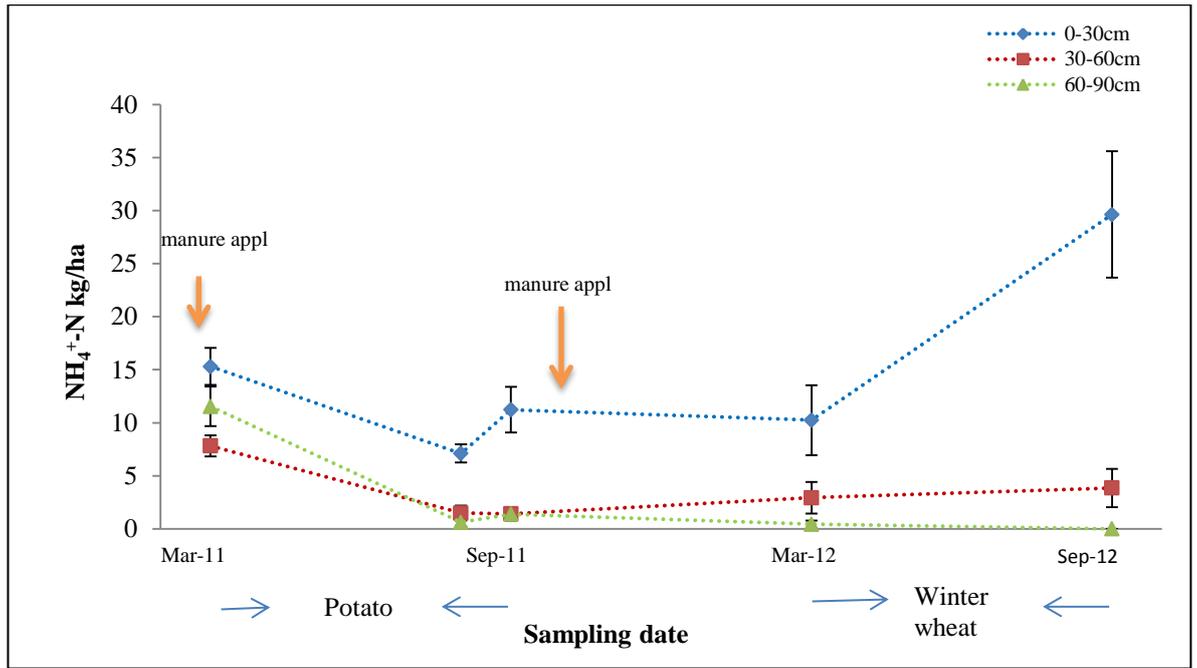


Figure 5.23 Soil NH₄⁺-N content (mean with SE) measured on different sampling time at depths 0-30, 30-60 and 60-90 cm CON ROT, ORG FE treatment during growing seasons 2011 and 2012.

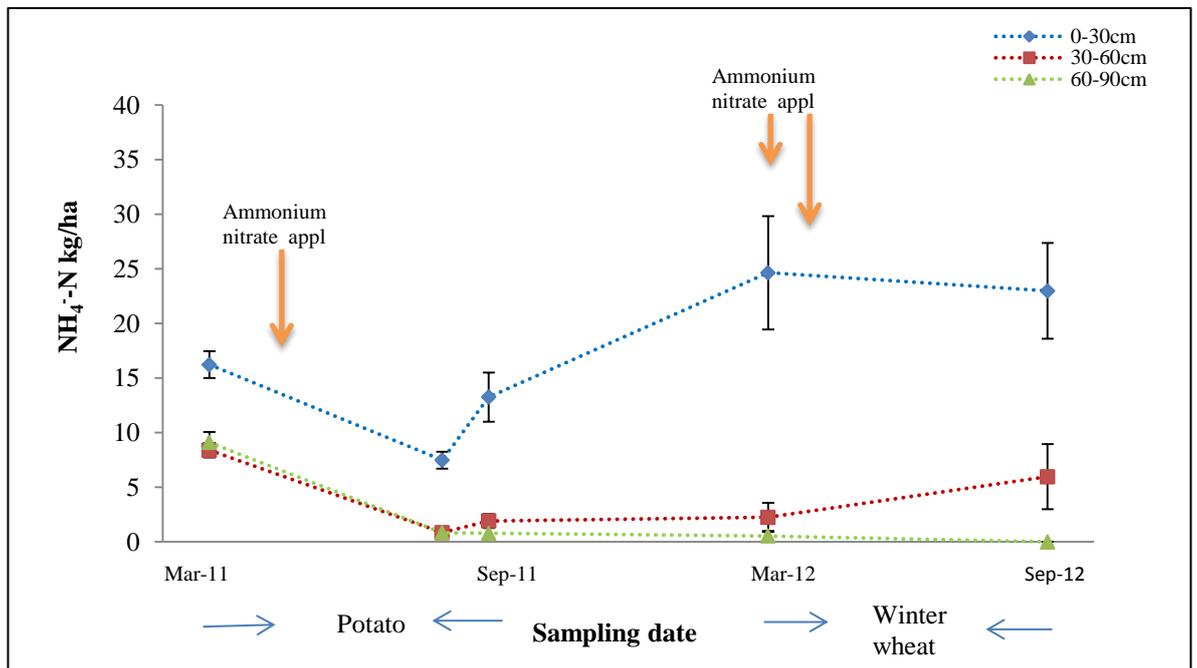


Figure 5.24 Soil NH₄⁺-N content (mean with SE) measured on different sampling time at depths 0-30, 30-60 and 60-90 cm for CON ROT, CON FE treatment during growing seasons 2011 and 2012.

5.4 Discussion

5.4.1 Impact of crop type

The mean total soil mineral nitrogen (SMN) content of 50 kg N ha⁻¹ measured in plots after potato harvest in both 2010 and 2011 is similar to the mean value (47 kg N ha⁻¹) measured in sandy soil (Shepherd and Lord, 1996) and those reported by Macdonald *et al.* (1997): in silty clay loam (55 kg N ha⁻¹) and sandy loam (68 kg N ha⁻¹) soils. Webb *et al.* (1997) reported a higher range of 79-180 kg N ha⁻¹ of soil mineral N content following potato. The mean values of postharvest soil nitrate-N (PHSNi) found following potato in our study were 24 and 34 kg N ha⁻¹ for 2010 and 2011 respectively. These amounts are typical of those found in a range of other studies using mineral fertilisers (Vos, 1999; Zebarth *et al.*, 2003; Zvomuya *et al.*, 2003; Bundy and Andraski, 2005; Hu *et al.*, 2012a) and composted cattle manure (Haase *et al.*, 2007; Nyiraneza and Snapp, 2007). Belanger *et al.* (2003) suggested that levels of PHSNi after potato harvest (0-90 cm depth) of less than 70 kg N ha⁻¹ indicated that the N fertiliser had not been applied to an excessive level. More work is needed to confirm whether this value can be used as a guide for farm practice.

The mean value of SMN content of 69 kg N ha⁻¹ measured in plots after cereal harvest in 2011 and 2012 is similar to the range measured by Macdonald *et al.* (1997) in a similar soil type (50 to 87 kg N ha⁻¹) and is also within the range reported by Dilz (1988) for winter wheat and within the range of 21-73 kg N ha⁻¹ for winter wheat and winter barley reported by Grylls *et al.* (1997). Chaney (1990a) reported a range of PHSNi after cereal harvest of 14 to 74 kg N ha⁻¹ in eight different sites with a range of soil types. The mean values of PHSNi content found in our study was 17, 28 and 35 kg N ha⁻¹ for spring wheat, winter wheat and spring barley respectively. Dilz (1988) reported a range of PHSNi of 14 to 35 kg N ha⁻¹ for winter wheat with optimum fertiliser rates of 200 kg N ha⁻¹. Especially in 2012, we cannot exclude the possibility of losses of nitrate before cereal harvest due to the very wet year; in the UK cereals stop accumulating soil N in July/ early August as they enter the ripening phase, therefore any amount of soil nitrate residues from fertilisers or that produced from mineralisation will be at risk of leaching earlier than harvest (Blankenau and Kuhlmann, 2000).

Several studies reported difference on the level of PHSNi after cereal harvest, Marley *et al.* (2013) reported 39 and 20 kg N ha⁻¹ to a depth of 90 cm for winter and spring barley

growing in loamy soils and receiving 250 kg N ha⁻¹ of ammonium nitrate and following legumes. Belanger *et al.* (1998) found 24 kg N ha⁻¹ of PHSNi after spring wheat harvest following potato. In sand clay soil Widdowson *et al.* (1987) measured 26 and 31 kg N ha⁻¹ of soil nitrate after winter wheat harvested in two different years where potato was the previous crops. At the economic optimum N rate Richards *et al.* (1996) reported that PHSNi after winter barley harvest following winter wheat ranged from 12-62 kg N ha⁻¹. In contrast values of 11-57 kg N ha⁻¹ were measured where no fertiliser N was applied (Richards *et al.*, 1996), the mean level of soil nitrate after harvest in plots receiving N fertiliser was only increased by 4 kg N ha⁻¹ compared with plots receiving no N fertiliser, suggesting that applying fertiliser N at the optimum rate does not increase the risk of nitrate leaching.

The amount of PHSNi measured after cereals harvest in our experiment is within the range reported above, however the differences between cereals on the amount of PHSNi may be confounded by year/rotation. Differences in the amount of PHSNi measured after cereal harvest could be also due to N uptake and its use efficiency, root depth, soil condition (Delogu *et al.*, 1998). Foulkes *et al.* (1998) reported that a higher amount of soil nitrate after spring barley than spring wheat is due to the longer nitrogen uptake period and higher nitrogen utilisation of spring wheat compared with spring barley. Thorup-Kristensen *et al.* (2009) reported that winter wheat is more efficient in using soil nitrogen than spring wheat and spring barley because winter cereals usually have deeper rooting than spring cereals. Differences in the nitrogen use efficiency between cereals was also reported by Baeckstrom *et al.* (2006). Differences in the amount of PHSNi measured after cereals harvest may also come from the mineralisation of the soil organic N that occurs after cereals stop utilising soil nitrogen resulting in a late season build-up of root zone nitrate levels (Richards *et al.*, 1996).

Comparing our results for SMN and PHSNi with results obtained from other experiments is difficult, because a large number of factors (and their interactions) can affect soil mineral N measured e.g. weather patterns, soil type, sampling date and crop management. In addition the differences in PHSNi can be due to differences in the hydrological properties including levels of the ground water table and the depth of the unsaturated layer (Grinsven *et al.*, 2012). Consequently during the data analysis reported above (section 5.3), sometimes there were significant differences between some plots as a result of complex interactions between treatment factors, however few

of these effects were seen consistently for season/crop combinations. However, the general robustness of the soil sampling and analysis procedures is further assured by the finding that the range of the soil mineral N measured is within the range typically reported in the literature.

In both experiments we found only very small differences in PHSNi following potato than cereals. It is often expected that there will be a higher leaching risk after potatoes than cereals due to differences in root distribution between the shallow rooting potato crops and deeper rooting cereals (Munoz *et al.*, 2005). Mineralisation of crop residues after harvest can increase the soil nitrate leaching over winter, these processes can be controlled by several factors (see chapter 2.3.2.1 literature), it has been reported that potato residues remaining after the crop harvest (if not desiccated) are mineralised more quickly than those returned in the cereal straw (Webb *et al.*, 1997). In our experiment little mineralisation of the organic potato residues may have been happened in the time between harvest and the soil sampling. During the potato harvest some of the haulms had been incorporated into the soil, however only some of the residues will have mineralised before the soil sampling took place. Even if the mineralisation occurred after the soil samples, it would be lost by leaching over winter (Webb *et al.*, 1997; Webb *et al.*, 2000b). The very cold weather during the winter 2010 and 2011 may reduce the mineralisation processes.

The NH_4^+ -N content measured to depth of 90 cm after cereals in our experiment was within the typical range measured by others e.g. Widdowson *et al.* (1987) measured a range of 36 to 50 of NH_4^+ -N kg ha^{-1} following winter wheat in sandy clay soils. Work by Westerman *et al.* (1994) found accumulation of NH_4^+ -N up to 60 kg ha^{-1} to 90 cm depth in the soil profile following long term annually applied ammonium nitrate at recommended rate where maximum yields were obtained; interestingly accumulation of NH_4^+ -N was also recorded in all plots that had no fertiliser. Accumulation of NH_4^+ -N was also recorded in subsoil depths at all sites. We measured higher NH_4^+ -N content to 90 cm depth after cereals than following potatoes. The higher NH_4^+ -N content may indicate incomplete nitrification processes and therefore accumulation of NH_4^+ -N (McEwen *et al.*, 1990). However, Widdowson *et al.* (1987) found a higher NH_4^+ -N content to 90 cm depth when the previous crops was potato compared with oats.

Bundy and Andraski (2005) also reported that following potatoes the 0-30 cm depth contained more than half of the PHSNi level found in the soil profile; in these experiments 53% of PHSNi was found in the topsoil. The PHSNi content within the surface 0-30 cm was correlated ($r^2 = 0.7$ and 0.9) with the PHSNi content within a 0-90 cm depth under all treatments after potato harvest in 2010 and 2011 respectively, and ($r^2 = 0.5$, 0.8 and 0.5) after spring wheat, winter wheat and spring barley respectively in 2011 and 2012. These results agree with those reported by (Belanger *et al.*, 2003), this relationship between the PHSNi content at 0-30 cm and 0-90 cm depth suggests that even shallower samples (0-30 cm) of PHSNi could be used to identify areas that have high risk of soil nitrate leaching during the winter and early spring.

Of course the amount of N actually leached may differ from that predicted by PHSNi depending on the soil type, mineralisation and denitrification rates overwinter and rainfall (Webb *et al.*, 1997; Webb *et al.*, 2000b). Some indication of leaching losses can be inferred from the proportion of the PHSNi that is either lost or carried over from harvest to the following spring. The soil NO_3^- concentration measured at 0-30 cm and 0-90 cm depths in March 2012 was 38 and 66 % respectively of the soil NO_3^- concentration measured from the same fields after potato harvest. (Zebarth *et al.*, 2003) found that spring nitrate concentrations were 10 to 66 % of those measured in autumn.

5.4.2 Impact of potato variety

We measured no effect of potato variety on the overall profile PHSNi in either 2010 or 2011 and no differences between the varieties were seen in the following cereal crops. Zebarth *et al.* (2003) also found no significant differences in nitrate leaching risk following 4 potato varieties grown in a similar soil type. However, the distribution of nitrate within the soil profile was affected by variety; in the top 0-30 cm depth, the difference in PHSNi content between Sante and Sarpo Mira was very small in both growing seasons, but in the deeper soil 30-90 cm plots growing Sante contained more nitrate than those growing Sarpo Mira. Kristensen and Thorup-Kristensen (2007) also found significant differences between nitrate concentrations in subsoil with a change in the potato cultivar. Higher PHSNi content is found where an early potato variety is grown when compared with a later variety; in our experiment the subsoil PHSNi was higher where the early variety Sante is grown than the late variety Sarpo Mira. Increasing N uptake with an increasing length of the growing season between potato

varieties was reported by (McPharlin and Lancaster, 2010). In these experiments there was a significantly lower N uptake by Sante than Sarpo Mira ($p=0.005$); both varieties were considered to have yielded well (33 t ha^{-1} for CONF, 27 t ha^{-1} for ORGF) and (35 t ha^{-1} for CONF, 27 t ha^{-1} for ORGF) in 2010 and 2011 respectively according to the long-term farm average (Rempelos *et al.*, 2013).

5.4.3 Effect of crop rotation

There was a marked effect of crop rotation in experiment 4; but no similar effect was seen for experiment 3. The organic rotation contains more legumes and a period in grass-clover ley (see chapter 3.2 site description). Both experiments are replicates with the same cropping pattern in the organic and conventional rotations since 2005; however, the organic rotation in Experiment 4 had 3 years of grass-clover ley (2005-2007) whereas the organic rotation in Experiment 3 had only 2 years of grass-clover ley (2005-2006). Our results showed that in Experiment 4 the soil nitrate-N through the season and PHSN_i was significantly increased in the organic crop rotation compared with the conventional rotation for both potato and cereal crops.

Previous crops and crop rotations have been shown to have an effect on nitrate leaching risk. For example, in a study comparing the effect of organic and conventional crop rotation on N leaching in Denmark, a rotation that included a legume green manure crop was found to have higher N leaching (Thomsen *et al.*, 2001). Zebarth *et al.* (2003) also found that PHSN_i was significantly higher when potatoes were grown following red clover hay compared with those grown following a cereal in 1999 and 2002. However the literature also reports that previous crops and crop rotations have no significant effect on nitrate leaching risk. For example (Honeycutt *et al.*, 1995) in similar soil type found no significant effect of crop rotation on PHSN_i after potato grown following a legume. Webster *et al.* (2003) also found that the prior crops (beans) had no effect on the soil mineral N measured after cereal harvest. Askegaard *et al.* (2011) have also reported no effect of crop rotations with and without an N₂-fixing crop compared with crop rotations with manure application on N leaching after spring barley and winter wheat in a sandy loam soil in Denmark.

In their multi-year experiment, Zebarth *et al.* (2003) found that in one year (2000), PHSN_i did not differ significantly among the rotation treatments, whereas as described above, in some years differences between rotations were seen. These results therefore

confirm that the influences of crop rotation on PHSNi and actual leaching loss will vary between years. This suggests that the effects arise as a result of interaction between the cropping patterns and weather which either affect crop growth or N loss processes. For example, at Nafferton, the rainfall in 2009 was 66 % higher than that in 2010 for the growing season (April to October); this difference in the rainfall pattern may have affected the growth or N fixation of the previous crop of beans or led to a different pattern of N mineralisation of the bean residues (Kayser *et al.*, 2010). There may also be long-term impacts on mineralisation resulting from the difference in the cropping sequences in the organic rotations before 2005. Eriksen *et al.* (2008) found increased nitrate leaching losses with an increased proportion of grass-clover ley in an arable rotation on a sandy loam soil. However, (Christensen *et al.*, 2009) found only short-term effects of increasing age of grass ley on sandy loam soils in Denmark; increased spring barley yields were only found in the first season and did not persist into the second and third following crops. Similar results were found with grass-clover leys (1-6 years) on a sandy loam soil in the UK (Johnston *et al.*, 1994).

Boehm *et al.* (2009) who also reported high losses of N released by legumes after high amounts of precipitation. In addition, the bean residues were incorporated earlier in autumn 2009 than in 2010 which may have increased the losses and reduced availability to the following potato crop in Experiment 3. Mitchell *et al.* (2000) concluded that early incorporation of crop residues increase the soil nitrate that is at risk of leaching compared with late incorporation. Wet conditions overwinter in 2009-2010 can be expected to increase the risk of soil NO_3^- losses through leaching and/or denitrification (Cameron *et al.*, 2013); though unfortunately no samples were taken in spring 2010 (before PhD work began) which could have helped verify this explanation. Slight differences in the rainfall and temperature patterns during the subsequent potato growing season may affect the potato growth and the crop's ability to recover the N released through mineralisation (Grylls *et al.*, 1997). These results confirm that PHSNi content can be highly variable between years and among fields even where there are the same preceding crops with similar management.

5.4.4 Impact of crop protection

Where crop yield is restricted by disease, this may result in both reduced N uptake and N use efficiency, and hence increased PHSNi level. This was confirmed by Dilz (1988)

and Macdonald and Gutteridge (2012) who found higher amount of soil mineral N content after poor crop harvest compared to those after healthy crops. And also as reported by Kristensen and Thorup-Kristensen (2007). However in these trials there were no major problems with disease reported see Rempelos *et al.* (2013) for a full report on potato disease) and perhaps as a result, difference between crop protection treatments did not have a significant effect on PHSNi after either potato or cereal harvest.

5.4.5 Impact of fertility management

5.4.5.1 Potatoes

Contrasting approaches to fertility management (ammonium nitrate vs. composted cattle manure) had no effect on the amount of PHSNi after potato harvest in both growing seasons. However the yield of potato in both growing seasons, 2010 and 2011, was about 21% higher with ammonium nitrate than where composted cattle manure was used, and overall N uptake was about 42% higher (Rempelos *et al.*, 2013), where ammonium nitrate was applied at rate of 180 kg N ha⁻¹ compared with composted cattle manure at rate of 175 kg total N ha⁻¹. Despite the fact that the total amount of N applied as in manure or fertiliser was very similar, the yield difference confirms that the readily plant available inorganic N in the composted cattle manure is lower than those in inorganic fertilisers (Alluvione *et al.*, 2010; Rashid *et al.*, 2013). In our experiment we also found that the increased availability of N for plant uptake from mineral N fertiliser persisted well into the growing season; in August soil samples, the PHSNi content was significantly greater in plots receiving ammonium nitrate than composted cattle manure at both 0-30 cm and 0-90 cm depth, but this difference disappeared after harvest. We found no negative relationship between potato yield and PHSNi as has been found previously (Webster *et al.*, 2003). However, in these experiments the spread in yield was relatively small and all yields were considered “good” for the farm which may explain the lack of such a relationship. Canali *et al.* (2010) also did not find significant differences in PHSNi with different rates of N organic fertilisers applied to potato crops, despite different yields. The uptake of N by crops can reduce the pool of SMN measured in the soil during the growing season very effectively, for example (Webb *et al.*, 2004) reported a range from 54 - 98% of the total amount of N outputs was as crops offtake.

It has been suggested that slowly available inorganic N from composted manure may increase PHSNi because composted manure may continue to release N through mineralisation of the organic N during the time when crop uptake rates decline or after crop harvest (Palmer *et al.*, 2013). However, we did not find higher PHSNi content in the organic plots following potato harvest as a result of continuing mineralisation of the organic N (Shepherd and Newell-Price, 2013). Blankenau and Kuhlmann (2000) also found no difference between the soil mineral N at 0-90 cm depth when either inorganic fertiliser or manure were applied to potato at rates of 247 kg N ha⁻¹.

In our experiments both the cattle manure and ammonium nitrate are applied at the recommended rates and the yields achieved indicated that we were close to, or below, the optimum. Shepherd and Lord (1996) also reported that any residues of applied fertiliser should be low when the fertiliser is applied at the recommended rate. Often in fertiliser response trials, increased PHSNi is seen at the highest rate of application e.g. Dilz (1988) and Lynch *et al.* (2008) found increased PHSNi when they applied composted cattle manure at rate of 300 kg N ha⁻¹ in loamy sand soil. However, Vos (1999) found that there were no differences in PHSNi where they had applied rates of N fertiliser ranging from 0-250 kg N ha⁻¹ for potato in a similar soil type, but in soil samples taken before potato harvest (August) they found that soil nitrate content did increase with increased fertiliser rate.

5.4.5.2 Cereals

In all the following cereal crops we found similar results to those reported for potato crops, fertility management (ammonium nitrate vs. composted cattle manure) had no effect on the amount of PHSNi content after cereal harvest in both growing seasons 2011 and 2012. As with the potatoes, cereal yields were higher where ammonium nitrate was used for winter wheat (3.8 t ha) and spring barley (5.4 t ha) compared with yield of (1.4 t ha and 2.0 t ha) respectively with composted cattle manure; this is a yield increases of 63% and 62%. However, there was no significant effect of fertility treatments on spring wheat yield (6.2 t ha) NEFG pers. comm.

In a similar soil type, Chaney (1990a) also found that the soil NO₃⁻-N losses after harvest did not increase significantly with fertiliser rate until the optimum N rate for wheat yield was exceeded a similar relationship for winter wheat following potato in

eight different sites in central and eastern England, Macdonald *et al.* (1989) also found no significant differences in leaching risk between plots receiving no fertiliser and those receiving N fertiliser at rates of 114-234 kg N ha⁻¹, their study confirmed that most of the nitrate at risk of leaching during the winter period comes from mineralisation and not from unused fertilisers, when these are applied at recommended rates. Glendining *et al.* (1996) also confirmed that rates of N fertiliser less than or equal to the optimum had little effect on PHSNi. Blankenau and Kuhlmann (2000) found that where the input of N fertiliser was 190-220 kg N ha⁻¹ between 60-93% of the N applied fertiliser was recovered in the crops at harvest, and they reported no significant difference in the SMN content after cereal harvest between plots receives optimum rate of N fertiliser and unfertilised plots.

In our experiment composted cattle manure had no effect on the soil nitrate at risk of leaching, this result is similar to the results obtained by Askegaard *et al.* (2011) who reported that use of composted manure improved cereal yield compared with control plots but had no effect on soil nitrate leaching. The low proportion of readily available of inorganic N in the composted manure combined with active crop N uptake may lower the amount of PHSNi found in the soil.

5.5 Conclusion

None of the range of crop management practices used in the Nafferton Factorial Systems Comparison trial markedly influenced the amount of PHSNi content following potato and cereal crops in 2010, 2011 or 2012. The experiment seeks to use optimal crop management practices under either organic or conventional guidance and all treatments successfully kept the average PHSNi at low levels suggesting a minimal leaching risk. However, a higher level of PHSNi was measured in some plots (up to 116 kg N ha⁻¹). As result of unmanageable in-field variability, even where recommended rates of N fertilisers are applied, higher risk of nitrate losses via leaching in some areas is to be expected. Our data suggest that reduction to below optimum rates will reduce crop yields but may not contribute to significant reductions in the amount of PHSNi in arable rotations with cereals or potatoes. Nonetheless this highlights the importance of deriving a realistic field-specific optimum rate from the general recommendations in order to minimise any residual N fertiliser after crop harvest.

While measurements of soil mineral N are useful, they give only a glimpse rather than a full picture of the soil N cycle. These results highlight the need for further research at Nafferton to underpin the understanding of the N dynamics in the Nafferton Factorial Systems Comparison trial including the quantification of N mineralisation, immobilisation, denitrification and volatilisation. Jahangir *et al.* (2012) reported that complete, rapid denitrification of soil NO_3^- in arable soil could occur in only several days under some conditions. (Powlson *et al.* (1986)) reported that a losses of ^{15}N through denitrification were double those by leaching in (silty) clay loam topsoils with clay loam subsoil, and that the denitrification processes was more related to the soil wetness during the 21 days after N application rather than the amount of rain. In these soils with a texture contrast between topsoil and subsoil (see Chapter 6), denitrification may be as important in driving N losses as leaching. In addition nitrogen tracer techniques could be used as a tool to help improve our understanding of the dynamics of the N cycle in arable rotations.

The PHSNi is considered to provide a useful measure of the nitrate in the soil (from unused fertiliser and mineralisation) which is at of risk of leaching. Higher soil mineral nitrogen (NO_3^- -N and NH_4^+ -N) content accumulated in top 0-30 cm than subsoil in both experiments. The good correlation between the soil nitrate at 0-30 cm and 0-90 cm depth of the soil profile that obtained in our experiment mean that rapid soil sampling (0-30 cm) could be used in arable rotations to identify areas that have potential risk of nitrate leaching during the winter and early spring. Overall the results obtained from our study are important to understand the effect of crop management, soil and environmental factors and their interactions on the PHSNi level and develop strategies to minimise nitrate losses via leaching.

6 Characterisation of soil physical soil properties controlling water movement in the soils of the NFSC trial

6.1 Introduction

Nitrate (NO_3^-) leaching depends on the movement of soil water to ground and surface water. Soil and geological properties, e.g. hydraulic conductivity, water potential, and the distribution of permeable and impermeable layers, influence both the rate and volume of drainage (Afyuni *et al.*, 1994; Addiscott, 1996b; Hillel, 1998). Hence knowledge of the hydrological pathways and the effect of soil properties on water transport within each soil type are essential (Afyuni *et al.*, 1994; Addiscott, 1996b; Stockdale, 1999; Bullock *et al.*, 2008; Whetter *et al.*, 2008). The study of water movement through agricultural soils is complicated, not only because of the large number of interacting processes and driving factors above and below-ground (Rowell, 1994), but also because of their variability in time and space (Bruce *et al.*, 1985).

Hydraulic conductivity depends on the size and continuity of the pores, which carry the water as it moves. Porosity is affected by soil properties such as texture, organic matter, structure, density, and their heterogeneity within the soil profile (Xu *et al.*, 2011) and they are also affected and altered by management practices especially cultivations in the plough layer. More soil pores are filled with water as soil water content increases, therefore hydraulic conductivity increases with an increase in soil moisture content (Hillel, 1998). When the soil pores are filled mostly with water, i.e. between saturation and field capacity, saturated flow occurs, driven mostly by the force of gravity (Hillel, 1998). Hence both the amount of water potentially found in the macropores (mobile water) and the saturated hydraulic conductivity (K_s), which quantifies the rate of water flow in a saturated soil, are key hydraulic parameters linked to drainage (Hu *et al.*, 2012b).

The objectives of this study were therefore to answer these questions:

Q1 – Are there any differences in physical properties with depth? This will help to explain the soil mineral nitrogen data (Chapter 4 and 5)

Q2 - Are there any differences in physical properties in soil profiles between plots where bromide was applied? This will help explain the results obtained from the bromide experiments (Chapter 7).

6.2 Methods

6.2.1 Soil profile description

Full soil profiles were studied on 14 September 2012. Three soil profiles were dug with a spade until the C horizon was reached on the edges of the NFSC experiment in the grass buffer strips in pits 1.5 long and 1m wide. Horizons were identified and described for each soil profile with field properties such as soil colour, texture, structure, consistence described according to the methods described by (Avery, 1980; Payton and Palmer, 1990) and classified according to the Soil Classification for England and Wales (Avery, 1980).

6.2.2 Soil sampling in the field

Soil samples were collected after clearing litter and residual grass from the soil surface. Topsoil was removed until the depth of 12.5 cm was reached. Undisturbed soil samples were taken from 3 depths (12.5 cm, 42.5 cm and 72.5 cm) to relate to the soil mineral N sampling depths; none of these depths fell at a horizon boundary (Table 6.1). Fourteen intact soil cores samples were collected from each depth in each soil profile, giving a total of 126 intact samples. The sampling was done using stainless-steel soil-core rings, 5 cm long and 5 cm diameter (Figure 6.1). Intact cores were taken using stainless steel rings to preserve the natural soil structure of the sample (at mm to cm scales) and represent the natural condition of the field soil. The stainless steel rings were gently pressed into the soil by hand then a wooden mallet was used to insert the rings into the soil until it was level with the soil surface (Figure 6.1). The rings filled with soil were removed carefully from the soil by digging around them to ensure an intact sample and excessive soil at the top and bottom was cut flush to the ring with a knife. Samples were repeated if large stones were found in the rings. For each depth, 5 undisturbed soil cores were kept intact for soil water characteristic measurement (Table 6.1). These cores were covered with plastic lids and placed in plastic bags to minimise any possible water loss by evaporation. The remaining cores were bulked in groups of 3 cores to give three composite samples for each depth. All soil samples were transferred to a refrigerator and kept at 4 °C at Newcastle University.

Table 6.1 *Horizon depths and depth of soil core samples collected with rings in three soil profiles excavated in the buffer strips of the NFSC experiment.*

Profile number	Horizon depth (cm)	Actual sample depth (cm)	No. of replicate intact cores	No. of composite samples (each 3 bulked cores)
1	0 - 31	12.5 – 17.5	5	3
1	32 - 52	42.5 – 47.5	5	3
1	53 - 90	72.5 – 77.5	5	3
2	0 - 32	12.5 – 17.5	5	3
2	33 - 49	42.5 – 47.5	5	3
2	50 - 90	72.5 – 77.5	5	3
3	0- 28	12.5 – 17.5	5	3
3	29 - 48	42.5 – 47.5	5	3
3	49 - 90	72.5 – 77.5	5	3



Figure 6.1 *Collection of undisturbed soil cores using stainless steel rings in the soil profile.*

6.2.3 Sample preparation and laboratory determination of basic properties

The composite soil samples were removed from the refrigerator in the next day and immediately weighed. Soil samples were then broken by hand and mixed in the bags, stones removed, sieved through a 4 mm sieve and homogenised, and weighed.

A subsample was taken to determine moisture content at 105°C for 24 hours. The bulk density was calculated using the known volume of the samples and the dry soil weight corrected, as needed, for stone weight and volume (Avery and Bascomb, 1982).

Volume of stone = stones weight/density (2.7)

Corrected of bulk density for stones weight and volume =
weight of dry soil / (volume of soil - volume of stones).

Soil pH was measured in a 1:2.5 soil: water mixture according to standard UK methods (Avery and Bascomb, 1982). 10 g of 2 mm sieved wet soil was placed in a plastic bottle with 25 ml of distilled water. The suspension was stirred well and left to stand for 15 minutes to equilibrate. The pH reading was taken with a glass electrode pH meter.

The remaining soils were air dried for approximately one week to a constant weight and any visible organic materials were removed. The soil was then ground to pass a 2 mm sieve and stored for further analysis.

6.2.4 Loss on ignition - Organic Carbon determination

The loss on ignition method (Avery and Bascomb, 1982; Rowell, 1994) was used to estimate soil organic carbon. Between 10 to 15 g of air dry soil was placed in a dry weighed crucible and the overall weight was recorded. The samples were dried overnight in an oven at 105°C and the next day the dry weight was recorded. The crucibles were then placed in a muffle furnace at 550°C overnight. The next day the samples were removed, cooled in a desiccator and the weight was recorded. The organic carbon content ($t\ ha^{-1}$) was estimated from the Loss on Ignition data using the widely used correction factor of 1.724 which assumes that soil organic matter contains about 58 % carbon (Howard and Howard, 1990; Sparks *et al.*, 1996).

6.2.5 Particle size distribution

The particle size distribution was measured using the sieving and sedimentation methods described by Avery and Bascomb (1982). The soil samples were treated with hydrogen peroxide to remove the organic matter and then dispersed by adding sodium hexametaphosphate solution and shaking overnight to ensure all aggregates had been dispersed to their primary particles. To determine the sand fractions, a nest of sieves was used to separate the sand particles into coarse sand ($> 600 \mu\text{m}$), medium sand ($212 \mu\text{m} - 600 \mu\text{m}$) and fine sand ($212 \mu\text{m} - 63 \mu\text{m}$) (Avery and Bascomb, 1982). The remaining suspension was agitated and made up to 1 litre in a measuring cylinder before sedimentation and pipette sampling to estimate silt and clay content (Figure 6.2).



Figure 6.2 *Measuring cylinders used during sedimentation of the soil samples*

6.2.6 Particle density

The method described by Avery and Bascomb (1982) and Rowell (1994) was used to determine particle density. Soil samples were first boiled to remove air, with about 12 g of < 2 mm oven dried soil weighed accurately boiled with 20 ml of water for 30 minutes. The suspension was then cooled in water at room temperature and transferred to a pre-weighed 100 ml volumetric flask, water was added to the mark, and the volumetric flask was then weighed. The particle density was calculated as follows:

Particle density =

$$\frac{\text{Mass of oven dry soil (g)}}{100 - (\text{Mass of suspension in the volumetric flask} - \text{Mass of oven dry soil} - \text{Mass of flask})}$$

Once the particle density was known then the total porosity was also estimated from the bulk density as follows:

Porosity = 1 - (bulk density / particle density).

6.2.7 Saturated hydraulic conductivity, Ks

The intact soil core samples were used to determine the saturated hydraulic conductivity (Ks) using a falling head permeameter (Berryman *et al.*, 1982; Craig, 2004) (Figure 6.3). This equipment was readily available in the School of Civil Engineering and is considered most appropriate for the measurement of rates of saturated hydraulic conductivity in sandy soils (Craig, 2004).

4 replicate intact soil cores were used for each profile and depth (36 cores in total). Soil cores were saturated with de-aired water from the bottom to allow soil air to escape from the top before beginning the test. A filter paper (Whatman No 54) was used to cover the base of a core to prevent soil loss from the bottom of the sample.



Figure 6.3 *Measuring K_s of intact soil cores using the falling head method.*

After the cores were connected to the plate, they were allowed to equilibrate to a steady state. For top soil (12.5 cm, 42.5 cm), equilibration took about 1 hour. Because of the low permeability of the deep samples (72.5 cm) these were left to equilibrate for 24 hours. Once the measurement period began, measurements of the water level in the standpipe were made after 15, 30 and 45 minutes. For each core, the measurement was made three times and the mean was calculated. The saturated hydraulic conductivity (K_s) of the core samples was then calculated by the use of the following equation:

$$K_s = a \times L \times \ln (h_0/h_1) / At$$

Where:

a is the cross sectional area of standpipe (cm^2).

L is the length of the soil sample core (cm).

A is the cross sectional area of core (cm^2).

t is the time for water level (relative to the water level in the reservoir) to fall from h_0 to h_1 .

h_0 is the initial height of water

h_1 is the final height of water

After the saturated hydraulic conductivity was determined, all soil core samples were kept saturated at 4 °C so that they could be transferred to the pressure plates (Section 3.2.8).

6.2.8 Determination of field capacity, plant available water and wilting point using pressure plates

Soil water content was measured at 0.05 bar, 2 bar and 15 bar using pressure plate apparatus (Figure 6.4). A low-pressure plate (0-1 bar) was used to measure the field capacity and (1-3 bar) for the easily available water with intact soil cores whereas high-pressure plate (15 bar) was used to measure the wilting point using disturbed soil (Hall *et al.*, 1977; Avery and Bascomb, 1982).

The water content measured at 0.05 bar, 2 bar and 15 bar are considered to be appropriate measures of field capacity (0.05 bar), easily plant available water (0.05 – 2 bar) and wilting point (15 bar), respectively, under British soil conditions (Hall *et al.*, 1977).

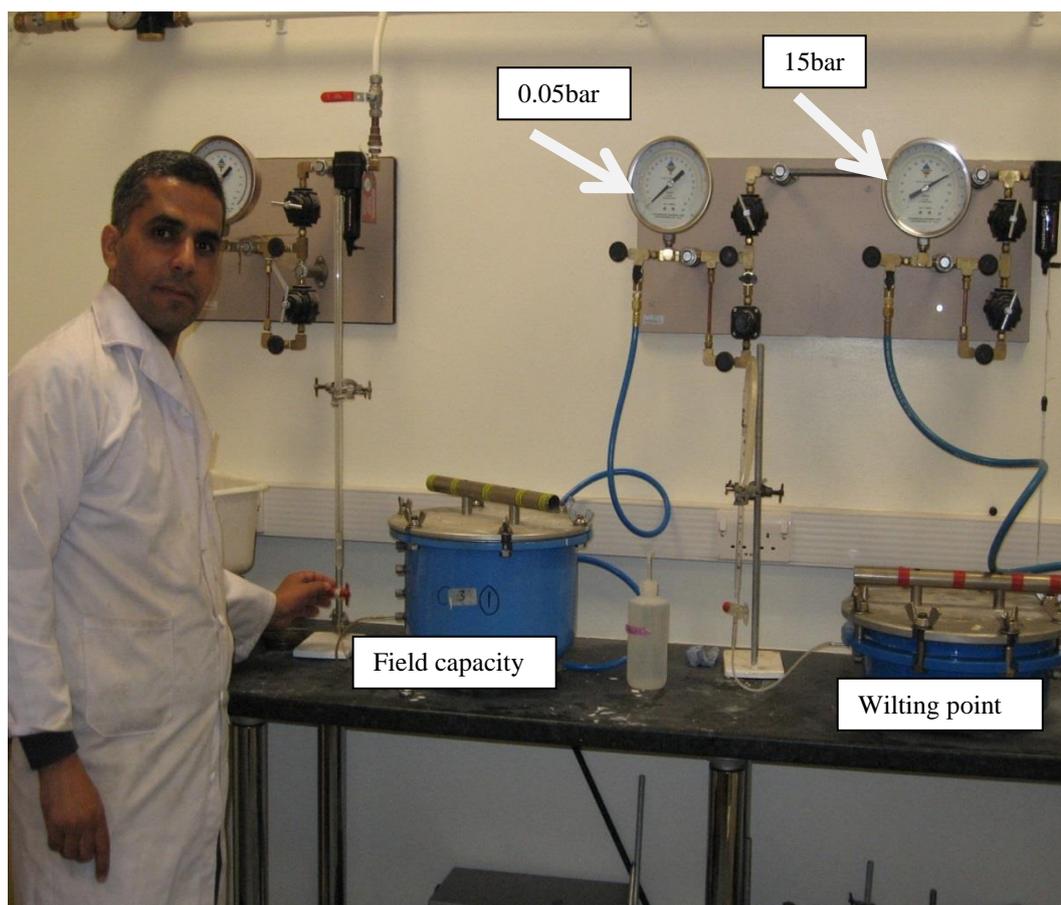


Figure 6.4 Soil pressure plate apparatus used to measure field capacity and wilting point.

To prepare the plates, a slurry of fine silica sand was prepared which was then placed on the porous ceramic plate to create good hydraulic contact between the sample and the plates. The plates were then transferred into the high-pressure chamber. A piece of fine mesh material was used to cover the base of each core to prevent soil loss from the bottom of the sample.

To determine field capacity (0.05 bar) and easily plant available water (0.05 - 2 bar), the intact saturated cores were carefully transferred to the low pressure plate. The pressure in the chamber was set at 0.05 bar forcing any excess water out of the cores through the micropores of the plate and out of the chamber through a small tube connected to a burette. The level of the excess water in the burette was monitored carefully until an equilibrium was reached; this required between 7 and 10 days. When equilibrium was attained, the soil samples were removed and weighed and then replaced in the pressure chamber and the pressure increased to 2 bars. When the second equilibrium was reached

(10 to 15 days), soil samples were removed and weighed and then dried (105°C for 24 hours); these data were converted to volumetric water content using the average bulk density determined for the field cores.

To determine wilting point (15 bar), 60g to 80g of disturbed soil was weighed into a soil core and packed carefully. Water was then added carefully from the bottom to saturate the soil so as not to trap air and then the repacked cores were transferred to the high-pressure plate. Pressure was carefully increased in the chamber until 15-bar pressure was reached; the samples were then left for a period of 15 to 25 days until equilibrium was attained. The soil samples were then removed and gravimetric moisture content determined (105°C for 24 hours); these data were converted to a volumetric water content equivalent to that of an intact core using the average bulk density determined for the field cores.

The relative porosity occupied by macropores (saturation to field capacity), water conducting mesopores (0.05 to 2 bar) and smaller mesopores (2 bar to 15 bar) as well as micropores (< 15 bar) were also estimated based on these water contents.

6.2.9 Pedotransfer functions for soil water content

Various moisture retention parameters can be estimated using regression equations from more easily measured soil properties such as the percentage of clay, silt and organic matter, and also bulk density.

Hall *et al.* (1977) developed the following regression equations for the calculation of soil water content at 0.05, 2 and 15 bars from the physical properties of soil samples collected from 261 of soil profiles from England and Wales:

$$\theta_{v(0.05\text{bar})} = 47.00 + 0.25 (\text{clay}) + 0.10 (\text{silt}) + 1.12 (\text{organic matter}) - 16.52 (\text{bulk density}).$$

$$\theta_{v(2\text{ bar})} = 8.70 + 0.45 (\text{clay}) + 0.11 (\text{silt}) + 1.03 (\text{organic matter}).$$

$$\theta_{v(15\text{ bar})} = 2.94 + 0.83 (\text{clay}) - 0.0054 (\text{clay})^2.$$

Gupta and Larson (1979) developed the following regression equations for the calculation of soil water content at 0.05, 2 and 15 bars based on easily measurable soil properties. They used from soil samples collected from 10 locations in eastern and central United States. The form of the equation used is:

$$\theta_p = a \times \text{sand (\%)} + b \times \text{silt (\%)} + c \times \text{clay (\%)} + d \times \text{organic matter (\%)} \times e \times \text{bulk density (g/cm}^3\text{)}.$$

Where:

θ_p is the predicted water content ($\text{cm}^3 \text{ cm}^{-3}$).

a, b, c, d and e are regression coefficients changing according to pressure.

	a	b	c	d	e
0.05 bar	0.007053	0.010242	0.01007	0.006333	-0.321
2 bar	0.000932	0.002643	0.006636	0.002717	-0.02214
15 bar	-0.000059	0.001142	0.005766	0.002228	0.02671

6.2.10 Statistical analysis

Data were collected from 3 plots, each plot was from a different block and each plot was sampled at 3 depths. For basic soil properties (soil particle size distribution, bulk density, organic matter, pH and soil water content at 15 bar), there were 3 replicate composite samples (from 3 core samples taken from the field). For soil water content at 0.05 and 2 bar and saturated hydraulic conductivity there were 4 replicate cores from each depth (horizon). This design allowed within profile variability to be separated in the analysis from between plot variability (3 plots). All data were tested for Normality test. Data of K_s were log-transformed; all other data had normal distributions without transformation.

Treatment effects due to plot (soil variability), depth (horizon) and their interactions on soil properties were tested using a General Linear Model using Minitab 16 software:

$$= \text{plot depth (plot} \times \text{depth)}$$

Differences between individual means were tested using Tukey's pair-wise comparisons following analysis of variance.

The mean values of the soil parameters measured from composite samples (soil particle distribution, bulk density, organic matter, pH and soil water content at 15 bar) and soil parameters measured from intact cores (soil water content at 0.05 and 2 bar and, saturated hydraulic conductivity), and calculated measures (porosity, macroporosity) were correlated to each other to assess any possible relationship among these soil properties. The mean values for each plot/horizon were used because the data were not paired (9 points). An additional correlation analysis between soil organic matter and soil texture (% clay) in the top soil was carried out; this used all the data from individual samples as these were paired (9 points). This analysis was carried out using Minitab 16 software and the significant relationships between the parameters are presented graphically using Sigma Plot 11.0 software.

6.3 Results

6.3.1 Soil profile description

The site was gently sloping to nearly level with gradients of 2° to 3° and there was only 5 m difference in the elevation between the highest (plot 1) and lowest (plot 3) plots. All plots showed evidence of cultivation with Ap horizons of c. 30 cm thickness overlying either a Bw or Bg horizon. The soils showed evidence of surface water gleying with stagnogleyic Brown Earth soils (Nercwys Series) found in plots 1 and 2, while in plot 3 (figure 7.1) the soil was classified as a Cambic Stagnogley (Brickfield Series). The differences between the profiles are nonetheless relatively small (The full description of the soil profiles is included in Appendix 1). Field texturing of soils by hand indicated that the soil in plot 2 had more sandy topsoil and Bw horizon (sandy loam and sandy clay loam respectively) than the equivalent horizons in the other plots (sandy clay loam and clay loam respectively).

6.3.2 Particle size distribution

6.3.2.1 Clay content

Plots – Clay content was very highly significantly higher in plot 3 than in plots 1 and 2 (Table 6.2). Mean clay percentage in plot 1 was also significantly higher than that measured in plot 2 when averaged over all depths (Table 6.2).

Depths – Clay content was very highly significantly different between the three horizons sampled (Table 6.1). The percentage of clay content was significantly higher at the 60-90 cm than the 0-30 and 30-60 cm depths. Clay content at 30-60 cm depth was also significantly higher than the 0-30 cm when averaged over all plots (Table 6.2).

Interaction between plots and depths – There was a very highly significant 2-way interaction between plots and depths (Table 6.2). In plot 2 there was no significant change in clay content with depth whereas in plot 3 clay content increased significantly with depth. In plot 1, the Bg horizon (60-90 cm) had significantly higher clay content than either the Ap (0-30 cm) or the Bw (30-60 cm).

Table 6.2 Clay content (%) of the samples taken at three depths 15, 45 and 75 cm which are considered to be representative of the 0-30, 30-60 and 60-90 cm horizons of the plots. Mean values of 3 replicate composite samples (each 3 intact cores) given, with \pm SE of the mean.

Depth cm	Plot 1	Plot 2	Plot 3	Mean
0-30	19.09 \pm 0.42 ^c	17.46 \pm 0.75 ^c	20.36 \pm 1.24 ^c	18.97C
30-60	19.68 \pm 0.24 ^c	18.62 \pm 0.30 ^c	24.00 \pm 0.12 ^b	20.77B
60-90	24.02 \pm 0.13 ^b	19.03 \pm 0.96 ^c	28.99 \pm 1.08 ^a	24.01A
Mean	20.93 ^b	18.37 ^c	24.45 ^a	

Mean values in the main table with the same lower case red letters are not significantly different; means (depth) in the final column with the same upper case letter are not significantly different; means in the final row (plot) with the same lower case letter are not significantly different (Tukey's $p > 0.05$).

6.3.2.2 Silt content

Plots –The mean percentage of silt was very significantly higher in plot 3 than plots 1 and 2 (Table 6.3). The mean percentage of silt was similar in plots 1 and 2 when averaged over all depths (Table 6.3).

Depths –Silt content was very highly significantly higher at 60-90 cm than that measured at 0-30 cm and 30-60 cm depths (Table 6.3). Silt percentages measured at 30-60 cm depth were also significantly higher than that measured at 0-30 cm depth when averaged over all plots (Table 6.3).

Interaction between plots and depths – there was very highly significant 2-way interaction among plots and depths (Table 6.3). There was no significant change in silt content with depth in plot 2 despite an increase from 20.08 to 24.97 between 15 and 45 cm depth, while silt content increased below 30 cm in plot 3 and in plot 1 at 60-90 cm depths (Table 6.3).

Table 6.3 Silt content (%) of the samples taken at three depths 15, 45 and 75 cm which are considered to be representative of the 0-30, 30-60 and 60-90 cm horizons of the plots. Mean values of 3 replicate composite samples (each 3 intact cores) given, with \pm SE of the mean.

Depth cm	Plot 1	Plot 2	Plot 3	Mean
0-30	20.82 \pm 1.38 b	20.08 \pm 2.19 b	19.96 \pm 1.19 b	20.29C
30-60	22.02 \pm 1.09 b	24.97 \pm 1.37 b	34.30 \pm 1.26 a	27.09B
60-90	34.11 \pm 1.18 a	24.44 \pm 0.04 b	32.83 \pm 1.11 a	30.46A
Mean	25.65b	23.16b	29.03a	25.95

Mean values in the main table with the same lower case red letters are not significantly different; means (depth) in the final column with the same upper case letter are not significantly different; means in the final row (plot) with the same lower case letter are not significantly different (Tukey's $p > 0.05$).

6.3.2.3 Sand content

Plots – Sand content was very highly significantly higher in plot 2 than plots 1 and 3 (Table 6.4). Mean sand content in plot 1 was also significantly higher than that of plot 3 when averaged over all depths (Table 6.4).

Depths – Sand content was very highly significantly higher in 0-30 cm than that measured at 30-60 cm and 60-90 cm depths (Table 6.4). Sand percentages measured at 30-60 cm depth were also significantly higher than that measured at 60-90 cm depth when averaged over all plots (Table 6.4).

Interaction between plots and depths there was very highly significant 2-way interaction between plots and depths (Table 6.4). There was no change in sand content with depth in plot 2, while sand content was decreased significantly with depth in plot 1 at 60-90 cm and in plot 3 both 30-60 and 60-90 cm had significantly lower sand content than the topsoil 0-30 cm (Table 6.4).

Table 6.4 Sand content (%) of the samples taken at three depths 15, 45 and 75 cm which are considered to be representative of the 0-30, 30-60 and 60-90 cm horizons of the plots. Mean values of 3 replicate composite samples (each 3 intact cores) given, with \pm SE of the mean.

Depth cm	Plot 1	Plot 2	Plot 3	Mean
0-30	60.09 \pm 1.73 a	62.46 \pm 1.45 a	59.68 \pm 0.40 a	60.74 A
30-60	58.30 \pm 0.96 a	56.42 \pm 1.52 a	41.70 \pm 1.35 b	52.14 B
60-90	41.87 \pm 1.27 b	56.53 \pm 0.92 a	38.19 \pm 1.99 b	45.53 C
Mean	53.42 b	58.47 a	46.52 c	52.80

Mean values in the main table with the same lower case red letters are not significantly different; means (depth) in the final column with the same upper case letter are not significantly different; means in the final row (plot) with the same lower case letter are not significantly different (Tukey's $p > 0.05$).

Sand and clay content were strongly negatively correlated ($r = -0.931$) as is expected. Sand content also has a lower variability with each horizon than either silt or clay content. Consequently % sand is used alone as an indicator of the soil texture from here on. Particle density averaged 2.49 for all samples with no significant effect of plot or soil depth found.

6.3.3 pH

Plots – There was no significant difference in the mean soil pH measured between plots 1 and 3 but mean soil pH in both these plots was significantly higher than plot 2 when averaged over all depths (Table 6.5).

Depths –Mean pH values measured at 60-90 cm depth were significantly greater than values measured at both depths 30-60 and 0-30 cm depth (Table 6.5).

Interaction between factors – There was significant 2-way interaction between plots and depths (Table 6.5). Similar soil pH values were observed in all horizons of plots 1 and 3; whereas lower pH values were measured in plot 2 in both the Ap (0-30 cm) and Bw (30-55 cm) horizons. There was no significant difference in pH at 60-90 cm (Table 6.5).

The increasing pH at 60-90 cm depth confirm that the underlying glacial till is calcareous supplying lime.

Table 6.5 pH of the samples taken at three depths 15, 45 and 75 cm which are considered to be representative of the 0-30, 30-60 and 60-90 cm horizons of the plots. Mean values of 3 replicate composite samples (each 3 intact cores) given, with \pm SE of the mean.

depth cm	plot 1	plot 2	plot 3	Mean
0-30	6.53 \pm 0.07 ab	6.15 \pm 0.09 c	6.58 \pm 0.07 ab	6.42B
30-60	6.54 \pm 0.06 ab	6.30 \pm 0.04 bc	6.62 \pm 0.08 ab	6.49B
60-90	6.71 \pm 0.11 a	6.83 \pm 0.03 a	6.79 \pm 0.05 a	6.78A
Mean	6.59a	6.43b	6.66a	

Mean values in the main table with the same lower case red letters are not significantly different; means (depth) in the final column with the same upper case letter are not significantly different; means in the final row (plot) with the same lower case letter are not significantly different (Tukey's $p > 0.05$).

6.3.4 Organic matter

Plots - Organic matter content was significantly higher in plot 1 than plot 3 which was also significantly higher than plot 2 when averaged over all depths (Table 6.6).

Depths – The mean percentage of organic matter at 0-30 cm depth was significantly higher than that observed at 30-60 cm depth, which was also significantly higher than that measured at 60-90 cm depth when averaged over all plots (Table 6.6).

Interaction between plots and depths – There was significant 2-way interaction between plots and depths (Table 6.6). The decline in organic matter content with depth was much smaller in plot 2 than in plots 1 and 3. The lowest value was observed in the Bg horizon (60-90 cm depth) in plot 3 (Table 6.6).

Table 6.6 Organic matter content (LOI, %) of the samples taken at three depths 15, 45 and 75 cm which are considered to be representative of the 0-30, 30-60 and 60-90 cm horizons of the plots. Mean values of 3 replicate composite samples (each 3 intact cores) given, with \pm SE of the mean.

depth cm	plot 1	plot 2	plot 3	Mean
0-30	3.62 \pm 0.10 a	2.94 \pm 0.04 b	3.31 \pm 0.03 a	3.29 A
30-60	2.72 \pm 0.09 b	2.21 \pm 0.07 c	2.75 \pm 0.03 b	2.56 B
60-90	2.36 \pm 0.11 c	2.15 \pm 0.02 c	1.73 \pm 0.07 d	2.08 C
Mean	2.90 a	2.43 c	2.60 b	2.64

Mean values in the main table with the same lower case red letters are not significantly different; means (depth) in the final column with the same upper case letter are not significantly different; means in the final row (plot) with the same lower case letter are not significantly different (Tukey's $p > 0.05$).

6.3.5 Bulk density

Plots – Mean bulk density values were similar in plot 3 and 1, while plot 2 had significantly lower bulk density when averaged over all depths (Table 6.7).

Depths – The mean bulk density was highly significantly greater at 60-90 cm depth than that measured at 30-60 cm depth which in turn was significantly higher than the values measured at 0-30 cm depth when averaged over all plots (Table 6.7).

Interaction between plots and depths – there was no interaction between plots and depths.

Bulk density values were compared with those determined from the samples taken in the plots using the hydraulic corer (Section 4.2.3). Results showed that there were no differences on the values of the bulk density between two methods ($p= 0.355$).

Table 6.7 Bulk density ($g\ cm^{-3}$) of the samples taken at three depths 15, 45 and 75 cm which are considered to be representative of the 0-30, 30-60 and 60-90 cm horizons of the plots. Mean values of 3 replicate composite samples (each 3 intact cores) given, with \pm SE of the mean.

Depth cm	plot 1	plot 2	plot 3	Mean
0-30	1.47 \pm 0.02 c	1.33 \pm 0.07 d	1.47 \pm 0.05 c	1.42 C
30-60	1.61 \pm 0.04 ab	1.51 \pm 0.01 bc	1.66 \pm 0.01 a	1.59 B
60-90	1.67 \pm 0.02 a	1.63 \pm 0.07 a	1.68 \pm 0.05 a	1.66 A
Mean	1.58a	1.49b	1.60a	1.56

Mean values in the main table with the same lower case red letters are not significantly different; means (depth) in the final column with the same upper case letter are not significantly different; means in the final row (plot) with the same lower case letter are not significantly different (Tukey's $p>0.05$).

6.3.6 Water content at Field Capacity (0.05 bar)

Plots – There was little difference in the values of water content at field capacity between plots. However, mean field capacity was slightly and significantly higher in plot 1 than plot 2 when averaged over all depths (Table 6.8).

Depths – There was little difference in the absolute values of water content at field capacity between depths (Table 6.8). However, mean field capacity was slightly and significantly higher at 60-90 cm than at 0-30 cm when averaged over all plots (Table 6.8).

Interaction between plots and depths — there was no interaction between plots and depths.

Table 6.8 Field capacity 0.05 bar (cm cm^{-3}) of the samples taken at three depths 15, 45 and 75 cm which are considered to be representative of the 0-30, 30-60 and 60-90 cm horizons of the plots. Mean values of 4 intact cores given, with \pm SE of the mean.

Depth cm	Plot 1	Plot 2	Plot 3	Mean
0-30	0.317 \pm 0.01	0.299 \pm 0.08	0.315 \pm 0.01	0.310B
30-60	0.325 \pm 0.01	0.308 \pm 0.01	0.327 \pm 0.01	0.320AB
60-90	0.329 \pm 0.01	0.319 \pm 0.01	0.336 \pm 0.01	0.328A
Mean	0.323a	0.308b	0.326ab	

Means (depth) in the final column with the same upper case letter are not significantly different; means in the final row (plot) with the same lower case letter are not significantly different (Tukey's $p > 0.05$).

Total porosity in the topsoil was 40 % of the soil volume or greater and this declined with depth in all plots, though plot 2 had markedly higher porosity at both 0-30 cm and 30-60 cm than plots 1 and 3 (Table 6.9). Macroporosity made up a significant proportion of the total porosity in the topsoil in all plots and this remained so for plot 2 at 30-60 cm. However, in general macropores declined with depth (Table 6.9) and macropores made up a very small proportion of pore space at 60-90 cm for plot 1 and for both 30-60 and 60-90 cm in plot 3. Because porosity is calculated, based on other properties already statistically analysed (see previous sections), therefore statistical analysis was not carried out for the porosity measures.

Table 6.9 Mean calculated total porosity and macroporosity for soil samples from three plots 0-30, 30-60 and 60-90 cm depth.

Depth (cm)	Plot 1	Plot 2	Plot 3
Total porosity $\text{cm}^3 \text{cm}^{-3}$			
0-30	0.400	0.454	0.414
30-60	0.365	0.402	0.341
60-90	0.340	0.355	0.344
Macroporosity $\text{cm}^3 \text{cm}^{-3}$ (as % total porosity)			
0-30	0.082 (20.5)	0.155 (34.1)	0.098 (23.7)
30-60	0.039 (10.7)	0.093 (23.1)	0.013 (3.8)
60-90	0.010 (3.1)	0.035 (9.9)	0.007 (2.0)

6.3.7 Soil water content at 2 bar

Plots – Mean water contents at 2 bar were significantly higher in plot 3 than plot 2 (Table 6.10). However there was no significant difference when comparing the mean values in plots 2 and 1 or plots 3 and 1 when averaged over all depths (Table 6.10).

Depths – Mean water contents at 2 bar measured at 60-90 cm depth was significantly higher than depths 0-30 and 30-60 cm, with no significant difference between these depths (Table 6.10).

Interaction between plots and depths – there was no interaction between plots and depths.

Table 6.10 Water content at 2 bar ($\text{cm}^3 \text{cm}^{-3}$) of the samples taken at three depths 15, 45 and 75 cm which are considered to be representative of the 0-30, 30-60 and 60-90 cm horizons of the plots. Mean values of 4 intact cores given, with \pm SE of the mean.

Depth cm	Plot 1	Plot 2	Plot 3	Mean
0-30	0.225 \pm 0.01	0.213 \pm 0.00	0.226 \pm 0.01	0.221B
30-60	0.234 \pm 0.01	0.227 \pm 0.001	0.250 \pm 0.00	0.237B
60-90	0.256 \pm 0.01	0.253 \pm 0.01	0.287 \pm 0.02	0.265A
Mean	0.239ab	0.231b	0.254a	0.241

Means (depth) in the final column with the same upper case letter are not significantly different; means in the final row (plot) with the same lower case letter are not significantly different (Tukey's $p > 0.05$).

6.3.8 Water content at wilting point (15 bar)

Plots – Mean water content at wilting point in both plot 3 and plot 1 was significantly higher than the average for plot 2 (Table 6.11), however there was no significant difference between plot 1 and 3 when averaged over all depths (Table 6.11).

Depths – there was very highly significant difference between the mean wilting point (15 bars) values measured between three depths across all plots (Table 6.11). The mean water content at wilting point at 60-90 cm depth was significantly higher than both other depths. Mean water content at wilting point at 30-60 cm was also significantly higher than 0-30cm depth when averaged over all plots (Table 6.11).

Interaction between plots and depths – there was no interaction between plots and depths.

Table 6.11 Wilting point (15 bar) of the samples taken at three depths 15, 45 and 75 cm which are considered to be representative of the 0-30, 30-60 and 60-90 cm horizons of the plots. Mean values of 3 replicate composite samples (each 3 intact cores) given, with \pm SE of the mean.

Depth cm	Plot 1	Plot 2	Plot 3	Mean
0-30	0.132 \pm 0.03	0.134 \pm 0.05	0.142 \pm 0.04	0.136C
30-60	0.155 \pm 0.01	0.144 \pm 0.01	0.148 \pm 0.00	0.149B
60-90	0.205 \pm 0.01	0.160 \pm 0.07	0.198 \pm 0.01	0.187A
Mean	0.164a	0.146b	0.162a	0.157

Means (depth) in the final column with the same upper case letter are not significantly different; means in the final row (plot) with the same lower case letter are not significantly different (Tukey's $p > 0.05$).

6.3.9 Saturated hydraulic conductivity (Ks)

Plots – The mean Ks values measured in plot 2 were significantly higher than other plots (Table 6.12). There were no significant differences in the mean values of the Ks measured between plot 1 and 3 when averaged over all depths (Table 6.12).

Depths – Mean K_s values were very highly significantly higher for 0-30 cm than other depths. The K_s values measured at depth 30-60 cm were also significantly higher than the values measured at 60-90 cm depth when averaged over all plots (Table 6.12).

Interaction between plots and depths – there was no interaction between plots and depths.

Table 6.12 Saturated hydraulic conductivity values (K_s) (cm day^{-1}) of the samples taken at three depths 15, 45 and 75 cm which are considered to be representative of the 0-30, 30-60 and 60-90 cm horizons of the plots. Mean values of 4 intact cores given, with \pm SE of the mean.

depth cm	Plot 1	Plot 2	Plot 3	Mean
0-30	2.213 \pm 1.92	5.354 \pm 0.43	1.798 \pm 0.43	3.122A
30-60	1.021 \pm 0.77	2.389 \pm 0.49	0.049 \pm 0.02	1.153B
60-90	0.026 \pm 0.01	0.092 \pm 0.02	0.004 \pm 0.00	0.041C
Mean	1.087b	2.612a	0.617b	

Means (depth) in the final column with the same upper case letter are not significantly different; means in the final row (plot) with the same lower case letter are not significantly different (Tukey's $p > 0.05$).

6.3.10 Correlation between soil physical properties

Sand content was strongly and positively correlated with log K_s , total porosity, macroporosity (Figure 6.5 a, b, c), and negatively with measured soil water content at 0.05, 2 bar and 15 bar (Figure 6.6 a, b, c). There was no significant overall relationship between SOM and the soil texture. However some indication of a positive relationship ($r^2=0.66$, $p=0.053$) was measured between SOM and clay content in the top soil.

Total soil porosity showed very highly significant and positive correlation with log K_s (Figure 6.7a), and negatively with soil water content measured at 0.05 (Figure 6.7b).

Macroporosity was very highly positively correlated with log K_s (Figure 6.8a). The soil water content measured at 0.05 bars was highly significant and negatively correlated with log K_s (Figure 6.8b).

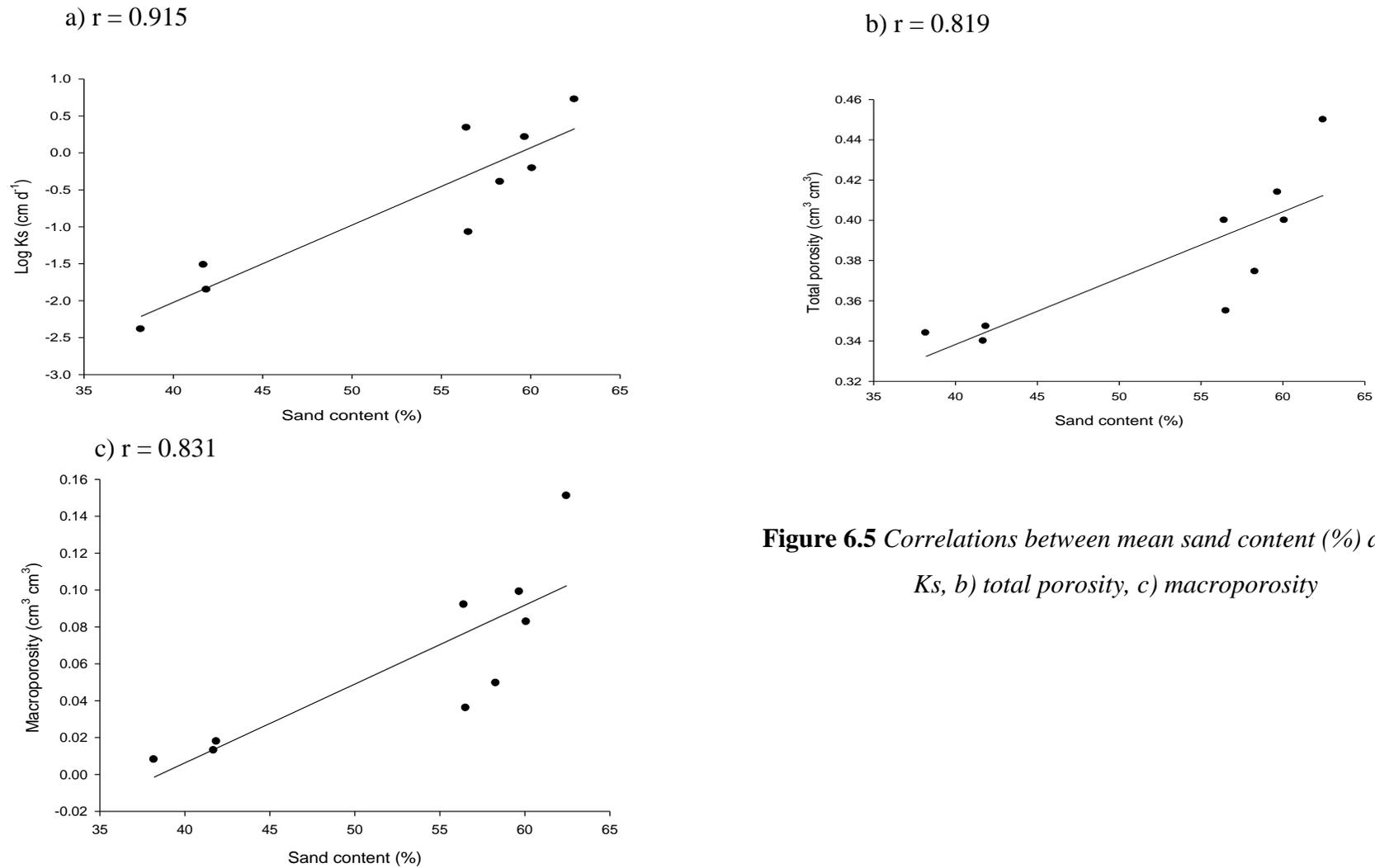


Figure 6.5 Correlations between mean sand content (%) and: a) log K_s , b) total porosity, c) macroporosity

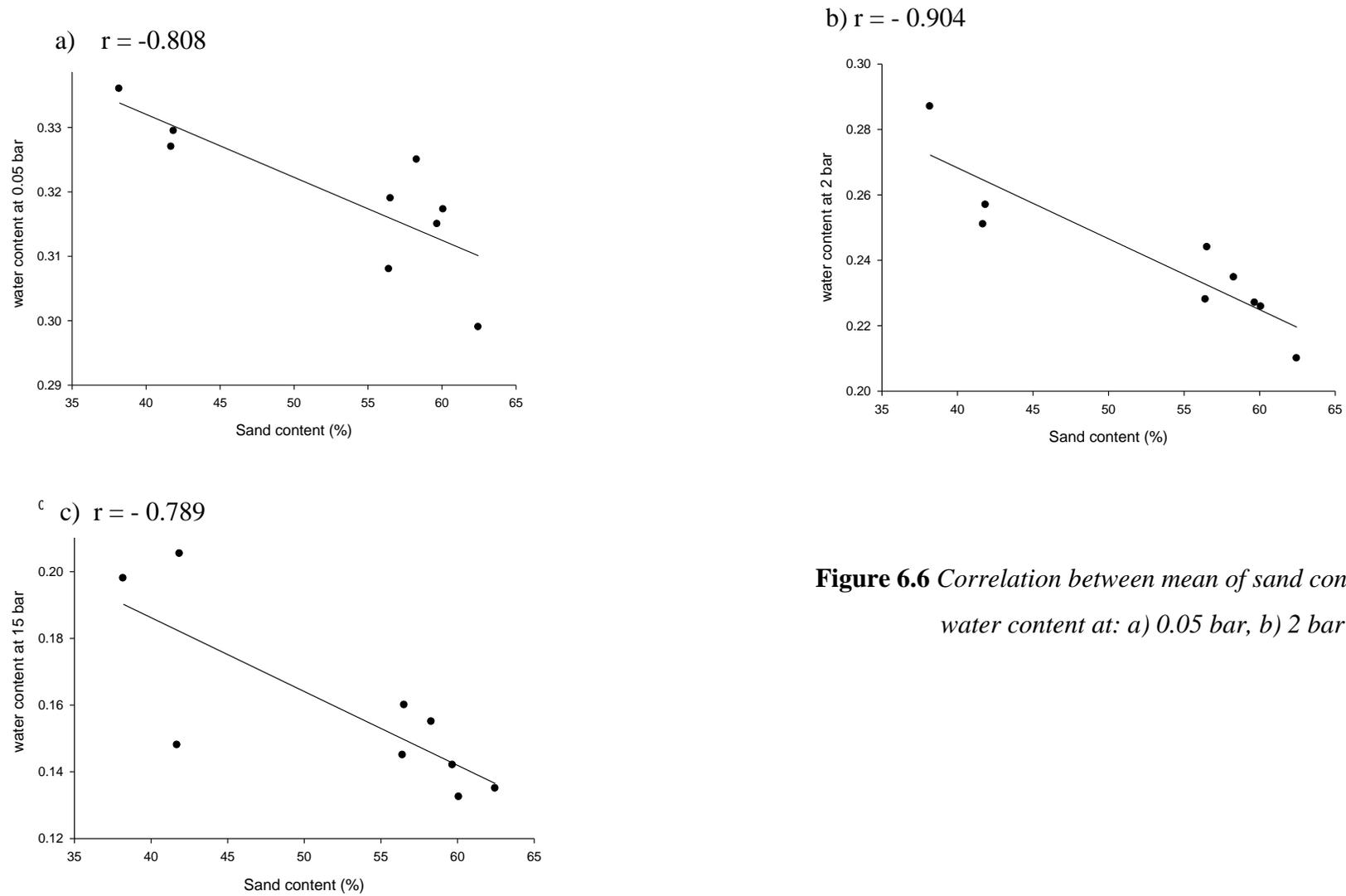


Figure 6.6 Correlation between mean of sand content (%) and water content at: a) 0.05 bar, b) 2 bar and c) 15 bar

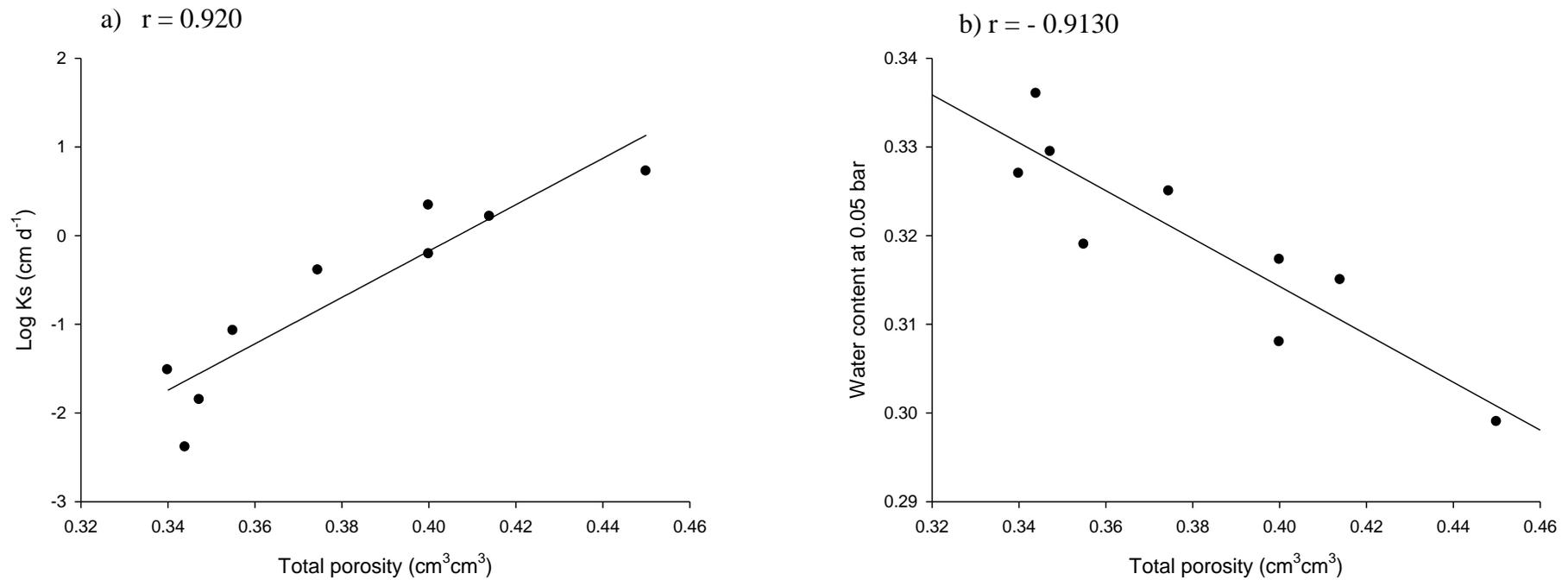


Figure 6.7 Correlation between mean total porosity and: a) $\log K_s$ and b) soil water content at 0.05 bar.

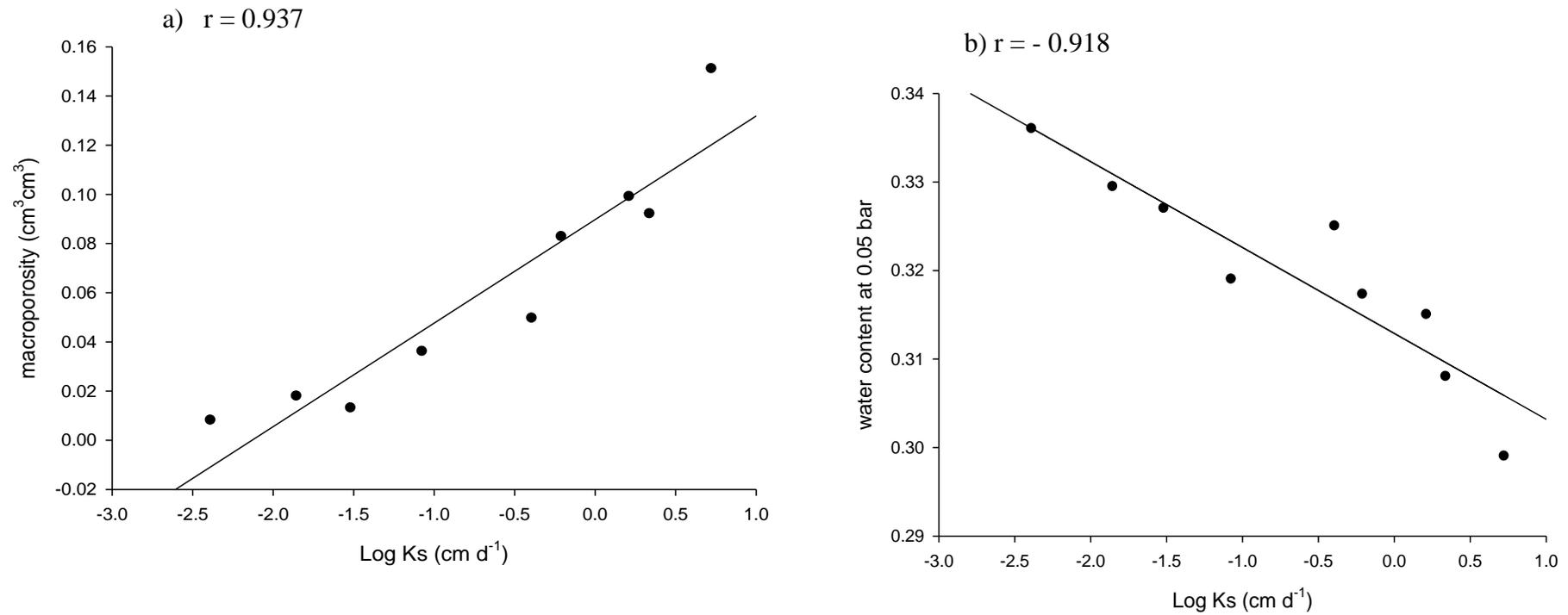


Figure 6.8 Correlations between $\log K_s$ and: a) macroporosity and b) water content at 0.05 bar

6.3.11 Evaluation of pedotransfer functions for soil water content

The estimation results of the soil water content at 0.05, 2 and 15 bars derived from the regression equation developed by Hall *et al.* (1977) did not agree with the measured data ($r < 0.21$). However results derived from Gupta and Larson (1979) equation showed interesting results. For water content at 0.05 bar the equation did not agree well with the measured data (Figure 6.9a), but a significant positive relationship was found between measured and predicted values for the soil water content at both 2 and 15 bar (Figure 6.9b and c). While the prediction of water content at 2 bar is close to the 1:1 line (Figure 6.9b), the prediction of wilting point is an overestimate compared with the measured values (Figure 6.9c; 3-4% higher). This will lead to an underestimate of soil available water content.

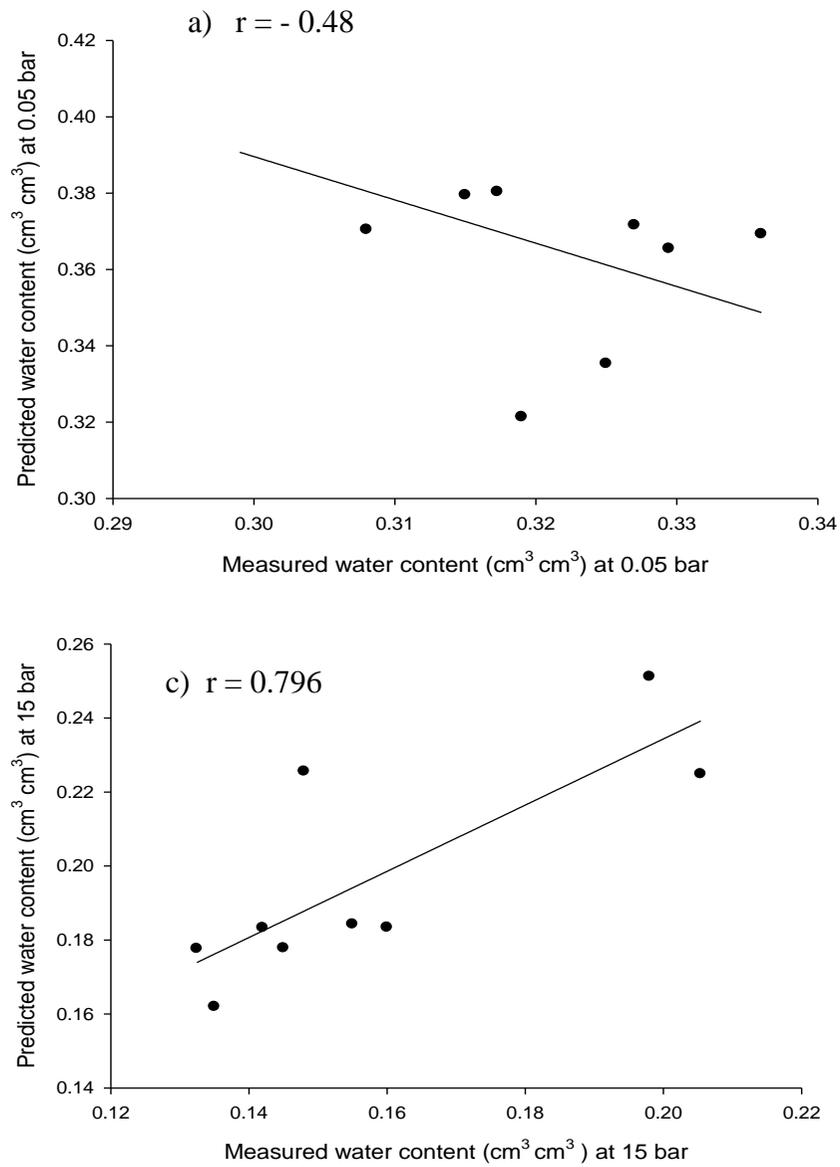


Figure 6.9 Predicted vs measured values of soil water content at a) 0.05 bar, b) 2 bar and c) 15 bar, using equations developed by Gupta and Larson (1979).

6.4 Discussion

As expected SOM decreased with depth (Powelson, 1993). However, despite the commonly found relationship between increased clay content and increased soil organic matter (Rowell, 1994), in our study there was no significant overall relationship between SOM and soil texture, the relationship was confounded as a result of the increase in clay content with depth. However as clay content in the top soil increased SOM also increased. In our study SOM also had no significant relationship with either soil water content at field capacity or saturated hydraulic conductivity. Over a larger range of SOM, Aparicio and Costa (2007) found no relationship between soil organic matter and topsoil texture (sandy clay loam, clay loam) but found a strong positive relationship between soil organic matter and water holding capacity and hydraulic conductivity, which they attributed to an increase in water retaining pores as result of increasing SOM (Hati *et al.*, 2006; Aparicio and Costa, 2007). Rawls *et al.* (2003) also found no significant effect of soil organic matter on soil water retention at low levels of SOM.

In these soil profiles, soil texture has the main effect on total soil porosity, the soil moisture characteristic curve and water movement. Soil water retained (at 0.05, 2 and 15 bars) increased and total porosity, macroporosity and saturated hydraulic conductivity (K_s) decreased with depth as sand content decreased. Higher sand content is associated with large pores which are responsible for the rapid movement of water and also with decrease moisture holding capacity, whereas clay creates a large number of small pores which decrease the permeability and increase the water holding capacity (Webster *et al.*, 1993; Hillel, 1998; Rab *et al.*, 2011).

In these soil profiles, increased soil depth and changes in soil texture had relatively small effects on meso- and micro-porosity (measured by the water retained at 0.05 bar and higher pressures) whereas large changes were observed in the macroporosity, i.e. the pores which are empty at field capacity. Wright *et al.* (1998) observed effects of cultivation on both the distribution and the continuity of the macropores which consequently affected the routes of water flow within the soil. Bathke *et al.* (1992) found that where sand content was higher in the Ap horizon and decreased with depth, both total and macroporosity decreased (from 16 % in the top 30 cm to 5 % at in the bottom soil) and saturated hydraulic conductivity declined from 4 cm day⁻¹ to 0.7 cm

day⁻¹. Both Afyuni *et al.* (1994) and Olatuyi *et al.* (2012b) also found that increased clay content with depth caused a decline in K_s and a slight increase in the amount of water held at field capacity in a cultivated clay loam soil. The decrease in hydraulic conductivity may consequently enhance water accumulation and subsurface lateral movement above the horizon with reduced permeability (Bathke *et al.*, 1992; Olatuyi *et al.*, 2012a). These measurements confirm the observations of gleying features in the soil profiles; a higher sand content was found in the Ap and Bw horizons than in the Bg which has a higher clay content which suggests that water will move quickly in the Ap and Bw horizons, but very slowly in the Bg horizon, with more rapid drainage expected in Plot 2 than in Plots 1 and 3.

The use of pedotransfer functions derived from Gupta and Larson (1979) to estimate the soil moisture characteristic curve gave good estimate of the soil water content at 2 bars but the predicted and measured data were not in agreement for the intact soil cores at the lower suction (0.05 bar). Water contents at high suction are considered to be mainly affected by the texture whereas water held in the soil at field capacity is affected by both the structure and texture of the soil (Hillel, 1998). Pollacco (2008) considers that soil texture and bulk density can be used to estimate the water content at field capacity as any effect of organic matter on porosity is already incorporated into measurements of bulk density. These data suggest that pedotransfer functions may be suitable to estimate soil water properties that are mostly texture driven.

6.5 Conclusion

In our study measured soil water content at 0.05, 2 and 15 bar increased and total porosity, macroporosity and saturated hydraulic conductivity (K_s) decreased with depth as sand content decreased. There was a strong positive relationship between macroporosity and $\log K_s$ suggesting that saturated hydraulic conductivity in this soil is mainly affected by the volume of macropores rather than their continuity. The observed changes in soil texture with depth will influence rates of infiltration by rainfall, the amount of water held in the soil (Bruce *et al.*, 1985; Afyuni *et al.*, 1994; Hillel, 1998; Rab *et al.*, 2011) and consequently the distribution and movement of soil water in the profile, which controls the movement and losses of solutes via leaching (Bathke *et al.*, 1992; Olatuyi *et al.*, 2012b). The measurements of high macroporosity (26 %) in the topsoil (giving high K_s) together with low macroporosity at 60-90 cm (5 %) giving very

low K_s) indicates that these soils are likely to show some subsurface accumulation and lateral movement of water within the soil profile.

In our study pedotransfer functions did not provide a good estimation of soil water content at field capacity and, as a result, the pedotransfer functions examined are not useful tools to predict macroporosity and the amount of mobile water in the soil profile. These properties, together with K_s , which control drainage (and consequently nitrate leaching) are strongly affected by structure as well as texture. Therefore, observations of the soil profile together with measurements of porosity (bulk density), ideally macroporosity, are needed to underpin field studies of nitrate leaching.

CHAPTER

7

7 Using bromide tracers to investigate the underlying hydrological pathways of nitrate movement in plots of the NFSC experiment

7.1 Introduction

Variation in soil physical properties within a field modifies hydrological processes and hence controls both the pathway and rate of solute transport within and out of the soil profile (Bathke *et al.*, 1992; Afyuni *et al.*, 1994; Logsdon, 2007; Bullock *et al.*, 2008; Thibodeau *et al.*, 2008; Whetter *et al.*, 2008). The direction of solute movement can determine the eventual receptor for any pollutants; if movement is dominantly vertical, any solutes may eventually end up in the ground water (Burt *et al.*, 1993; Bullock *et al.*, 2008; Olatuyi *et al.*, 2012b) or if movement is lateral, local surface waters such as streams and rivers will be the main receptor (Burt *et al.*, 1993; Afyuni *et al.*, 1994; Bullock *et al.*, 2008; Olatuyi *et al.*, 2012a). Many authors have used Br tracing in field and laboratory, in our experiments Br has been used in the field. There are a number of problems associated with carrying out bromide experiment on columns in the laboratory these problems were reviewed by (Beven *et al.*, 1993; Bronswijk *et al.*, 1995) and include 1) Using the soil column experiment (repacking or undisturbed soil cores) do not take into account the spatial variability of the soil properties in both horizontal and vertical direction because of the soil repacking and small column sizes. 2) It may also not represent the real conditions in the field including the rainfall patterns and evapotranspiration. 3) The free surface at the base may create an artificial lower boundary to the soil sample while in the field there would be suction to water table below. 4) Soil cores will be restricted because of the restricted size of the column and

taking the cores may cut some of the structural flow pathways. 5) Possible flow along the sides of the cores.

The use of soluble tracers can help to study and monitor the transport of NO_3^- through soils and also help improve our understanding of the underlying hydrological processes (Bullock *et al.*, 2008; Thibodeau *et al.*, 2008; Whetter *et al.*, 2008) Bromide has been used to study hydrological pathways with both vertical and lateral movement of bromide observed. For example, Whetter *et al.* (2008) used bromide tracer and found that different soil profile properties and topography (crest, midslope, depression) influenced the amount of vertical and lateral redistribution of Br^- . Olatuyi *et al.* (2012a) also found evidence of lateral movement over the surface or in the surface soil with 5-10% of the applied Br recovered outside the area in which it was applied. Afyuni *et al.* (1994) measured some lateral movement of Br^- in the interfluvium where the slope gradient was small; hence it is important to consider lateral as well as vertical pathways for solute movement even in gently sloping sites. To obtain more information on the hydrological pathways for nitrate leaching under field conditions in the plots of the NFSC experiment at Nafferton farm, two experiments were established in 2011 and overwinter 2011-12 using a bromide tracer to test whether:

- a significant amount of bromide can move laterally in these soils and the relative importance of this hydrological pathway compared with vertical transport.
- location within the field affects the main hydrological pathways for movement of solutes (both vertical and lateral).

7.2 Material and Methods

7.2.1 Site description

Two separate experiments were carried out using bromide as a conservative tracer to study the hydrological pathways within the soils of the NFSC experiment. Experiment 1 took place during late spring 2011 (March-May 2011) and Experiment 2 (an overwinter experiment) took place between 7 November 2011 and 1 May 2012. The experiments were located within the NFSC field with experiment 1 taking place in three plots of the NFSC (plots A, B, C) and Experiment 2 taking place in the adjacent buffer grass strips (Plots 1, 2, 3; Figure 7.1); sites were selected in order to be representative of the plots within which mineral N profiles were studied (Chapter 5). Each plot used for

the bromide tracer experiments was 6 m × 12 m. The slope in the field was gentle c. 3° as seen in the soil profile descriptions in Appendix 1.

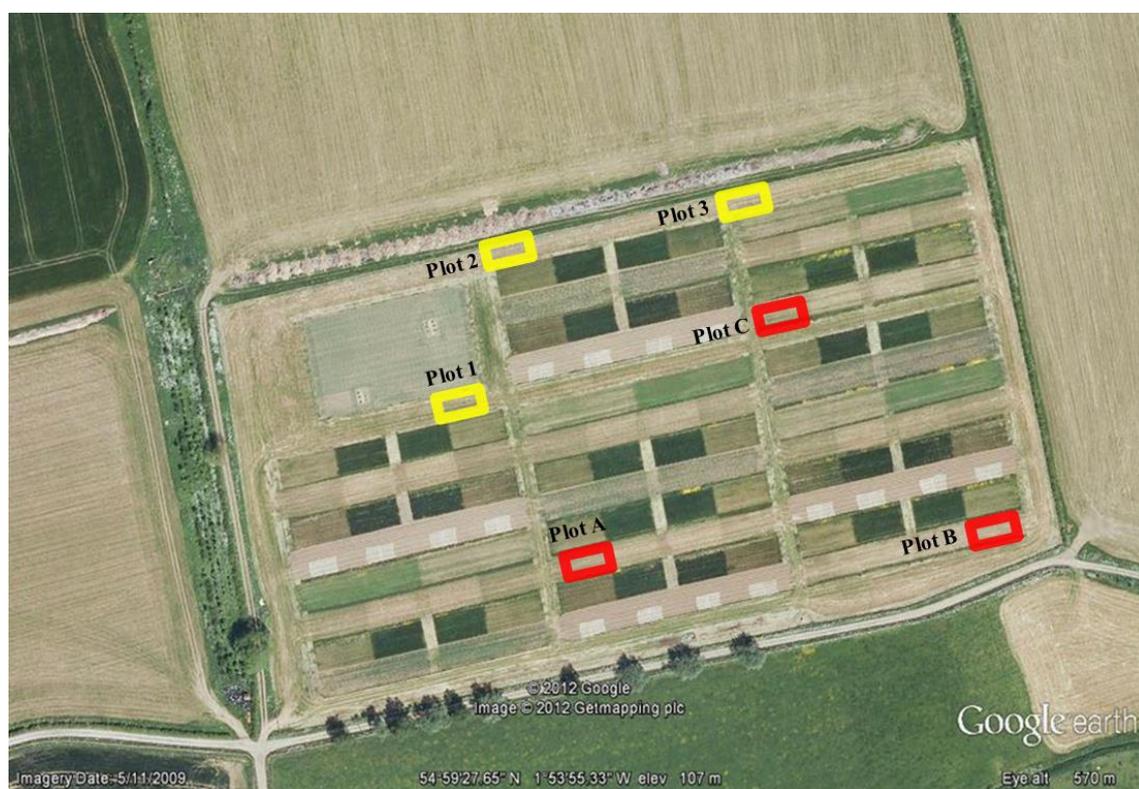


Figure 7.1 The location of bromide plots experiments, red plots experiment 1, and yellow plots experiment 2.

7.2.2 Experiment 1 – field design

For experiment 1, 30 porous suction cups were installed at either 30 cm or 60 cm depth (15 suction cups for each depth, 5 at each depth per plot) in three replicate plots/areas within the NFSC under grass-clover ley. Each plot was within the organically managed treatments; the plots had been planted to spring barley undersown with grass-clover ley in spring 2008 and the plots were managed for silage in 2009, 2010 and 2011 with three harvests per year. No additional fertility inputs were made to the plots in this period. The depths were chosen to represent the plough layer (0-30 cm) and the effective root zone (0-60 cm). Within the plot there was 3 m between the groups of cups installed at 30 cm and 60 cm depth. Each group of suction cups (at either 30 cm or 60 cm) was arranged in a circle (1 m radius) with one suction cup installed in the centre (Cs)

(source, S) and the 4 remaining cups (C_U , C_L , C_R and C_D) equally spaced on the perimeter of the circle (Figure 7.2). In each circle one cup was placed directly downslope of the centre (downslope, C_D).

7.2.3 Experiment 2 – field design

The design of experiment 2 was similar to the design used in the experiment 1; however, following that experiment some minor modifications were made. The previous results of experiment 1 indicated that bromide was only recovered at the source cup (C_S) and downslope locations (C_D). Hence in this experiment the upslope porous cup (C_U) was therefore removed and placed between the source (C_S) and the downslope cup (C_D), 75 cm downslope from C_S (C_{D2} ; Figure 7.3). The suction cup samplers used in the second experiment were the same cups as had been used in the first experiment after reconditioning and cleaning.

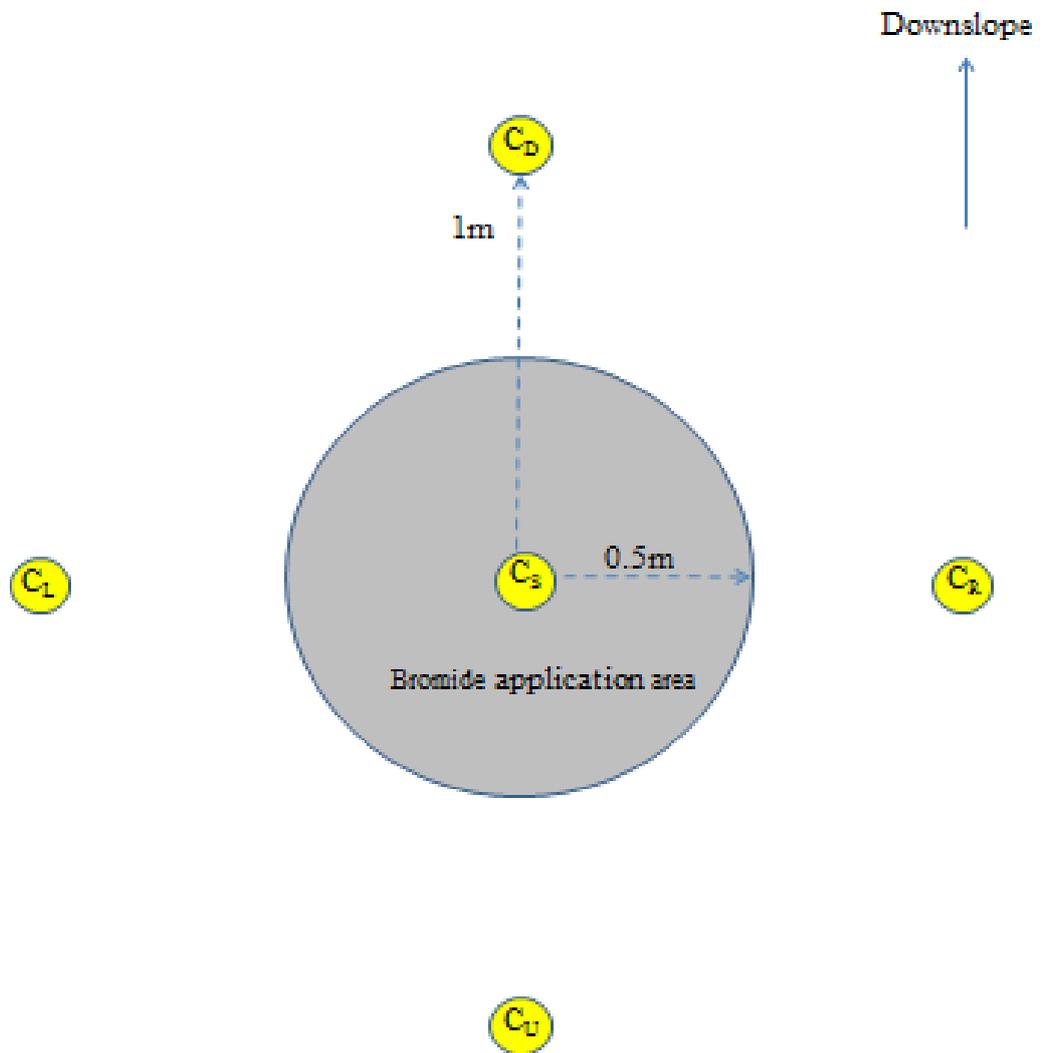


Figure 7.2 Detail of experimental design in the field for experiment 1 showing location of the bromide application (to a circle of 0.5 m radius; Source), and the porous cup samplers. One porous cups was placed at the centre of the source area (C_S) and 4 porous cups (C_U , C_L , C_R , C_D) were placed at 1m from C_S with C_D immediately downslope of C_S .

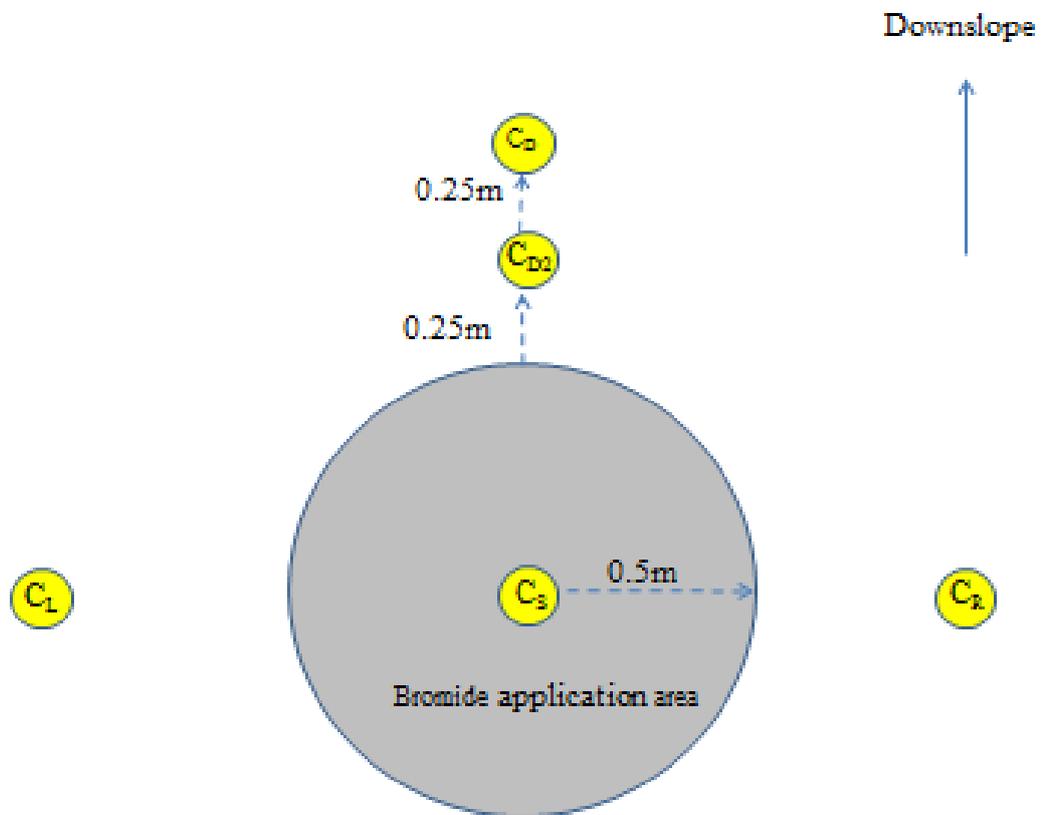


Figure 7.3 Detail of experimental design in the field for Experiment 2 showing location of the bromide application (to a circle of 0.5 m radius; Source), and the porous cup samplers. One porous cup was placed at the centre of the source area (C_S) and 3 porous cups (C_D , C_L , C_R) were placed at 1m from C_S with C_D immediately downslope of C_S ; an addition porous cup sampler C_{D2} was placed between C_S and C_D , 75 cm from C_S .

7.2.4 Installation of porous ceramic cups

The porous ceramic suction cup samplers used were similar to the cups described and used by many authors e.g. (Lord and Shepherd, 1993; Webster *et al.*, 1993; Curley *et al.*, 2011) and were purchased from Van Walt Limited, Prestwick Lane, Grayswood, Haslemere, Surrey United Kingdom (Walt, 2010). Each porous ceramic cup (80 mm long and 30 mm outside diameter with a pore size of 1 μm) was attached to long PVC tube (Figure 7.4). A rubber plug, 30 mm outside diameter, with a stainless steel tube passing through the centre was fitted to the open end of the PVC tube, a nylon tube was then attached to the steel tube and sealed with clips. A vacuum could be applied by connecting a pump to the nylon tube; once the vacuum had been applied the tube was clamped. Before installing the porous ceramic cups, which were new when used in Experiment 1, they were cleaned using the method described by (Curley *et al.*, 2010). All the ceramic cups were rinsed with water three times, a vacuum was applied and the cups were left in deionised water for three days. The cups were then flushed with dilute acid (1 N HCl) and finally rinsed with deionised water before taking them to the field.



Figure 7.4 Porous ceramic cups attached to sampling tubes as used in the experiments.

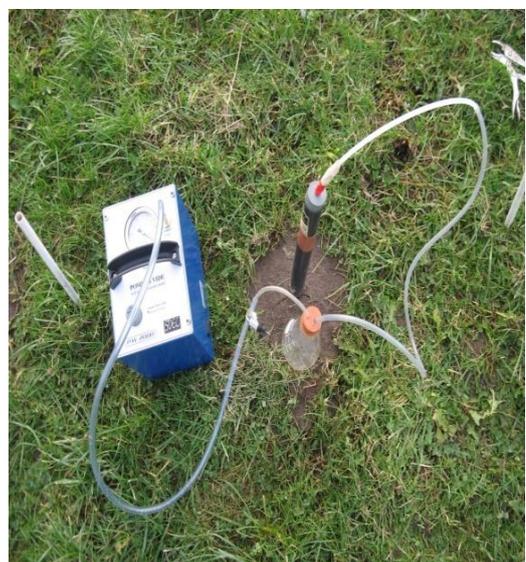
The installation method used in this experiment is similar to that used by (Webster *et al.*, 1993). To install the porous suction cups, vertical holes were made using a hydraulic soil sampler that had a diameter similar to that of the cups (Figure 7.5); this ensured good hydraulic contact between the cups and the soil (Curley *et al.*, 2010). The soil surface was cleaned to prevent any soil material falling into the holes and the soil from both topsoil and lower soil was kept separately and all stones and gravel were removed. Fine silica sand was used at the base of hole to create good contact between the soil and the ceramic cups. The silica sand was mixed with water to make thick slurry and placed into the holes; the amount used was enough to cover the ceramic cups in each hole. All the suction cups were then inserted down into the bottom of the holes, so that each porous suction cup was totally surrounded by the silica slurry (Figure 7.5). All the holes were backfilled with stoneless soil from same the depth until *c.* 15 cm from the soil surface. A layer of 10 cm of sodium bentonite powder (Mineral, 2010) was then added to form a plug to isolate the porous ceramic cups and prevent any possible preferential flow of water down the hole. The holes were then repacked to just proud of the soil surface with the remaining soil.

For experiment 1, the porous ceramic cups were installed on 26 February 2011. For experiment 2, the porous cups were installed on 17 November 2011.

Immediately after installation was complete, suction was applied to all the ceramic cups and water was removed from the cups to ensure all of them were working well and to increase the effectiveness of contact between the ceramic cups and the silica sand. The porous ceramic cups were then left for one week. After that a suction of 50 kPa was applied using a pump and left for 24 hours (Figure 7.5). The next day all the solution was removed from the porous cup and discarded. To remove the soil solution, a sampling bung perforated by two small diameter plastic tubes was attached to the PVC tube; one plastic tube reached the bottom of the cups to suck all the soil solution from the cup, the other shorter tube was used to create a vacuum within the collection bottle which in turn sucked the soil solution from the cup into the collection bottle. All the soil solution in the collection bottle was transferred into labelled bottles.



a) Careful installation into augered hole b) Backfilling to create hydrological isolation



c) Plot layout with source area outlined by cup d) Sampling of soil solution collected

Figure 7.5 Installation of porous ceramic cup samplers

7.2.5 Tracer application

On 4 March 2011 (experiment 1) and 1 December 2011 (experiment 2), bromide tracer of 300 kg NaBr ha⁻¹ (equivalent to 23.29 g Br⁻ m⁻²) was applied to the soil surface within a circular source area (0.5 m diameter) centred at Cs. The bromide solution was prepared by dissolving 23.561 g of NaBr in 500 ml of deionised water (giving an application of 18.299 g Br⁻ to the source area; 0.785 m²). The amount of water used for the application was enough to make sure all the bromide was dissolved and spread uniformly and also to minimise run off. To reduce the risk of runoff, bromide was applied on a day where there was no rain forecast. The bromide solution was applied evenly across the soil surface using a manual hand pump sprayer.

In both experiments, the plots were uncovered and received ambient rainfall. However, in experiment 1, little rainfall was recorded in April and no rainfall was recorded in the first four days of May and no soil solution could be obtained from the porous ceramic cups. Therefore, on 4 May 2011, 25 mm of irrigation was used to simulate the rainfall (a typical total rainfall in the month of May). The irrigation (of 176.7 litres) was, however, applied to a restricted circle of 3 m diameter centred on the source to eliminate any possible changes in the hydrological properties between the main circle and the surrounding area that might be caused by the irrigation. The irrigation water was applied slowly and uniformly distributed over the circle to minimise any possible erosion or runoff.

No irrigation was applied in experiment 2.

7.2.6 Sampling of soil solution

Soil solution samples were collected from the porous cups every 15 days or immediately following any significant rainfall event until the soil had dried to such an extent that solution samples could not be obtained. To obtain soil solution samples a vacuum of 50 kPa (0.5 bar) was applied to the porous ceramic cups using a battery powered Vacuum Pump (Model PAV2000-12 Volts) manufactured by Van Walt, SDEC France company). The sampler tube was connected to the pump's air inlet nozzle and the pump switched on; about 15 seconds was needed to obtain 50 kPa. The clip on the sampler's tube was closed strongly to retain the vacuum in the sampler, the pump was

then switched off and disconnected from the tube. The sampler was then left for approximately 2 to 5 hours to provide a sample of the soil solution on the day of sampling.

Soil solution was drawn into the porous suction cups due to the pressure gradient caused by the partial vacuum. Between 15 ml and 60 ml of soil solution was obtained from each porous ceramic cup at each sampling time; the volume of the solution was recorded. Deionised water was used to clean the small tube and the sampling bottle after sampling each suction cup to prevent any contamination between the samples. About 4-6 hours was needed to collect the solution from 30 cups. All samples were transferred to prewashed polyethylene bottles and stored in a freezer at temperature of -20 °C. Before analysis for bromide and nitrate, samples were thawed and then filtered through a syringe filter (0.2 µm pore size, 25 mm diameter).

7.2.7 Calculation of total bromide loss using porous ceramic cups

In order to calculate bromide loss, the amount of drainage during the period of two experiments was estimated using data collected at the weather station at Nafferton farm. The method used for estimation of drainage is described in full in Section 3.4.

As with Lord and Lord and Shepherd (1993), the same estimate of drainage was used for all cup samplers on each occasion; the drainage volume at each sampling point was not estimated separately. The total bromide loss past each depth in each plot was calculated using the trapezoidal rule (Lord and Shepherd, 1993), where the total amount of bromide loss (kg ha^{-1}) is the area under the plot of bromide concentrations against cumulative drainage (mm). The area under the plot of Br^- concentration against drainage was calculated as the sum of the areas of the trapezia resulting from the Br^- concentration at successive sampling occasions ($C_1, C_2 \text{ mg l}^{-1}$), and the drainage volume between sampling occasions ($v \text{ mm}$). The total amount of bromide leached in each sampling interval in kg ha^{-1} was then :

$$\text{Br}^- \text{ leached} = 0.5(C_1 + C_2) v / 100.$$

7.2.8 Soil sampling

Before the installation of porous cups and the application of bromide tracer, a manual soil auger (3 cm diameter) was used to collect initial soil core samples to determine soil water content and the background concentration of bromide for all three plots. Soil samples were taken on the 20 February 2011 (experiment 1) and 10 November 2011 (experiment 2). All augered holes were outside the area of tracer application to prevent any possible hydrological changes that might result from the destructive sampling. In each plot four cores were collected to 90 cm, each was divided into 3 layers (0-30, 30-60, 60-90 cm) and the depths were chosen to match the mineral N sampling and represent rooting zones. It was not possible to sample deeper than 90 cm because the length of the available soil auger was 100 cm. For each plot a single composite sample for each layer was placed into plastic bags, and stored in a freezer at temperature of -20 °C.

After the porous cup sampling in experiment 1 was complete, detailed soil sampling was carried out on 2 June 2011 to determine final bromide recovery, 88 days after bromide application. 10 soil core samples were taken in/around each circle of porous cup samplers giving replicate sets of samples per plot (Figure 7.6). Only one soil core sample position was in the source area (S_S) near the cup position and 3 core samples were located left (S_L) and right (S_R) of the source area and one core upslope (S_U). 6 cores were located downslope (S_{D1} , S_{D2} , S_{D3} , S_D , S_{D4} and S_{D5} ; Figure 7.6). Soil core samples were taken using a hydraulic soil sampler and the core was divided into 0-30 cm, 30-60 cm and 60-90 cm sampling depths. In total, 180 soil samples were taken and the samples were stored as described as above.

At the end of experiment 2, soil core samples were collected on 2 May 2012. 10 soil cores were collected for each circle of porous cup samplers inside each plot (Figure 7.7) giving replicate sets of samples per plot. Only one soil core sample position was in the source area (S_S) near the cup position and 2 cores samples were located left (S_L) and right (S_R) of the source area. 6 cores were located downslope (S_{D1} , S_{D2} , S_{D3} , S_D , S_{D4} , S_{D5} and S_{D6} ; Figure 7.7). All processes of sampling were similar to those described above.

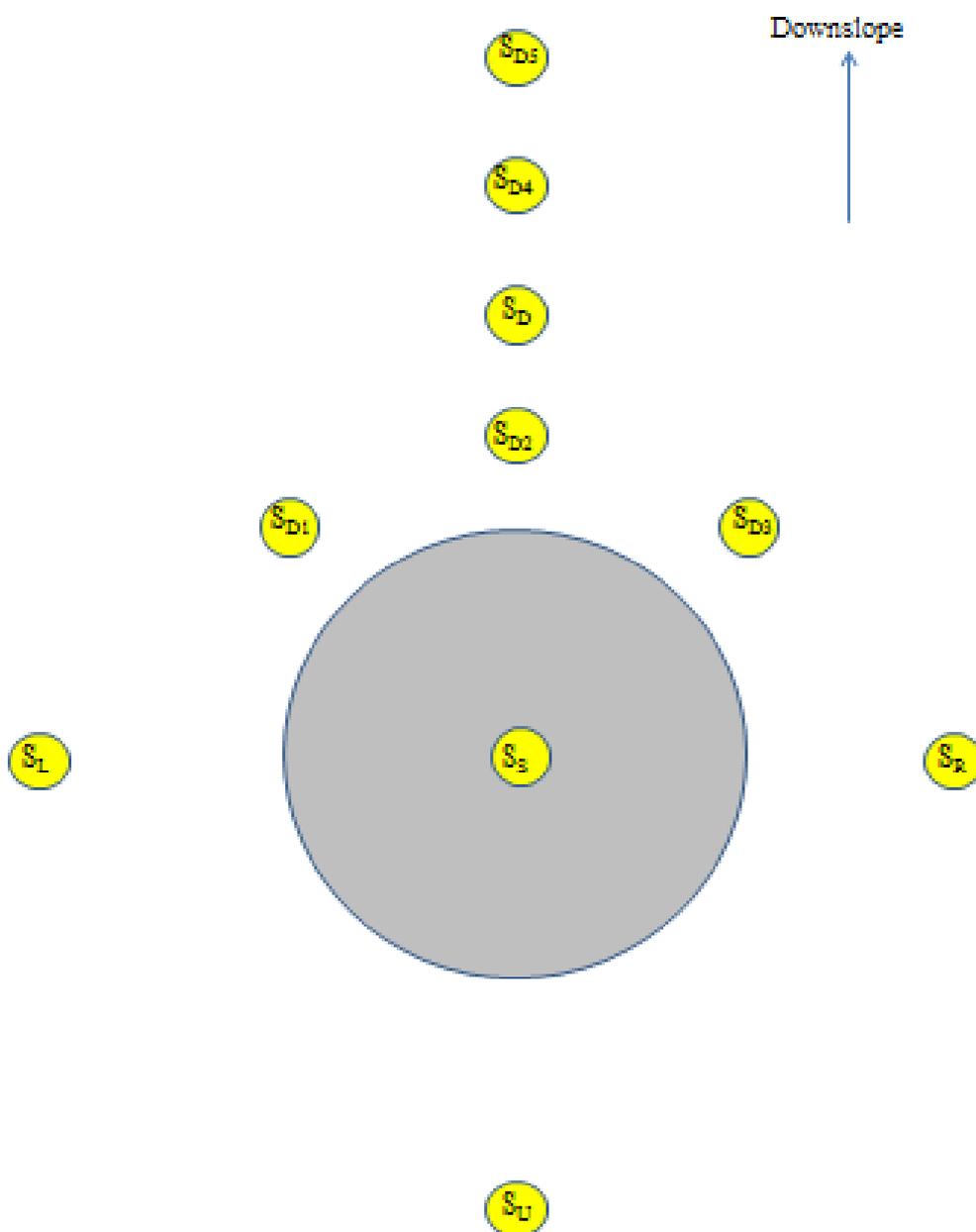


Figure 7.6 Detail of experimental design in the field for Experiment 1 showing location of the soil sampling points for bromide recovery following application (to a circle of 0.5 m radius). Samples were taken at the centre of the source area S_S and outside source area S_U , S_L and S_R , and downslope S_{D1} S_{D2} S_{D3} S_{D4} S_{D5} .

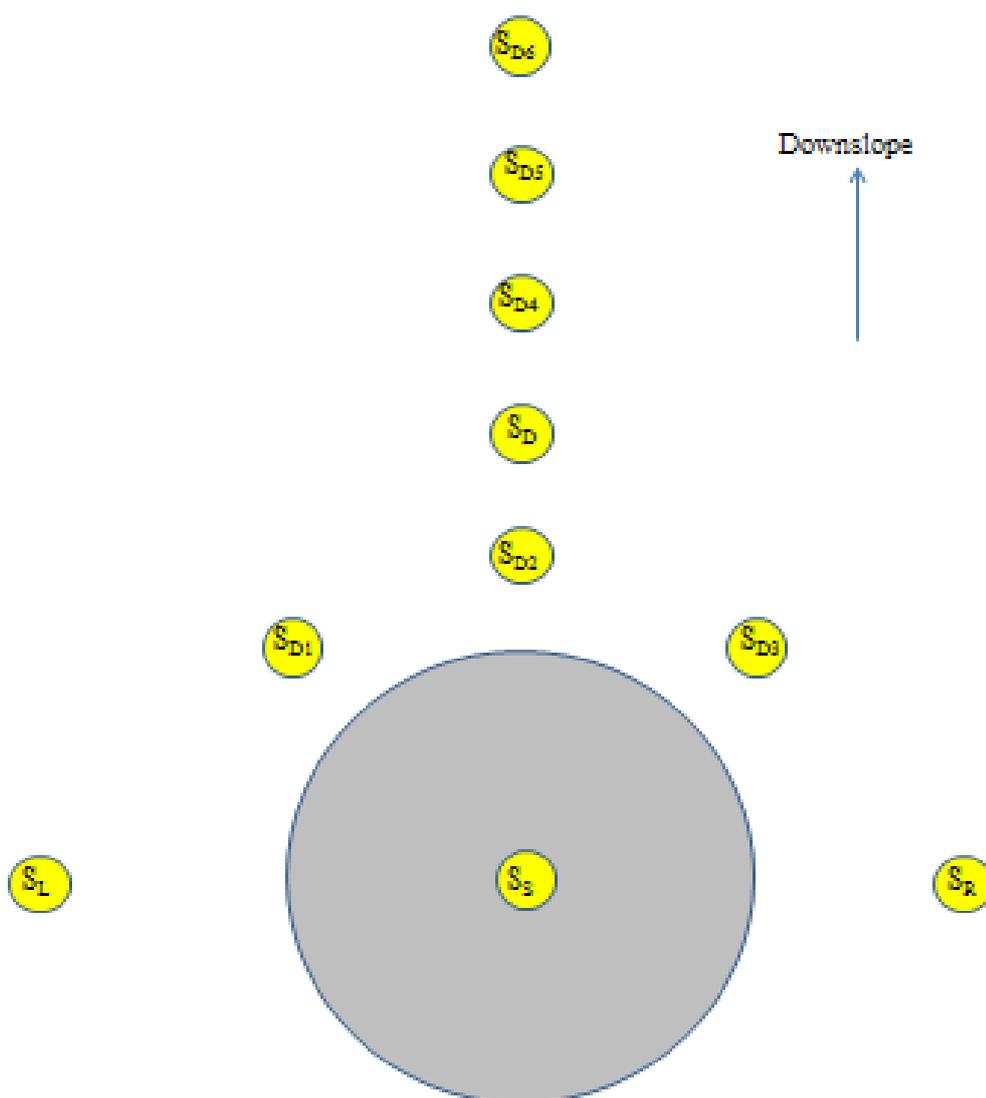


Figure 7.7 Detail of experimental design in the field for Experiment 2 showing location of the soil sampling points for bromide recovery following application (to a circle of 0.5 m radius). Samples were taken at the centre of the source area S_s and outside source area S_L , S_R , and downslope S_{D1} S_{D2} S_{D3} S_D S_{D4} S_{D5} S_{D6} .

7.2.9 Soil extractions

Soil samples were taken from the freezer and left for 1 to 3 hours to thaw. All soil samples were mixed and sieved (< 4 mm) to ensure that each composite sample represented the layer and avoid any variability of bromide concentrations that could be found over a small distance. The soil water content of each soil sample for each depth was determined gravimetrically using *c.* 75 g of moist soil (105°C for 24 hours). Soil bulk density was determined for each sample collected using the hydraulic corer by drying and weighing an intact portion of the core of known length; average bulk density values for each soil depth were used to convert the gravimetric soil water content to volumetric water content (Martin, 1993; Gebregiorgis and Savage, 2007).

Preliminary extractions were made first using a 1:1 ratio (20 g soil and 20 ml deionised water) and a 1:2 ratio (10 g soil and 20 ml deionised water); however, the extraction solutions obtained had a strong dark brown colour and were very difficult to filter using a 0.45 µm syringe filter. Hence the extraction method was changed to a ratio of 1:5 as described by Kessavalou *et al.* (1996) this ratio produces less colouration in the solution. Briefly, 8 g of soil was weighed into a polypropylene extraction bottle, 40 ml deionised water was added and the extraction bottle was placed on a shaker at 300 rpm for one hour. The resulting suspension was centrifuged at 4500 rpm for 15 minutes at a temperature of 15 °C and filtered (Whatman 42) into extraction bottles. In order to reduce the intensity of dark colour, samples were refrozen at -20 °C for three days and taken from the freezer and left for 3 hours to thaw. Once thawed a brown coloured material precipitated to the bottom of the tube and was removed by filtering through syringe filters (0.25µm cellulose acetate membrane) ahead of Br⁻ determination.

7.2.10 Analysis of bromide in soil solutions and soil extracts

Concentrations of bromide and nitrate in the soil extracts and samples collected from the porous ceramic cups were determined using ion chromatography. The Ion Chromatograph used is in the Environmental Engineering teaching laboratory and is a Dionex ICS-1000 with an AS40 auto sampler. The column is an Ionpac AS14A, 4 x 250 mm analytical column. The flow rate is 1 ml min⁻¹, the eluent is 8.0 mM Na₂CO₃/1.0 mM NaHCO₃ solution and the injection loop is 25 µl.

Bromide standards (0.2, 0.6, 1.0, 2.0, 4, 5, 10, 20, 30, 40 and 50 ppm) were prepared using sodium bromide salt, a sample of de-ionised water was also used as blank. These standards were used as samples in each sample run to check the accuracy of the ion chromatography.

7.2.11 Preliminary determination of the efficiency of the bromide extraction (ratio 1:5)

The bromide extraction method of 1:5 soil water ratio recommended by Kessavalou *et al.* (1996) was evaluated in a bromide recovery experiment. About 5 grams of each 12 soil samples (6 topsoil and 6 subsoil) were incubated for 24 hours with 2.5 ml of bromide solution (20 ppm and 40 ppm). All the samples were then extracted and prepared for analysis as described above. A soil sample without bromide and a water sample without bromide were also used. The concentration of bromide in the extract was determined using ion chromatography and the percentage of bromide recovered was calculated as follows:

Amount of bromide added =

Br ppm × volume of bromide solution added.

Amount of bromide extracted =

reading from ion chromatograph × (volume of bromide solution added + volume of water added).

Efficiency of extraction (%) =

(amount of bromide extracted/ amount bromide added) × 100

Most of the applied bromide was recovered in the soil samples (Table 7.1) showing no marked Br⁻ adsorption by the soil.

Table 7.1 Efficiency of bromide extraction with water using an extraction ratio of 1:5.

Bromide added ($\mu\text{g g}^{-1}$)	Depth (cm)	Br ⁻ recovery (%)	Br ⁻ recovery			
			Mean	SD	SE	CV%
50	0-30	94.74-97.01	96.09	1.19	0.688	1.23
50	30-60	90.68-96.35	93.69	2.84	1.64	3.03
100	0-30	91.51-95.99	93.57	2.26	1.31	2.42
100	30-60	90.09-94.05	91.78	2.04	1.18	2.22

7.2.12 Calculation of bromide recovery in soil

Bromide concentrations in soil samples per unit volume were determined from the soil extracts and the measured soil bulk density for each sampling depth. The soil cores collected from within the source area (S_S) were used to estimate the vertical redistribution of the bromide applied to the soil surface in the source area. Bromide concentrations mg kg^{-1} at each soil sample position and depth are converted to g Br^- . For vertical redistribution the average mass of Br^- (g) in S_S from each sampling depth in each replicate area was used for recovery calculations, recovery values from each sampling depth were summed to give total Br^- recovery in the 90 cm profile within the source area for each plot.

Soil cores collected from outside the source area (S_{D1} , S_{D2} , S_{D3} and S_D) were used to estimate any lateral redistribution of bromide. Calculation of overall Br^- recovery in soil is then dependent on how the Br^- concentrations determined for the soil cores are scaled up to the plot scale using two methods to allocate the representative volume of soil sampled outside the source area.

In the first method, Br^- recovery was estimated using methods similar to those described by Whetter *et al.* (2008) and Tilahun *et al.* (2005). However the design of the experiment is completely different. The design of the first method of allocation is shown in (Figure 7.8). Soil cores collected from downslope (S_{D1} , S_{D2} , S_{D3} and S_D) were considered to represent the plot segment of which they were the centre; this allows any lateral redistribution of bromide to be estimated. For the lateral redistribution the average concentration of g Br^- at each downslope sample from the same depth at each replicate plot was used for recovery calculations, recovery values from each sampling depth were summed to give total Br^- recovery in the 90 cm profile for each downslope

position, the sum of the recovery in areas centred on S_D , S_{D2} , and S_{D3} in each plot was used for lateral recovery.

In the second method of allocation for the calculation of lateral Br^- recovery, the positions of downslope samples (S_D , S_{D1} , S_{D2} , S_{D3} and S_{D4}) were considered to represent edge concentrations. The concentration of Br^- at S_{D1} was zero therefore we assumed no Br^- had moved beyond this point, at S_{D3} Br^- concentrations were measurable and we assumed there might be some Br^- beyond this point, therefore an additional “imaginary sample” S_{DX} was located beyond S_{D3} , and the concentration at S_{DX} was assumed to be zero. The concentration of Br^- in each area was then calculated as the average of the measured Br^- concentrations at each edge position. For the lateral redistribution the average concentrations of g Br^- in each area from each sampling depth were summed to give total Br^- recovery in the 90 cm profile for lateral recovery.

For both methods, the quantity of Br^- in each segment were calculated by multiplying the area of the segment (Figure 7.8) and (Figure 7.9) with the Br^- concentration estimated according to the allocation methods described above.

e.g. For Method 1

In segment S_D Quantity of Br^- =

concentration in soil core (0-30cm) at S_D x area of the S_D segment x layer depth (30cm) +
 concentration in soil core (30-60cm) at S_D x area of the S_D segment x layer depth (30cm) +
 concentration in soil core (60-90 cm) at S_D x area of the S_D segment x layer depth (30cm)

For Method 2

In segment between S_D and S_{D2} Quantity of Br^- =

(concentration in soil core (0-30cm) at S_D + concentration in soil core (0-30cm) at S_{D2} / 2)
 x area of the segment (segment between S_D and S_{D2})
 x layer depth (30cm) and same calculation for 30-60, 60-90 cm.

The total recovery was estimated from the sum of the mass of Br^- in each segment:

Br^- recovery % = 100 x (total Br^- measured (g) / total amount of Br^- (g) applied).

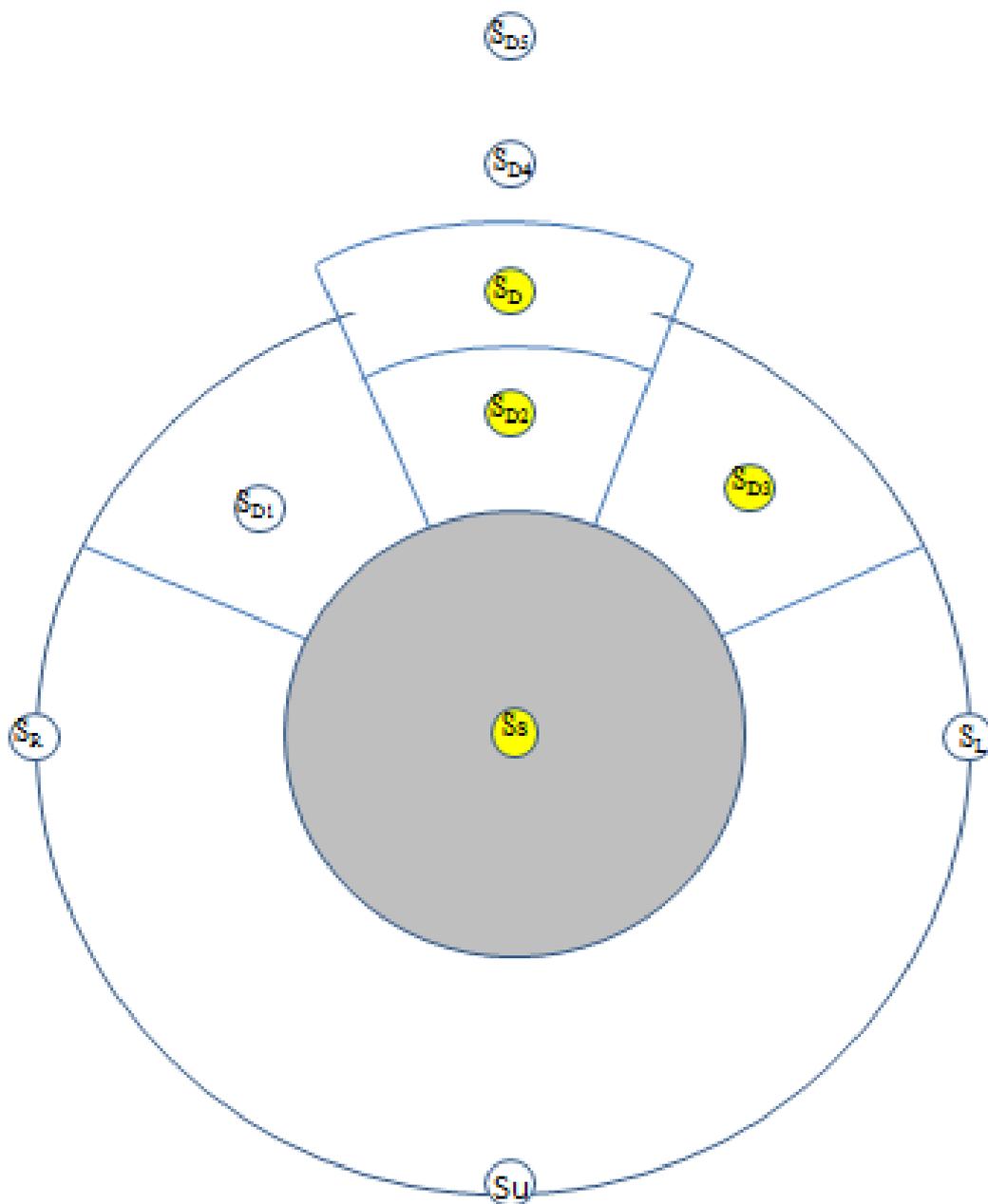


Figure 7.8 Lateral recovery– allocation of representative areas for each soil sample in Method 1. Area of bromide application indicated in grey (source). Soil cores indicated by blue circles had measurable bromide, soil cores indicated by white circles had no measurable bromide.

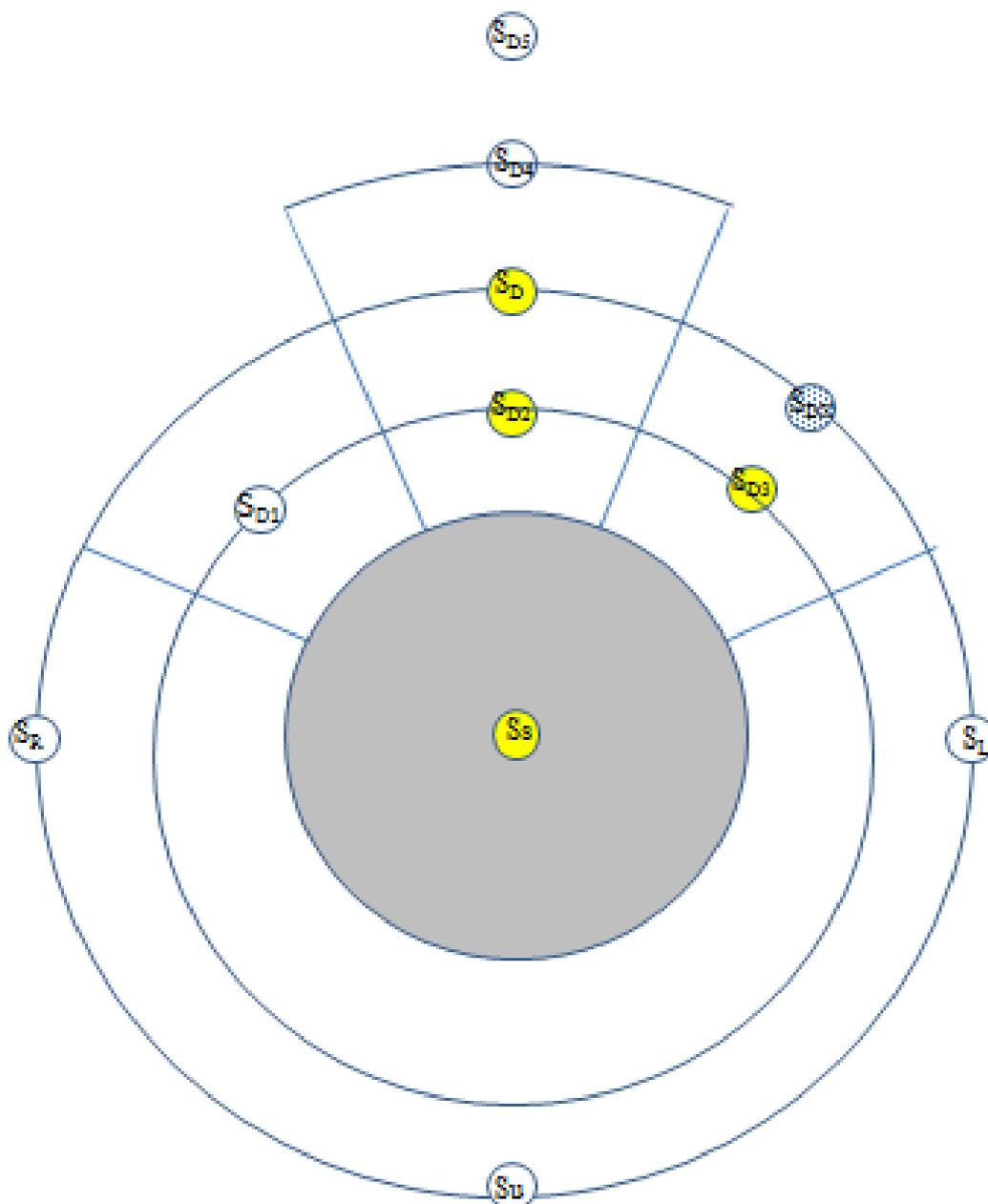


Figure 7.9 Lateral recovery—allocation of representative areas for each soil sample in Method 2. Area of bromide application indicated in grey (source). Soil cores indicated by blue circles had measurable bromide, soil cores indicated by white circles had no measurable bromide. For this method an additional “imaginary sample” S_{Dx} with no measurable bromide was added.

7.2.13 Statistical analysis

Cup data were collected from three replicate plots and two depths. However in experiment 1 bromide was detected in only two sample positions and so only these data were included in the statistical analysis. In experiment 2, bromide was detected in three sample positions. The effect of sample position, depth and their interactions on the total amount of bromide passing through the cups were tested statistically using a General Linear Model (GLM) using Minitab 16 software:

= depths sample positions (depths x sample positions)

The residuals were tested for normality. Data from experiment 1 was transformed using square roots. Data for experiment 2 had normal distribution. Differences between individual means were tested using Tukey's pair-wise comparisons following analysis of variance.

Soil samples used to calculate bromide recovery were collected from all 3 plots with two replicate subplots (one associated with the cups at 30 cm and one associated with the cups installed at 60 cm). The effect of plots, subplots, sample position, depth (3 plots x 2 subplots x 3 sample position x 3 depths) and their interactions were analysed as complete factorial analysis of variance using a General Linear Model (GLM) using Minitab 16 software. All data were tested for Normality. Data of soil samples collected for Br⁻ recovery in experiment 2 were transformed using square roots. All other data had normal distributions. Subsequently the complete factorial analysis of variance was repeated for each depth separately. This then allowed the variance to be allocated treating the depth as a split plot. Differences between individual means were tested manually using Tukey's pair-wise comparisons of analysis of variance with reference to published tables.

7.3 Results

7.3.1 Weather patterns during the experiments

During experiment 1 (March – June 2011), air and soil temperatures increased (Table 7.2) and calculated evapotranspiration also showed a marked increase. The cumulative rainfall during experiment 1 was 70.4 mm and the estimated drainage was 19 mm in the same period (Figure 7.10). In experiment 1, bromide was applied at the end of the winter period and the rainfall in the two months prior to the start of the experiment was 72.3 mm with an associated estimated drainage of 59 mm (Figure 7.10).

Before the start of experiment 2, the cumulative rainfall was 150 mm (September to November 2011 (Figure 7.10), and the measured soil water content in soil samples collected on 14 September 2011 indicated that the soil was already at field capacity; estimated total drainage from September to November 2011 was 38 mm. During experiment 2, the monthly average daily air temperature (December 2011 – April 2012) ranged from 1.71 °C to 7.4 °C, the coldest period was in January and the highest temperatures were recorded in March (Table 7.2). Spring 2012 was wetter and cooler than 2011. During the experimental period, the cumulative rainfall was 224 mm (December 2011 to April 2012, Figure 7.10) with an estimated associated total drainage of 180 mm (Figure 7.10).

Table 7.2 Monthly relative humidity, air temperature and soil temperature data for experiment 1, and experiment 2. Values are means. Data obtained from weather station at Nafferton farm.

2011	March	April	May	June		
Mean relative humidity (%)	83.7	75.5	72.9	81.0		
Mean Air Temperature (°C)	5.37	9.76	10.48	12.38		
Mean Soil Temperature (°C)	5.30	11.01	12.48	14.94		
2011-2012	Dec	Jan	Feb	March	April	May
Mean relative humidity (%)	87.0	80.5	84.7	82.9	91.6	91.8
Mean Air Temperature (°C)	4.63	1.71	4.89	7.40	5.59	9.12
Mean Soil Temperature(°C)	5.25	3.30	5.20	7.29	7.14	10.18

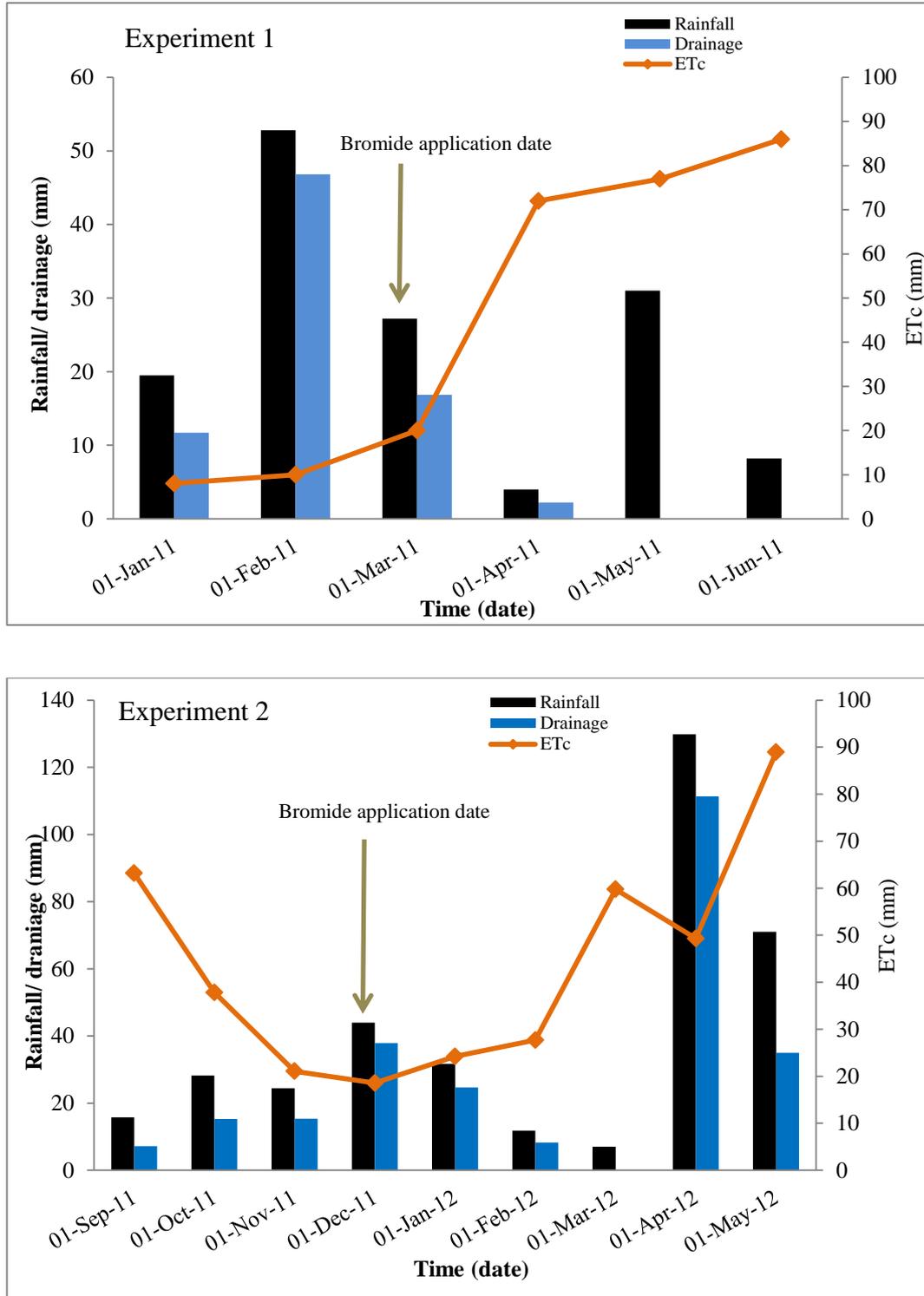


Figure 7.10 Total monthly rainfall, evapotranspiration and drainage during bromide experiments spring 2011 and overwinter 2011/2012. Rainfall was measured at the weather station of Nafferton farm, evapotranspiration was estimated using the Penman-Monteith equation for the whole period January to June 2011 for experiment 1, and from September 2011 to May 2012 for experiment 2.

7.3.2 Experiment 1 - Bromide concentrations measured in porous ceramic cups

A total of 150 soil solution samples were collected from the experimental plots during experiment 1. No drainage occurred between the last two sampling dates (7 April to 25 May 2011).

At source (Cs)

At the source, the mean concentration of Br^- of soil solution extracted from the porous ceramic cups at 30 cm depth ranged from 9.3 to 28.0 mg l^{-1} (average 20.2 mg l^{-1}) and at 60 cm the mean Br^- concentration ranged from 0.31 to 5.5 mg l^{-1} (average 2.9 mg l^{-1}). One week after Br^- application (following 8 mm of cumulative drainage) the bromide concentration at 30 cm depth increased markedly from zero to 12.7 mg l^{-1} and then increased further to 28.0 mg l^{-1} two weeks after application (13.8 mm of cumulative drainage, Figure 7.11). The bromide concentration then declined slightly but not significantly until the end of the experiment.

A trace amount (0.31 mg l^{-1}) of bromide was measured in soil solution extracted from the porous ceramic cups at 60 cm depth 7 days after bromide application (8 mm of cumulative drainage, Figure 7.11). Average Br^- concentration increased at 60 cm depth to reach an average concentration of 5.5 mg l^{-1} after 19 mm of cumulative drainage at the end of the drainage period (Figure 7.11).

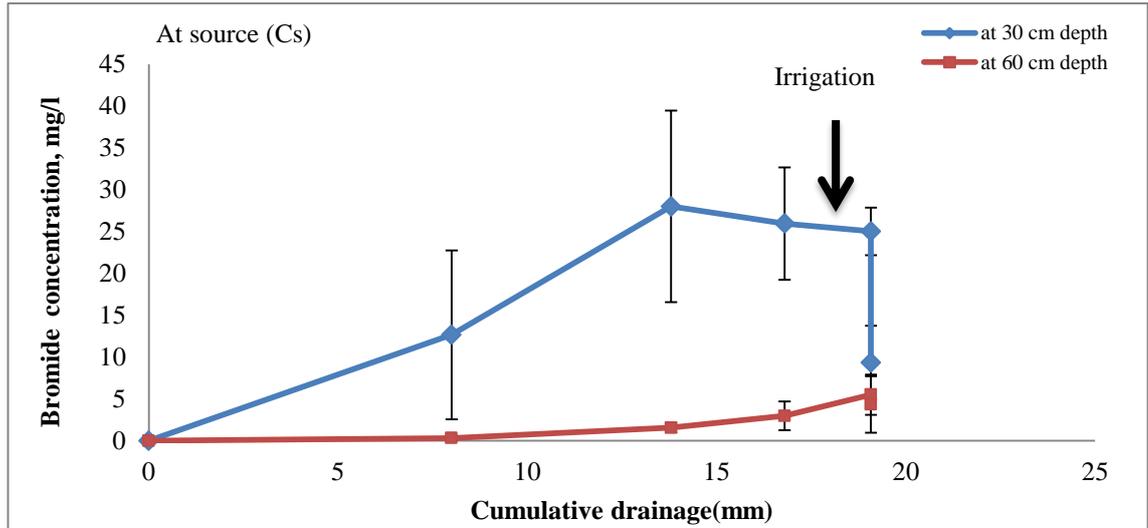


Figure 7.11 Br^- concentrations ($mg\ l^{-1}$) at source extracted from porous ceramic cups at 30 and 60 cm depth during experiment 1. Mean values for three plots given (with \pm SE of the mean) plotted against estimated cumulative drainage (mm).

Outside the source area

No bromide was detected in the soil solution samples taken from the porous cups at 30 and 60 cm in most of the positions outside the source area. However, bromide was detected in samples from the cup (C_D) which was located immediately downslope of the source.

At C_D , the mean concentration of Br^- of soil solution extracted from the porous ceramic cups at 30 cm depth increased from zero to around $3\ mg\ l^{-1}$ 14 days after Br^- application (13.8 mm of cumulative drainage; Figure 7.12). On the last sampling occasion (81 days after application) bromide concentrations of $6.0\ mg\ l^{-1}$ were measured (Figure 7.12).

The mean concentration of Br^- of soil solution at 60 cm depth at C_D was measurable but low ($0.26\ mg\ l^{-1}$) following 13.8 mm of cumulative drainage and then increased slightly with the highest concentration of $1.0\ mg\ l^{-1}$ measured in the last sampling event (Figure 7.12).

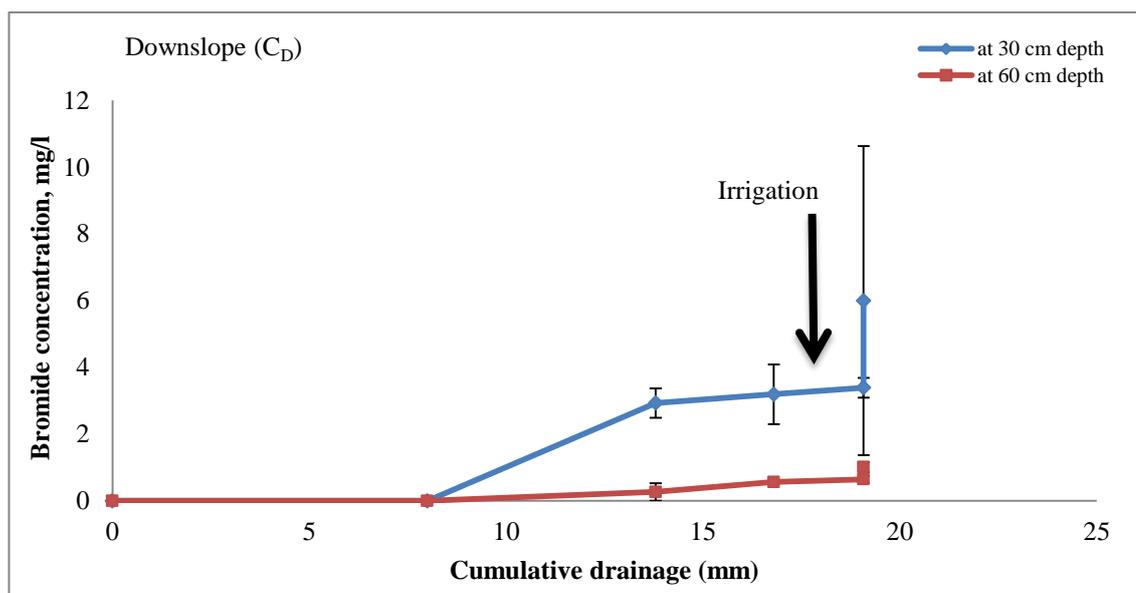


Figure 7.12 Br^- concentrations ($mg\ l^{-1}$) downslope of the source extracted from porous ceramic cups at 30 and 60 cm depth during experiment 1. Mean values for three plots given (with \pm SE of the mean) plotted against estimated cumulative drainage (mm).

The amount of bromide detected by the porous cups in the source area was very significantly higher than at the downslope position (Table 7.3). The amount of bromide which moved past 30 cm in the source area was very significantly higher than the all other depths and locations; similar amounts of bromide moved vertically past 60 cm in the source area or laterally from the source area which was detected passing 30 cm downslope (Table 7.3).

Table 7.3 Quantity of Br^- ($kg\ ha^{-1}$) which passed the cups at 30 and 60 cm depths for experiment 1. Mean values for three plots given with $\pm SE$ of the mean.

Sample depth cm	C _s	C _D	Mean
30	2.58±0.98 ^a	0.33±0.03 ^b	1.46 A
60	0.33±0.10 ^b	0.12±0.03 ^b	0.23 B
Mean	1.45 ^a	0.22 ^b	0.84

Within the body of the table, means followed by the same lower case red letter are not significantly different (Tukey's $p > 0.05$); means for each row (sample depth) followed by the same upper case letter are not significantly different; means for each column (position) followed by the same lower case letters are not significantly different.

7.3.3 Experiment 1 – nitrate concentrations measured in porous ceramic cups

Nitrate concentrations measured in the soil solution during the late winter period varied from 1.5–31.3 $mg\ NO_3^-\ l^{-1}$. Very low nitrate concentrations were measured especially at 30 cm once active plant growth had started (on the last sampling occasion). There was little temporal variation during the late winter period but there were marked differences between plots (Figure 7.13). Plot B had significantly higher nitrate concentrations measured at 30 cm (average 26.5 $mg\ NO_3^-\ l^{-1}$) than plots A and C (11.1 and 7.1 $mg\ NO_3^-\ l^{-1}$, respectively). Plots A and B had similar concentrations of nitrate measured at 60 cm; Plot C had much lower concentrations (Figure 7.13). Overall the amount of nitrate moving past 60 cm in this period in all plots was small $< 1.5\ kg\ NO_3^-\ kg\ ha^{-1}$.

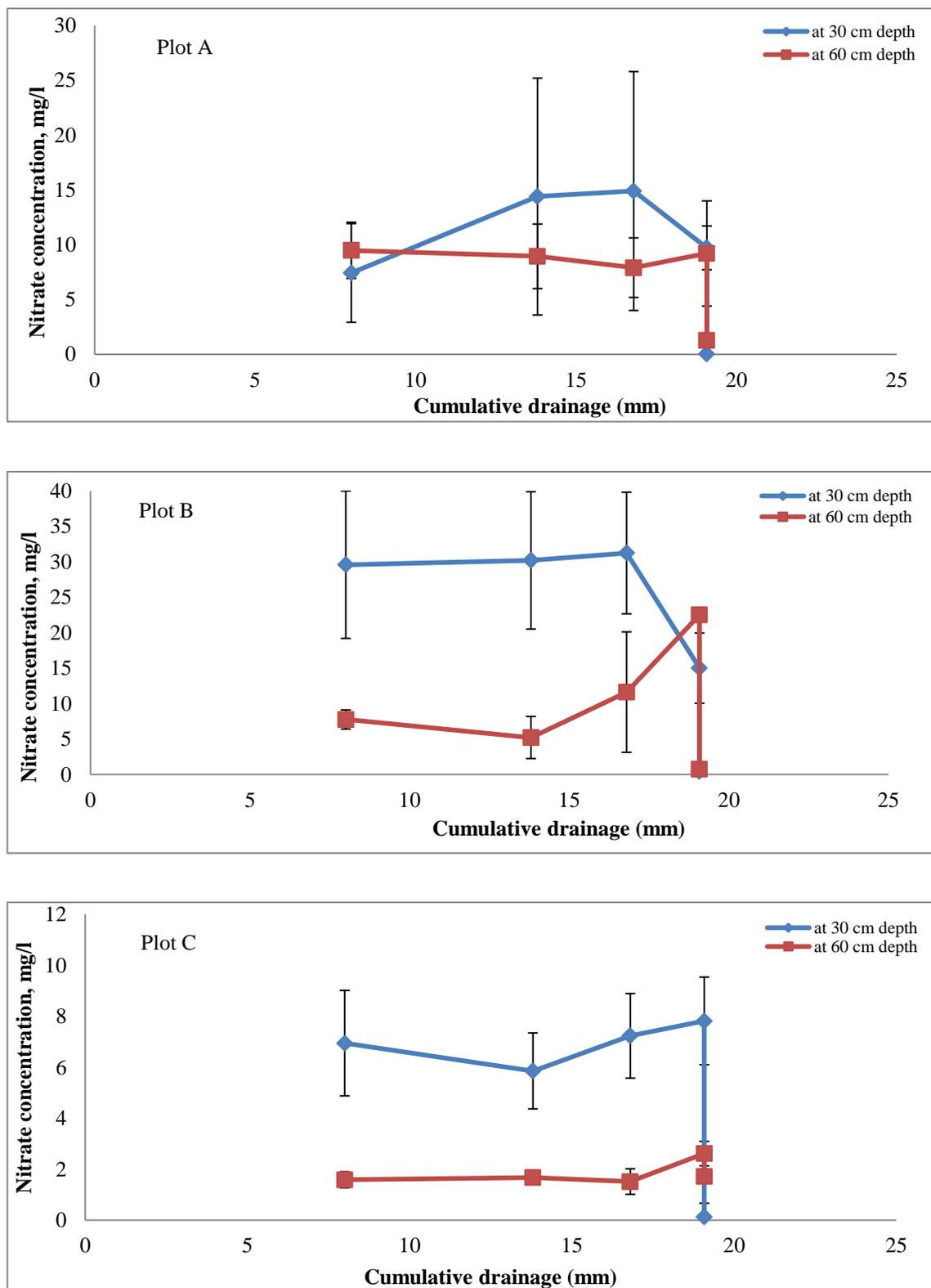


Figure 7.13 NO_3^- concentrations ($mg\ l^{-1}$) extracted from porous ceramic cups at 30 and 60 cm depth during experiment 1, plotted against a cumulative drainage (mm) for plots A, B and C. Mean values for 5 cups given with \pm SE of the mean.

7.3.4 Experiment 2 – Bromide concentrations measured in porous ceramic cups

A total of 390 soil solution samples were collected between November 2011 and May 2012 in experiment 2.

At source (Cs)

At the source (Cs) the concentration of Br⁻ of the soil solution extracted from the porous ceramic cups at 30 cm depth during the experiment period ranged from 27.6 to 342.6 mg l⁻¹ (average 180.7 mg l⁻¹) and at 60 cm the Br⁻ concentration ranged from 34.7 to 192.0 mg l⁻¹ (average 89.1 mg l⁻¹).

When the first soil solution sample was taken after surface application of the Br⁻ tracer (day 20, 24 mm drainage), the concentration of bromide at 30 cm depth was already 27.6 mg l⁻¹ (Figure 7.14). Bromide concentrations increased in soil solution at 30 cm to reach a maximum of 342.6 mg l⁻¹ on 23 Feb 2012 (after 71 mm drainage; 85 days after application). Br⁻ concentrations in soil solution then declined with a second broader peak observed in April (maximum 199 mg l⁻¹; 104 mm cumulative drainage, 134 days after application). Bromide concentration in the soil solution at 30 cm was 49.3 mg l⁻¹ when sampling ceased on 30 April 2012 (180 mm cumulative drainage, 152 days after tracer application; Figure 7.14).

The concentration of bromide in the porous cups at 60 cm depth when the first soil solution sample was taken was already 34.7 mg l⁻¹. High bromide concentrations (> 100 mg Br l⁻¹) were seen at 60 cm depth until 71 days after Br⁻ application (65 mm cumulative drainage). A subsidiary peak (133 mg l⁻¹) was observed after 125 mm cumulative drainage (141 days after bromide application; Figure 7.14). Bromide concentration at 60 cm subsequently exceeded that at 30 cm and was 94.6 mg l⁻¹ when sampling ceased on 30 April 2012 (182 mm cumulative drainage, 152 days after tracer application; Figure 7.14).

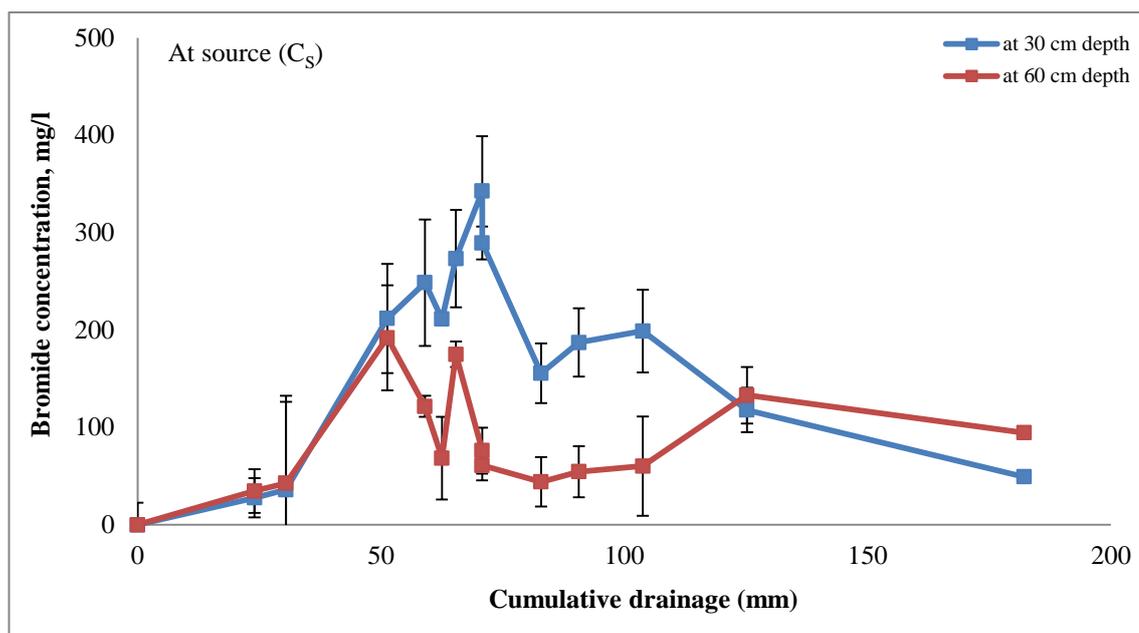


Figure 7.14 Br^- concentrations ($mg\ l^{-1}$) at source extracted from porous ceramic cups at 30 and 60 cm depth during experiment 2, plotted against a cumulative drainage (mm), 2011-2012. Mean values given with \pm SE of the mean.

Outside the source area

No bromide was detected in the soil solution samples taken from the porous cups at 30 and 60 cm in most of the positions outside the source area. However, bromide was detected in samples from the cups (C_{D2} , C_D) which were located immediately downslope of the source.

Downslope at C_{D2} the mean Br^- concentrations of soil solution extracted from the porous ceramic cups at 30 cm depth ranged from 0.30 to 28.2 $mg\ l^{-1}$ (average 12.8 $mg\ l^{-1}$) and ranged from 0.85 to 4.8 $mg\ l^{-1}$ at 60 cm depth (average 2.18 $mg\ l^{-1}$). The first trace Br^- concentration appeared at 30 cm 29 days after of bromide application (30 mm cumulative drainage; Figure 7.15). A broad peak where Br^- concentration was increased significantly above background ($> 17.5\ mg\ Br\ l^{-1}$) was seen between 59 and 100 mm cumulative drainage. Bromide concentration in the soil solution at 30 cm was 1 $mg\ l^{-1}$ when sampling ceased on 30 April 2012 (180 mm cumulative drainage, 152 days after

tracer application; Figure 7.15). However, at 30 cm, concentrations in individual plots varied widely throughout the sampling period.

At 60 cm depth (C_{D2}), no bromide was detected until 6 January 2012 when 3.31 mg l^{-1} was recorded (37 days after application, 51 mm cumulative drainage). The concentration of bromide in soil solution at 60 cm peaked at 4.78 mg l^{-1} (59 mm of cumulative drainage, 57 days after application). At the final sampling (180 mm cumulative drainage, 152 days after tracer application) bromide concentrations at 60 cm were 1.70 mg l^{-1} (Figure 7.15).

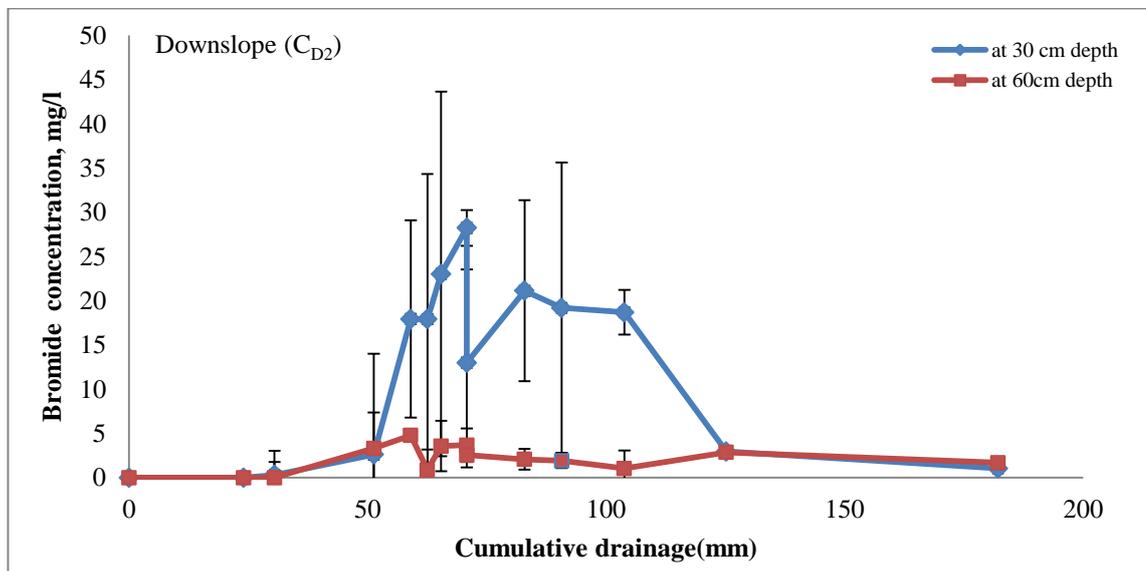


Figure 7.15 Br^- concentrations (mg l^{-1}) downslope of the source (C_{D2} , 25 cm outside source area) extracted from porous ceramic cups at 30 and 60 cm depth during experiment 2, plotted against a cumulative drainage (mm) during experiment 2011-2012. Mean values for three plots given with \pm SE of the mean.

Further downslope, 50 cm outside the source area (C_D) the mean Br^- concentrations of soil solution extracted from the porous ceramic cups ranged from 0.00 to 1.79 mg l^{-1} (average 0.85 mg l^{-1} at 30 cm depth and 0.18 mg l^{-1} at 60 cm depth. A trace amount of bromide (0.1 mg l^{-1}) was first detected at 30 cm depth 29 days after bromide application (Figure 7.16). The amount of bromide detected at C_D was small but the concentrations showed a broad peak during the monitoring period (maximum at 30 cm was 1.79 mg l^{-1} after 70 mm of cumulative drainage; 96 days after bromide application; Figure 7.16). A

similar broad low peak was seen at 60 cm depth with Br^- concentrations of 0.16 to 0.20 mg l^{-1} (59 - 82 mm cumulative drainage; Figure 7.16). No Br^- was detected at either 30 or 60 cm depth on the last sampling occasion.

The amount of bromide moving past the porous cups in the source area at both 30 and 60 cm depth was very significantly higher than at either downslope position; but there was no significant difference between the downslope positions (Table 7.4). The variability in Br^- between cups at 30 cm in the source area (C_S) (8.1%) was much less than downslope (67% for C_{D2} and 49% for C_D); variability at 60 cm was even greater.

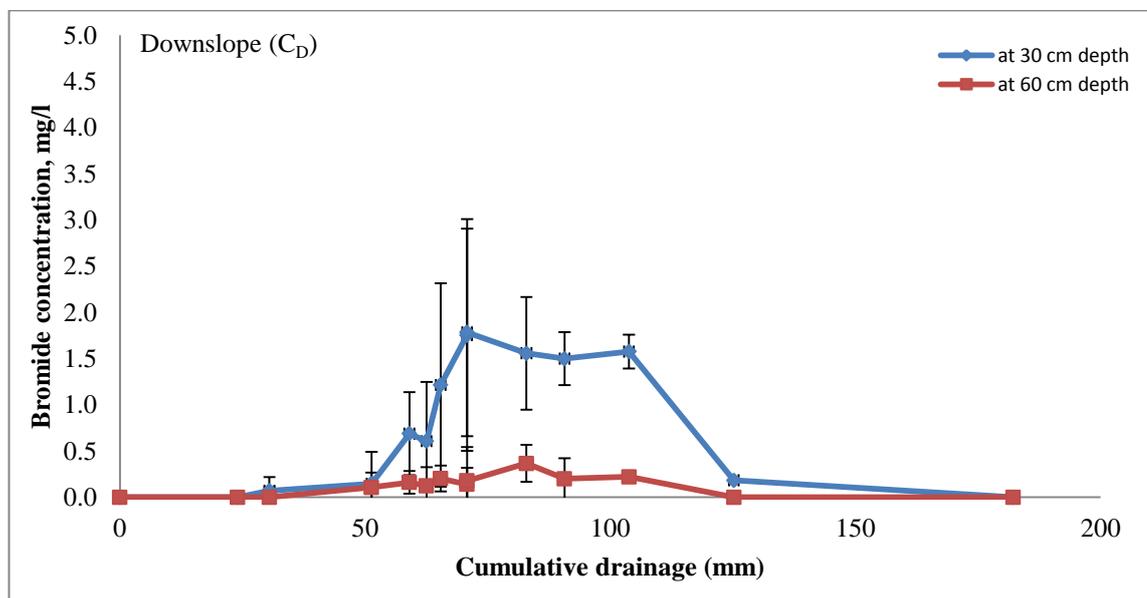


Figure 7.16 Br^- concentrations (mg l^{-1}) 50 cm downslope from the source extracted from porous ceramic cups (CD) at 30 and 60 cm depth during experiment 2, plotted against a cumulative drainage (mm) during experiment 2011-2012. Mean values for three plots given with \pm SE of the mean.

Table 7.4 Quantity of Br⁻ (kg ha⁻¹) which passed the cups at 30 and 60 cm depths by the end of the experiment. Mean values for three plots given with ± SE of the mean.

depth cm	C _S	C _{D2}	C _D	Mean
30	224.33±18.1a	12.75±8.52b	0.73±0.36b	79.27 A
60	155.86±22.5a	2.99±2.08b	0.15±0.14b	53.00 B
Mean	190.09a	7.87b	0.22b	66.13

Within the body of the table, means followed by the same lower case red letter are not significantly different (Tukey's $p > 0.05$); means for each row (sample depth) followed by the same upper case letter are not significantly different; means for each column (position) followed by the same lower case letters are not significantly different.

7.3.5 Experiment 2 – Nitrate concentrations measured in porous ceramic cups

Nitrate concentrations measured in the soil solution overwinter in experiment 2 varied from 0.1 – 51.7 mg NO₃⁻ l⁻¹. There was marked temporal variation overwinter with a peak of nitrate concentration seen between 40 and 80 mm cumulative drainage and some differences in the temporal pattern and peak concentrations between plots (Figure 7.17). Overall the amount of nitrate moving past 60 cm in this period in all plots was 11.2, 13.0 and 7.4 kg NO₃⁻ kg ha⁻¹ for plots 1, 2 and 3 respectively.

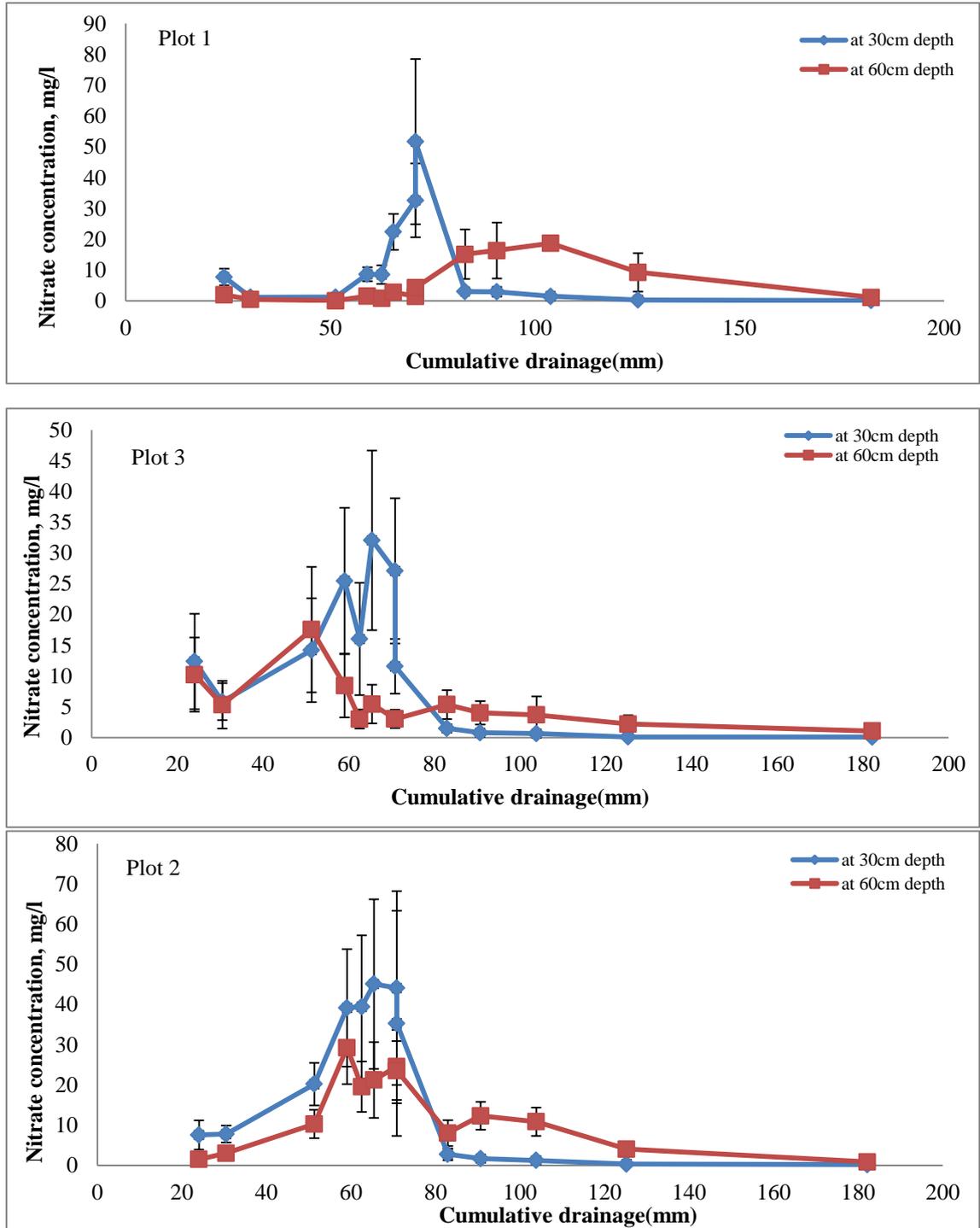


Figure 7.17 Mean NO_3^- concentrations (mg l^{-1}) extracted from five replicate porous ceramic cups at 30 and 60 cm depth in each plot during experiment 2, plotted against cumulative drainage (mm). Mean values given with \pm SE of the mean.

7.3.6 Experiment 1 - Bromide recovered in soil

No detectable background bromide was measured in the soil samples collected before experiment 1. At the end of the experiment, no bromide was detected at locations S_{D1} , S_{D4} , S_{DL} and S_{DR} (Figure 7.8). Hence these data were not included in further statistical analysis.

Plots and Subplots - there was no significant difference in the mean bromide concentrations (across all subplots, depths and sample positions) between the replicate plots or sub-plots.

Depth - bromide concentrations were significantly higher ($p = <0.001$) in the topsoil (0-30 cm; 10.24 mg kg^{-1}) than at both 30-60 cm and 60-90 cm depths. Concentrations measured at 30-60 cm (4.62 mg kg^{-1}) were also significantly higher than the concentrations at 60-90 cm (1.67 mg kg^{-1}) when averaged over all plots, subplots and sample positions (Table 7.5).

Sample position - bromide concentrations were significantly higher ($p = <0.001$) within the source area S_S (13.24 mg kg^{-1}) than in S_{D2} (1.84 mg kg^{-1}) and S_{D3} (1.45 mg kg^{-1}) when averaged over all plots and depths. The average total bromide concentrations (0-90 cm) was 39.74 mg kg^{-1} at S_S , 5.54 mg kg^{-1} at S_{D2} and 4.38 mg kg^{-1} at S_{D3} averaged across plots, subplots and depths (Table 7.5).

Interaction between factors - there was a significant 2-way interaction ($p = <0.01$) between sample position and depth; all two and three way interactions were not significant.

At the source (S_S) the sample from 0-30 cm depth had the highest bromide concentration (average across plots of 24.84 mg kg^{-1}) with about twice the amount detected in the 30-60 cm depth (10.82 mg kg^{-1}) (Table 7.5).

The relative difference between top-soil and sub-soil concentrations of Br^- was similar at the other sample positions. At S_{D2} the average concentration of bromide measured between the plots at 0-30 cm (2.97 mg kg^{-1}) and was higher than the average measured between 30-60 cm (1.73 mg kg^{-1}) depth (Table 7.5). At S_{D3} the mean concentration of

bromide measured in all plots at 0-30 cm was 2.92 mg kg⁻¹ with 1.32 mg kg⁻¹ at 30-60 cm; (Table 7.5).

Table 7.5 Br⁻ concentrations (mg kg⁻¹) measured in soil samples at 0-30, 30-60 and 60-90 cm depth in three plots 88 days after application of NaBr in experiment 1. Samples were collected at the source (Ss) where Br⁻ was applied and down slope (25 cm) outside the source area (S_{D2}, S_{D3}). For full description see figure 7.6 and 7.7. Values are means ± SE.

Depth cm	Ss	S _{D2}	S _{D3}	Mean
0-30	24.84 ^a ± 2.03	2.97 ^d ± 0.57	2.92 ^d ± 0.67	10.24A
30-60	10.82 ^b ± 2.28	1.73 ^d ± 0.51	1.32 ^d ± 0.41	4.62B
60-90	4.07 ^c ± 2.10	0.82 ^d ± 0.44	0.13 ^d ± 0.13	1.67C
Mean	13.24a	1.84b	1.45b	

Within the body of the table, means followed by the same lower case red letter are not significantly different (Tukey's $p > 0.05$); means for each row (sample depth) followed by the same upper case letter are not significantly different; means for each column (position) followed by the same lower case letters are not significantly different.

79 % of the applied bromide was recovered on average within the source area where the bromide was applied with 47% at 0-30 cm, 23% at 30-60 cm and 9% at 60-90 cm depth. Recovery of Br⁻ within the source area was higher for plot B than for plots A and C.

The average total recovery of the surface applied bromide to all plots was 85.4 % when calculated using the first area allocation method (Table 7.6) and 101.2 % when calculated using the second method (Table 7.7). Overall the highest estimated total recovery (vertical and lateral) was found for plot B and the lowest was for plot C whichever approach was used to estimate lateral recovery (Table 7.6) and (Table 7.7). However, the estimated bromide recovered laterally (downslope) was 6 % and 22 % for the first and second method respectively. Consequently losses of bromide from the system were predicted by the first method (14.6%), whereas the second method did not predict any losses of Br⁻ (-1.2%).

Table 7.6 Mean recovery and loss of Br^- applied (18.29 g Br^-) to the source area on 4 March 2011 as estimated using first method from bromide concentration measured in the soil samples for experiment 1.

Plot	Vertical (g Br^-)	Vertical recovery (%)	Lateral (g Br^-)	Lateral recovery (%)	Total mass (g Br^-)	loss	Total recovery (%)	Total loss (%)
1	14.09	77.0	0.85	4.7	14.95	3.34	81.7	18.2
2	17.03	93.1	0.61	3.4	17.65	0.64	96.5	3.5
3	12.39	67.7	1.89	10.3	14.28	4.01	78.1	21.9

Table 7.7 Mean recovery and loss of Br^- applied (18.29 g Br^-) to the source area on 4 March 2011 as estimated using the second method from bromide concentration measured in the soil samples for experiment 1.

Plot	Vertical (g Br^-)	Vertical recovery (%)	Lateral (g Br^-)	Lateral recovery (%)	Total mass (g Br^-)	loss	Total recovery (%)	Total loss (%)
1	14.09	77.0	3.75	20.5	17.84	0.45	97.5	2.5
2	17.03	93.1	4.33	23.7	21.36	-3.07	116.8	-16.8
3	12.39	67.7	3.95	21.6	16.35	1.94	89.4	10.63

7.3.7 Experiment 2 - Bromide recovered in soil

No detectable background bromide was measured in the soil samples collected before experiment 2. At the end of the experiment, no bromide was detected at locations S_{D1} , S_{DL} and S_{DR} (Figure 7.8). Hence these data were not included in further statistical analysis.

Plots and sub-plots - there was no significant difference in the mean bromide concentrations (across all depths and sample positions) between the replicate plots or subplots.

Depth - bromide concentrations were significantly higher ($p < 0.005$) in the topsoil (0-30 cm; 8.07 mg kg^{-1}) than at both 30-60 cm and 60-90 cm depths. Concentrations measured at 30-60 cm (4.30 mg kg^{-1}) were also significantly higher than those at 60-90 cm (1.88 mg kg^{-1}) when averaged over all plots, subplots and sample positions (Table 7.8).

Sample position - bromide concentrations were significantly higher ($p < 0.005$) within the source area S_S (12.19 mg kg^{-1}) than at S_{D2} (3.46 mg kg^{-1}), S_{D3} (1.78 mg kg^{-1}) and S_D (1.57 mg kg^{-1}) when averaged overall plots, subplots and depths. The average total bromide concentrations (0-90 cm) was 36.58 mg kg^{-1} at S_S , 10.39 mg kg^{-1} at S_{D2} , 5.36 mg kg^{-1} at S_{D3} and 4.72 mg kg^{-1} at S_D averaged across plots, subplots and depth (Table 7.8).

Interaction between factors - there was no significant interaction between plots, subplots, sample position and depth.

Table 7.8 Br^- concentrations ($mg\ kg^{-1}$) measured in soil samples at 0-30, 30-60 and 60-90 cm depth in three plots 88 days after application of NaBr in experiment 2. Samples were collected at the source (Ss) where Br^- was applied and down slope (25 cm) outside the source area (S_{D2} , S_{D3}) and 50 cm downslope of the source (S_D). For full description see figure 7.6 and 7.7. Values are means \pm SE.

Depth cm	Ss	S_{D2}	S_{D3}	S_D	Mean
0-30	19.17 \pm 3.37	7.15 \pm 2.10	2.97 \pm 0.93	3.01 \pm 1.15	8.07 A
30-60	11.17 \pm 2.87	2.51 \pm 1.20	2.02 \pm 0.93	1.51 \pm 0.74	4.30 B
60-90	6.24 \pm 2.31	0.72 \pm 0.47	0.36 \pm 0.24	0.20 \pm 0.20	1.88 C
Mean	12.19 a	3.46 b	1.78 c	1.57 c	

Means for each row (sample depth) followed by the same upper case letter are not significantly different; means for each column (position) followed by the same lower case letters are not significantly different. (Tukey's $p > 0.05$)

74 % of the applied bromide was recovered on average within the source area where the bromide was applied with 36.5% at 0-30 cm, 24% at 30-60 cm and 13.5 % at 60-90 cm depth. Recovery of Br^- within the source area was higher for plot 2 than for plot 1 and 3.

The average total recovery of the surface applied bromide to all plots was 85.6 % (\pm 4.4) when calculated using the first area allocation method (Table 7.9) and 99.5 % (\pm 7.6) when calculated using the second method (Table 7.10). Overall the lowest estimated total recovery (vertical and lateral) was found for plot 3 whichever approach was used to estimate lateral recovery (Table 7.9) and (Table 7.10). However, the estimated bromide recovered laterally (downslope) was 12 % and 26 % for first and second method respectively. Consequently losses of bromide from the system were predicted by the first method (14.4%), whereas the second method did not predict any losses of Br^- (0.5%).

Table 7.9 Mean recovery and loss of Br⁻ applied (18.29 g Br⁻) to the source area on the 01 Dec 2011 as estimated using first method from bromide concentration measured in the soil samples for experiment 2.

Plot	Vertical (g Br ⁻)	Vertical recovery (%)	Lateral (g Br ⁻)	Lateral recovery (%)	Total mass (g Br ⁻)	loss	Total recovery (%)	Total loss (%)
1	14.36	78.5	2.10	11.5	16.47	1.82	90.0	9.9
2	15.89	86.9	0.58	3.2	16.48	1.81	90.1	9.9
3	10.31	56.4	3.72	20.4	14.04	4.25	76.8	23.2

Table 7.10 Mean recovery of Br⁻ applied (18.29g Br⁻) to the source area on the 01 Dec 2011 as estimated from bromide concentration measured in the soil samples using second method for experiment 2.

Plot	Vertical (g Br ⁻)	Vertical recovery (%)	Lateral (g Br ⁻)	Lateral recovery (%)	Total mass (g Br ⁻)	loss	Total recovery (%)	Total loss (%)
1	14.36	78.5	4.78	26.2	19.15	-0.86	104.7	-4.7
2	15.89	86.9	4.08	22.3	19.97	-1.68	109.2	-9.2
3	10.31	56.4	5.15	28.2	15.47	2.82	84.6	15.4

7.4 Discussion

Bromide tracer was applied as a solution to the soil surface and on both occasions the soil was at or very close to field capacity. Therefore we would expect the added solute to be drawn rapidly through the soil pores and redistributed within 1-3 cm of the top surface of the soil, following saturation of the soil surface associated with the application (Hillel, 1998). The wet soil conditions at application are likely to promote faster Br^- transport and equilibration with soil solution at / or just below the soil surface through diffusion (Afyuni *et al.*, 1994). The Br^- concentrations measured in the porous cups in both Experiment 1 and 2 indicate that some rapid flow through the soil to depth occurs – preferential flow. The maximum measured Br^- concentrations were much higher in Experiment 2 than Experiment 1; the drainage volume over Experiment 1 (19 mm) was much lower than estimated even for the first period of sampling in Experiment 2 (24 mm). At this similar drainage volume the concentrations measured at 30 cm were nearly identical (28 mg Br l^{-1} in experiment 1; 28 mg Br l^{-1} in experiment 2) indicating that the hydrological properties of the topsoil were similar in the plots used in both experiments. However, the difference between the concentrations measured at 60 cm (6 mg Br l^{-1} in experiment 1; 35 mg Br l^{-1} in experiment 2) suggests a higher variability in hydrological properties governing preferential flow in the 30-60 cm horizon.

Watson and Luxmoore (1986) studied preferential flow in a tension infiltrometer and found that preferential flow was responsible for about 73% of the water transport. Where preferential flow of water to depth occurs, surface applied solutes may bypass the bulk of soil and be found deeper in the soil more quickly than predicted by soil matrix flow drainage (piston flow) only (Iragavarapu *et al.*, 1998). Figure 7.14 shows an early peak (192 mg l^{-1}) of Br^- in the cups at 60 cm depth after only 50 mm of estimated drainage that was significantly faster than would be predicted by piston flow. In order to obtain predictions of the depth of bromide moved with by preferential flow, the measured field data were compared with the simple piston flow model; (Rose *et al.*, 1982; Wierenga *et al.*, 1991) reported that during infiltration and redistribution of a known amount of water, the distance moved by the solute peak is given by:

$$Z_s = Q/\theta_{fc}$$

Where: Z_s is the depth of the solute peak beneath the surface (mm);

Q is the equivalent of depth solution (mm);

θ_{fc} is the volumetric water content of the soil at field capacity.

The previous equation was used to compute the average depth of the bromide peak; the position of the Br^- peak is theoretically located behind the wetting front (Rose *et al.*, 1982). The computed position of the bromide peak resulting from piston flow alone after 51.3 mm drainage was around 16.4 cm. Thus preferential flow (in part of the soil profile) was responsible for leaching the surface applied Br^- to 60 cm depth after 51.3 mm drainage. Water that flows preferentially through the macropores does not need to displace the water in the smaller pores (Al-Sibai *et al.*, 1997). Hence when Br^- enters the macropores preferential flow was effective in moving Br^- downward with relatively less water flow than that required to replace the water originally held in the micropores.

Rice *et al.* (1986) found that 5 fold greater amounts of Br^- were transported to depth than predicted by simple water balance, and explained the difference by preferential macropore flow. Wang *et al.* (2012) also found that nitrate concentrations measured in porous cup samplers in the subsoil peaked before those installed in the topsoil of undisturbed lysimeters with silt loam texture, due to preferential flow through the macropores.

In experiment 1, there is evidence of some preferential flow after only 8 mm of cumulative drainage; however, the larger drainage volumes in experiment 2 suggest that preferential flow of the surface applied bromide was most effective after 30 mm of cumulative drainage. Bathke *et al.* (1992) reported that it is not necessary for the pores which are largely responsible for preferential flow to extend fully to the soil surface to conduct water or solute deeper into the soil profile. The data from experiment 2 suggest that once the main solute front of Br^- had diffused and equilibrated to a depth of around 8 cm (as predicted from the drainage volumes by the piston flow model), the soil solution enriched in Br^- reached some larger pores from where rapid macropore flow conducted it deep into the profile (preferential flow). Once the solute peak resulting from the single application of bromide at the soil surface was leached further into the soil profile as cumulative drainage increased there was a gradual decrease in the Br^- concentration at the 60 cm depth, as preferential flow now conducted water from close to the soil surface which was no longer Br^- enriched to 60 cm. In experiment 2, the estimated amount of Br^- moved by preferential flow past 60 cm is 59 kg ha^{-1} which represents about 20% of the amount of bromide applied at the soil surface. This is similar to the range found by Everts and Kanwar (1990) who found in, arable soil found

that 12-24% of the applied bromide moved by preferential flow. Cullum (2009) reported that 28-35% of applied bromide moved by preferential flow in tilled soils and 18-55% moved by preferential flow under no-till management. In silt loam soil Perkins *et al.* (2011) and Addiscott (1993) found that 43% of applied bromide also moved to depth of 1m by preferential flow.

As cumulative drainage increased (Experiment 2) the Br⁻ concentrations measured in the porous cups show that both preferential and piston flow had a role in moving Br⁻ through the soil profile. Even after the peak Br⁻ concentration after 59 mm drainage, the Br⁻ concentration continued to increase at the 30 cm cup Figure 7.14 indicating that piston flow moved Br⁻ through the soil. The measured Br⁻ peak at 30 cm depth after 70.8 mm of cumulative drainage matches a computed peak depth of 25 cm by piston flow (Rose *et al.*, 1982). During piston flow mixing and transfer of water between the macropores and meso/micropores of the soil matrix takes place as the rate of flow is slow enough to allow mixing of the soil solution and added solute (Al-Sibai *et al.*, 1997). Hence solute peaks moved by piston flow are often broader than those resulting from preferential flow. After 120 mm of cumulative drainage the Br⁻ concentration continued to decline at the 30 cm cup while increasing at 60 cm depth, thus showing that piston flow had moved Br⁻ from the top 0-30 cm depth to the depth between 30-60 cm depth. Wang *et al.* (2012) found that micropores may have a reasonable hydraulic conductivity and will contribute a significant amount of drainage over a period of time, the contribution of the piston flow through the meso/micropores reflected in this study by the ongoing Br⁻ tail. Roth *et al.* (1991) also showed that a solute applied uniformly to the soil surface (with sandy clay loam: 0-30 cm, 30-90 cm clay loam texture), infiltrated and moved through the soil profile both slowly through the soil matrix by piston flow and rapidly by preferential flow. Both Izadi *et al.* (1993) and Afyuni *et al.* (1994) have reported that the uniform surface applied bromide may infiltrate and move through soil profile with both piston and preferential flow.

Two methods (porous cup samplers with estimated drainage and soil sampling) were used to measure Br^- leaching in this experiment (Table 7.11). The quantity of Br^- (kg ha^{-1}) measured in soil core samples taken at the end of the experiment was compared with an estimate of Br^- in soil (kg ha^{-1}) derived from the porous ceramic cup data:

Quantity of Br^- remaining at 0-30 cm =
 (quantity of applied Br^-) – (quantity of Br^- which passed the cup (C_S) at 30 cm depth)

Quantity of Br^- remaining at 30-60 cm =
 (quantity of Br^- which passed the cup (C_S) at 30 cm depth)
 – (quantity of Br^- which passed the cup (C_S) at 60 cm depth)

The data show very good agreement between these two methods (Table 7.11). Good agreement was found between these methods for bromide leaching by Williams and Lord (1997) and Magesan *et al.* (2007) and for nitrate leaching by Lord and Shepherd (1993) and Webster *et al.* (1993).

Table 7.11 Quantity of Br^- in the soil at the end of experiment 2 in the area where Br^- was surface applied. A comparison of the measured data with estimates based on the amount of Br^- moved past the porous cup samplers.

Depth (cm)	Br^- measured in soil from core samples (kg ha^{-1})	Br^- estimated as remaining in soil from cups (kg ha^{-1})
0-30	84.52	75.68
30-60	53.95	68.46

There was no attempt to measure surface run-off in these experiments; however, no sign of runoff from the test sites was noted on any occasion during the experiments. Therefore any lateral Br^- movement is assumed to occur in response to the lateral movement of water within the soil. Detection of Br^- outside the area in which it was applied (Figure 7.12, Figure 7.15 and Figure 7.16) clearly shows that even on this gentle slope part of the applied bromide tracer was transported laterally through the soil. Measured Br^- in the soil samples outside the source area after the experiment (Table 7.5 and Table 7.8) confirm that lateral transport of Br^- has occurred. Observations of both lateral and vertical movement of surface applied Br^- agree with those reported by

(Bathke *et al.*, 1992; Afyuni *et al.*, 1994; Bullock *et al.*, 2008; Olatuyi *et al.*, 2012b) The lateral movement may be explained in part by the soil physical properties in the plots (described in full in Chapter 6). The higher clay content and lower Ks in the Bg horizons are likely to reduce the ability of this horizon to transmit soil water vertically (Waddell and Weil, 2006). This may lead to lateral flow at the junction of the Ap/Bw and Bg horizons. Waddell and Weil (2006) also reported that increased clay content in the soil profile in their study between 60-90 cm (associated with low Ks) caused Br⁻ to move laterally outside the area of Br⁻ application.

In experiment 2, Br⁻ concentration measured in C_{D2} (25 cm from the source) was one order magnitude smaller than at the source (Ss); and downslope C_D (50 cm from the source) was 2 orders of magnitude lower than the source. A similar result was reported by Olatuyi *et al.* (2012a) who observed a rapid decline of Br⁻ concentration measured at distance of 25 cm from the point source, with further decline at increased distance downslope. Afyuni *et al.* (1994) detected Br⁻ laterally at a distance of 150 cm from the edge of the source but found that, in one season, the maximum concentration occurred between 10 to 45 cm downslope. In both downslope locations the topsoil had higher Br⁻ concentrations than soil below 30 cm depth; this may indicate that most of the bromide moved laterally within the topsoil. Patra and Rego (1997) reported that the lateral movement of Br⁻ outside the microplot accounted for 15% of the amount of Br⁻ (300 kg ha⁻¹) applied. Olatuyi *et al.* (2012a) reported that *c.* 15% the applied Br⁻ was recovered outside the source area (laterally within 125 cm) from the edge of the point source application. These estimates are very similar to the lateral bromide recovery estimated in Experiment 2 (12 % and 26 %) using the first and second allocation methods, respectively (Table 7.9; Table 7.10)

These soils are thought to be sub-surface drained (Section 3.2). However, we do not think that this subsurface drainage affected the water movement in the soil profiles studied as no drain pipes or permeable backfill were found in the plots during the description of soil profiles (Section 6.3.1) or the routine soil sampling for soil mineral N (Section 5.2.4) which suggests that any drains are installed with wide spacing. Castle *et al.* (1984) reported that traditionally drain spacing can be between 30 to 60 meters where drains are installed at depths between 0.75 to 1.0 m.

7.5 Conclusion

In these experiments we clearly showed that a small amount of bromide (> 12%) moved laterally as well as vertically in the soils of the NFSC. The lateral transport of bromide may have been a response to the measured decline in the macroporosity and increase in clay content with depth (Chapter 6). Both piston flow and preferential flow were responsible for the transport of surface applied bromide downward through the soil profile. The observed mechanisms which controlled the bromide concentration in the soil matrix and governed its transport in the soil profile are very likely to be effective in nitrate transport.

Over one typical drainage season (c. 300 mm), the results of this study show that soluble mobile compounds present at the soil surface in autumn may be moved via leaching as a result of piston flow to depth of c. 75 cm. Up to 20 % of the soluble compounds in surface-applied fertiliser or manure (e.g. nitrate) may be transported quickly by preferential flow to deeper depth and may be lost from the rooting zone before crop growth resumes in spring. The speed with which bromide moved through the soil profile in our study suggests that it is possible for nitrate to move below 60 cm as a result of preferential flow following only small amounts of drainage (25 mm) and hence fertiliser applied early in spring may also be at risk of significant nitrate losses.

8 Evaluation of advice to farmers aimed at minimising nitrate leaching from arable rotations

8.1 Introduction

Environmental problems linked to nitrate losses from soil via leaching to surface and ground water have been widely recognised (Section 2.1). These problems have led to the development of legislation and recommendations that aim to reduce nitrate concentrations in surface and ground water (Worrall *et al.*, 2009). In 1991 the EC Nitrate Directive (91-67/EEC) was adopted across the European Union. The Nitrate Directive requires Member States to introduce a Code of Good Agricultural Practice to control nitrate losses and to protect against nitrate pollution, which all farmers should follow on a voluntary basis. In the UK specific Nitrate Vulnerable Zones were designated (Lord *et al.*, 1999; Worrall *et al.*, 2009; van Grinsven *et al.*, 2012) in these areas farmers must comply with mandatory measures or rules that are similar to, although in some cases more strict than, the guidance on good practice.

The most prevalent source of information used by farmers to guide land management decisions has been shown to be other farmers (Garforth *et al.*, 2003). Facilitated farmer groups (e.g. the Landcare approach in Australia) are also a commonly reported means of sharing knowledge and promoting learning among farmers. Producer groups, environmental focus farms and Monitor Farms are also being successfully used as a means of knowledge sharing in the UK (Macgregor and Warren, 2006). There are a number of other routes by which farmers get management information including the farming press, industry reports, government publications etc. Garforth *et al.* (2003) indicate that the appropriate form of knowledge transfer will vary and, except where the task is simply that of making information available, facilitation to provide assistance or support in using the information is also important. Uptake into changed practice may

not be limited by access to information, but rather farmers' adoption, understanding and integration of that knowledge into practice (Deugd *et al.*, 1998).

Since the EC Nitrate Directive was introduced, a range of recommendations aiming to reduce nitrate leaching have been made available to farmers and land owners directly from government (Worrall *et al.*, 2009) but also through industry bodies (Dampney *et al.*, 2000). Through these recommendations farmers have been asked to meet specific environmental standards, and provided with guidance on how to meet these standards. Such recommendations have been offered in booklets, as software packages and online (Dampney *et al.*, 2000).

The aim of this chapter is therefore to evaluate the existing information on minimising nitrate leaching from arable rotations that is available to farmers and improve current recommendations, if needed. The objectives are therefore to:

- 1- Collate the existing information on nitrate leaching from arable rotations that is available to farmers.
- 2- Evaluate the likely effectiveness of these recommendations in minimising losses of nitrate via leaching by using the PhD research findings.
- 3- Suggest improvements to current recommendations, if needed

8.2 Existing information and recommendations

In this brief review I will collate recommendations from key examples of the main sources of information that are available to farmers. In particular I will use:

1. **Government** - the main route of information directly provided by the government is Protecting our Water, Soil and Air: A Code of Good Agricultural Practice for farmers, growers and land managers (COGAP, 2009).
2. **Research reviews** – the recommendation and the advice that produced by research group who are experts in nitrogen management and included in the recent EU knowledge transfer project (N-TOOLBOX) will be reviewed.
3. **Industry**- The recently updated released guide for nutrient management (Tried&Tested, 2014) will be reviewed.

8.2.1 Defra (2009) Protecting our Water, Soil and Air: A Code of Good Agricultural Practice for farmers, growers and land managers (COGAP).

Background

The Code of Good Practice is a management tool for farmers and land managers to support profitable management of crops and the land, while protecting the environment in the UK. The Code was written in 2009 for all UK farming systems. COGAP contains many recommendations that have been developed by several government bodies and organisations. It covers a broad range of issues including minimising ammonia and nitrous oxides loss to air, eutrophication, fertiliser and manure storage and application, use of cover crops in arable rotation, grazing management, and much more. The recommendations relating to the reduction of nitrate losses via leaching to surface and ground water include advice on efficient use of inorganic fertiliser and organic manure, soil fertility, management of livestock manure, buffer strips close to water bodies and waste management. In the following section key recommendations on minimising nitrate leaching for arable land are selected and directly copied (shown in italic text).

COGAP also directs farmers to additional specific advice particularly that contained in the Fertiliser Recommendations for crops (also known as the Fertiliser Manual RB209) (DEFRA, 2010). This manual contains recommendations for farmers and managers that allow them to select appropriate rates of fertilisers (both inorganic fertiliser and manures) to supply crop nutrients required, provide financial benefit and protect the environment. Recommendations from RB209 which are related to minimising nitrate leaching for arable land are selected and directly copied (shown in italic text after the recommendations taken from COGAP).

Key recommendations on minimising nitrate leaching for arable land

General points

- *Pay particular attention to how, when and the amount of nitrogen fertiliser and organic manure you apply to meet crop requirements.*
- *Maintain green cover on the land for as much of the year as possible.*
- *You should incorporate into the soil slurry that has been surface broadcast (spread by splash plate). You should do this immediately and at the latest within 6 hours.*

- *You should incorporate solid manures into the soil as soon as possible and at the latest within 24 hours.*

Specific recommendations

- *You should carefully work out the amount of nitrogen fertiliser needed for each crop in each field (the crop nitrogen requirement). You should not exceed the crop nitrogen requirement, as this increases the amount of nitrate lost by leaching so harming the environment as well as being a waste of money. You should take into account the amount of nitrogen supplied by the soil (the soil nitrogen supply). This will depend on the type of soil, previous cropping, rainfall and any organic manure you have applied. There are various recommendation systems available to help you (Fertiliser recommendation RB209). Where the soil nitrogen supply is high, soil analysis for mineral nitrogen can provide a more precise guide to fertiliser requirement.*
- *You should keep accurate records of the amounts and dates of applications of manufactured nitrogen fertilisers, organic manures ... to help work out how much nitrogen fertiliser is needed for future crops.*
- *You should not apply more than 250 kg of total nitrogen in organic manures to any given hectare in any 12 month period. Also, you should ensure that the amount of crop available nitrogen does not exceed the crop nitrogen requirement, which may mean applying less than this maximum amount. There are simple on-farm kits which can measure the nitrogen in animal slurries that is readily available to crops (the Sludge Use in Agriculture Regulation 1989, SI NO 1236), or you can use look up tables (Fertiliser recommendation RB209).*
- *Livestock manures, such as cattle manure and pig slurries and poultry manure, and liquid digested sewage sludge contain a relatively high proportion of readily available nitrogen (i.e. greater than 30% of total nitrogen is present in a readily available form). You should apply these in late winter or spring when crops can use the nitrogen efficiently. Where practically possible you should not apply them in the autumn and early winter months. This is particularly important on sandy shallow soils where the risk of nitrate leaching is greatest.*
- *You can spread organic manures that do not contain much readily available nitrogen (i.e. less than 30% of total N is readily available) such as farmyard*

manure, sewage sludge cake and compost made from green waste at any time, if field conditions are suitable to avoid causing run-off.

- *You should not apply organic manures when...the soil is waterlogged, flooded, frozen hard or snow-covered; or*
- *You should not apply organic manures where there is a significant risk of nitrogen getting into surface water via run-off, taking into account in particular the slope of the land, weather conditions, ground cover, proximity to surface waters, soil conditions and the presence of land drains.*
- *You should not apply organic manures within 10 meters of surface waters, including field ditches; or-50 metres of a spring, well or borehole.*
- *It is important to apply manufactured nitrogen fertiliser only at times when the crop can use the nitrogen. You should not apply it to grass between 15 September and 15 January and other crops between 1 September and 15 January unless there is a specific crop requirement at that time.*
- *You should spread manufactured nitrogen fertiliser as accurately as possible and at the right rate. You should not apply it directly to surface waters (including ditches).*
- *You should not apply manufactured nitrogen fertiliser when the soil is waterlogged, flooded, frozen had or snow-covered.*
- *Plan to sow autumn-sown crops as early as possible....Crops sown in early September will take up more nitrate than later sown crops....*
- *In autumn cultivate the land as close to sowing the next crop as possible. This will reduce the build-up of nitrate in the soil and can be especially beneficial after a crop, such as vining peas or oilseed rape, which leave residues containing a lot of nitrogen. You can often leave residues of late harvested crops, such as root crops, undisturbed until the following spring, unless the soil is compacted and there is a risk of run-off or soil erosion.*
- *Incorporating crop residues that do not contain much nitrogen, such as cereal straw, into the soil in autumn will help to reduce the amount of nitrate leached and to maintain or increase soil organic matter.*
- *By considering, slope, soil type, and the position of the surface waters and water supplies, you should identify fields or parts of fields where livestock manure and dirty waters should never be spread. These non- spreading areas should be marked on a farm map (in red).*

- *You should not apply livestock manures. When: The soil is waterlogged or... is frozen...is snow covered...is cracked down to field drains o backfill or... heavy rain is forecast within the next 48 hours.*
- *You should limit application to no more than 250kg of total nitrogen hectare in any 12 month period.*

Fertiliser Manual (RB209).

- **Nitrate:** *Fertiliser or manures should not be applied to steeply sloping, frozen-hard, snow- covered or water-logged soil or during rain as these conditions greatly increase the risks of runoff.*
- **Nitrate:** *The risk of loss of nitrate by leaching can be reduced by ensuring that the amounts of nitrogen applied from all sources are no greater than the crop requires and by applying nitrogen in organic manures and fertiliser under suitable conditions close to the time when the nitrogen in them is needed for crop growth.*
- **Organic manure:** *The amount of total nitrogen in applied organic manures must not exceed 250kg/ha in any 12 months period at the field level. In some situations, lesser amounts maybe appropriate. For example, the amount of crop available nitrogen supplied by organic manures should not exceed the amount of nitrogen recommended for the next crop.*
- *Manure applications before spring sown crops (e.g. root crops, cereals) should be made from late winter onwards to minimise nitrate leaching losses, particularly where high readily available N manures are applied.*

8.2.2 N-TOOLBOX

Background

N-TOOLBOX is a knowledge transfer project that was funded by The European Union (2009-2012) and written by (Julia Cooper, 2012). The project focuses on identification and testing of practical solutions to the problem of nitrate contamination within the agriculture sector and the work was carried out by Newcastle University, UK; Louis Bolk Institute, Netherlands; Aarhus University, Denmark; and University of Madrid, Spain. Further project description and the project outputs can be found at <http://research.ncl.ac.uk/nefg/N-TOOLBOX/>. In the following section key

recommendations on minimising nitrate leaching for arable land are selected and directly copied (shown in italic text).

Key recommendations on minimising nitrate leaching for arable land

- *Use dynamic simulation models to predict N supply from soil organic matter and recent additions of residues.*
- *Assess crop N status during the season and adjust side/top-dress N application rates accordingly e.g. chlorophyll meters.*
- *Use in season soil tests to measure minerals N levels and adjust side/top-dress N application rates accordingly.*
- *..... the soils with greatest risk of N losses to water from manure application are those which are freely draining... Losses can also be high when manure is applied to a drained arable clay soil. The study concluded that “the risks appear to be greatest where there is good connectivity between the soil surface and field drains, i.e. fissures and cracks” (Defra, 2005). Therefore, care should be taken when using manure on all types of soils.*
- *Time application of manures to coincide with crop demand (e.g. apply in spring rather than autumn.*
- *Use a decision support tool to plan nutrient applications that includes estimates of manure N release over the season.*
- *Use a nitrification inhibitor with injected slurry to reduce leaching of N.*
- *Maintain a green cover as much as practicable – use a cover crop if necessary and drill autumn-sown crops early.*
- *Use starter fertilisers and banding for vegetables.*
- *Apply autumn nitrogen only to those crops that need it – avoid unnecessarily early applications in spring.*
- *Use appropriate controls to minimise pest, disease and weed infestation.*
- *Maximize crop N uptake potential by selecting high yielding varieties and controlling pests and disease.*
- *Compost of high N crop residues.*
- *Grow deep rooted crops following shallow rooted crops to pump N from deep in the soil back to the surface.*
- *Predict optimum N application rates for crops: Research on the use of the range of approaches to predict N supply tends to focus on reducing the quantity of N-*

fertiliser application whilst maintain similar or increasing crop yields...use diagnostic tests... use of SPAD reading to adjust fertiliser N rates...use weather forecasting in the determination of crop N demand.

- *Best management practices for N fertilisers use on crops:...N application should be made in multiple small dose when plant demand is greatest.. Splitting application of fertiliser is usually very effective in allowing crop N uptake and minimizing leaching loss, especially in soils that are easily prone to leaching....where rainfall is frequent...Farmers are now advised that in temperate climate, winter cereals crops should not be N fertilised in autumn...the use of polymer –coated urea can substantially reduce N losses in the field..*
- *Modify tillage practices to reduce N losses to water...Delaying cultivation until just before the next crop can delay the release of nitrate and hence decrease the N leaching risks as it allows subsequent crops to assimilate N as they become established... Reducing overall tillage intensity may be an option for farmers with suitable structure and aeration status which depend on soil texture and climate...poorly drained soils (these tend to be clayey) are usually unsuitable for zero tillage...No tillage has also been linked to greater mineralization and increased amount of organic matter...as well as enhanced macropore flow ...in the medium/ long term minimum tillage practices may increase leaching risks as macropores channels in the topsoil, which can act as preferential flow paths, remain intact, applied N fertiliser may bypass the root zone and reach deeper soil layers...thus extra attention should be paid to the timing of N fertiliser application in reduced tillage systems.*
- *Do not apply manure to high-risk areas. ... Avoid application of manure to areas of the land where is a high risk of direct flow to watercourses. This includes: a)areas that are directly adjacent to a watercourse, borehole or road culvert, b) shallow soils over fissured rock or cracked soils over field drains, c)areas with a dense network of open (surface) drains, or d) wet depressions (flushes) draining to a nearby watercourse.*
- *Apply manure to land when conditions are optimum: time manure application to coincide with periods when there is a low risk of nutrient runoff or leaching....manure should be applied to the land at a time when the growing crop can use its available nutrients; this implies application in the spring.*

- *Attention to weather predictions is important whenever manure is applied to land. Avoiding applications before a heavy rainfall is expected should reduce the risk of surface runoff or leaching.*
- *Estimate the release of N from mineralization of recently applied manure...Use manure N availability tables that provide an estimate of the percentage of total N in manure that is available to the next crop....Use a software tool like MANNER-NPK to predict the fertilizer nitrogen value of field applied manures, Use a dynamic simulation model like NDICEA that will include mineralisation from recently added manure in its estimate soil nitrogen supply.*
- *Test manure for available N content before use: Determine the available N content of manure before its use in the field, either by sending samples for testing, or by using an on-farm testing method.*
- *In arable systems: Cultivate arable land for spring crops in the spring instead of in the autumn.... It is estimated that N leaching could be reduced by about 10 and 15 kg N ha⁻¹ in systems without and with manure application respectively... .*
- *Use a catch crop.....Catch crops are cover crops grown to catch available N in the soil and thereby prevent N leaching losses. They are usually planted after harvest of the main, commercial crop and left to grow during the non-growing season instead of leaving the land fallow.*
- *Incorporation of high C: N ratio residues to promote immobilization of mineral N: Straw or other high C: N ratio residues are incorporated into the soil after crop harvest to act as a “sponge” that holds inorganic N in the soil during the season when no crop growth is occurring...Reductions in N leaching of as high as 25% have been reported.*
- *Include N fixing green manures in the rotation as an alternative to manufactured N fertilizers....Thus the risk of N leaching is reduced if N fixing green manures are included in the rotation as an alternative to manufactured N fertilizers.*

8.2.3 Tried & Tested Nutrient Management Plan:

Background

The Tried & Tested tools and resources are available to farmers on-line [<http://www.nutrientmanagement.org>] to provide them with support for nutrient management planning. The resource have been produced by professional agricultural

advisers and approved by Defra and Environment Agencies in the UK. These resources help farmers to use fertilisers and organic manure on arable land in a way that optimises yield and, at the same time, reduces losses of crop nutrients. The nutrient management plan is available on-line. The web page has links to several useful sites including ADAS, the Environment Agency and others which also provide very useful information related to agricultural management. The second edition of Tried & Tested Nutrient Management Plan provides useful recommendations focussed on more efficient use of nutrients and reducing the losses of these nutrients, including nitrogen. The plans include two forms which give guidance to farmers on how to record nutrient use, at farm and field level including data related to applied fertilisers, manure and soil analysis. Other useful documents that are also available through the links online include Think Manure, Think soil, and New to Nutrient Management Guide.

The Tried and Tested Nutrient Management plan also refers to existing information; of particular relevance here is the booklet developed by ADAS Managing Livestock Manures and Making better use of livestock manures on arable land (ADAS, 2001).

In the following section key recommendations on minimising nitrate leaching for arable land from the main Tried and Tested resources and then the ADAS booklet are selected and directly copied (shown in italic text).

Key recommendations on minimising nitrate leaching for arable land

- *Determine the supply of nutrients from the soil*
- *Look up crop nutrient requirement at that level of soil supply*
- *Estimate the supply of nutrients from any organic manures applied*
- *Incorporate organic manure as soon as possible and within 24hours if land is sloping and within 50m of surface water that could receive run-off (NVZ Guidance Leaflet 8).*
- *Never apply manufactured nitrogen fertiliser, or organic manures, if soil is water-logged, flooded or snow-covered or has been frozen for more than 12 of the preceding 24 hours....*

Managing Livestock Manures

- *To minimise the impact of variable manure N supply, you should supply no more than 50-60% of the crop N requirement from manures.*
- *Manure application should not supply more than 250 kg/ha total N per year.*

- *For spring cereals and spring oilseed rape, manure application should be made from January onwards to minimise nitrate leaching losses, particularly for high available N manures. Rapid incorporation will minimise ammonia losses. Slurries and poultry manures can also be topdressed following drilling.*
- *For potatoes and sugar beet manure management should be the same as for spring cereals. Excessive application rates, particularly of poultry manures, should be avoided, as this can depress tuber dry matters and in beet, root amino-N levels can be increased, depressing sugar yields.*

Making better use of livestock manures on arable land – ADAS booklet.

- *....to make optimum use of the N contained in organic manures, they should be applied at times of maximum crop uptake- generally during the late winter/spring period.*
- *Speedy of manure incorporation is required e.g. by ploughing to conserve readily available N... the amount of N leached is mainly related to the manure application rates, readily available N content and timing of application....where practically possible, application during the autumn / early winter period should be avoided, as over winter rainfall is likely to wash nitrate out of the soil before crops can use it. Delaying application, particularly of high available N manures, until the late winter or spring will increase the utilisation of manure N and reduce nitrate pollution.*
- *Soil mineral nitrogen: Where there is uncertainty about the level of residual mineral N present in the soil, such as following long-term manure use or where manures have been applied at unknown rates, sampling for soil mineral N (SMN) is recommended*
- *...recommends that manure applications should not supply more than 250kg/ha total N per year. This is a sensible agronomic rate that will reduce pollution risk... Manures are commonly applied.....prior to drilling winter cereals
Potatoes....manure management should be the same as for spring cereal. Excessive application rates of manure should be avoided.*
- *Closed periods in NVZ for applying manufactured nitrogen fertilisers begin on 1 September...*

8.3 Evaluation of the likely effectiveness of these recommendations in minimising nitrate leaching by using the PhD research findings

When the recommendations collated in Section 8.2 are reviewed together, it can be seen that there is a large amount of overlap between the recommendations and the information provided by these different routes (Table 8.1). This is not surprising as the recommendations are largely developed from the same underpinning base of research and experience drawn from practice.

Many of the recommendations shown above (Section 8.2) cover aspects of the soil nitrogen cycle, plant nitrogen use and its management which were not studied in detail during the studies carried out as part of this thesis, therefore in the following sections, I will focus on the recommendations directly linked to the research carried out in this PhD and report in Chapters 4-7.

8.3.1 Do not exceed crop nitrogen requirement

This recommendation is included in COGAP, N-TOOLBOX and Tried & Tested. *Recommended rates from RB209 (selected to match the soil type and Index for the NFSC trial) are:*

Wheat, Autumn and Early Winter sown – Nitrogenapply nitrogen at the following...220 kg N ha⁻¹... half should be applied at the start of stem extension (not before April), and half at least 2 weeks later (not after early May) (page 105).

Wheat spring sown – Nitrogen: total nitrogen rate...180 kg N ha⁻¹ (page 110).

Barley spring sown – Nitrogen: total nitrogen rate...140 kg N ha⁻¹ (page 111).

Potatoes –Nitrogen: total nitrogen rate...150-180 kg N ha⁻¹ (page 121).

Several studies have shown that applying nitrogen fertilisers, at rates above the economic optimum, may lead to an increase in postharvest nitrate which is at risk of losses via leaching over winter (Macdonald et al., 1989; Lord and Mitchell, 1998; Chambers et al., 2000). The current recommended rates are reported by COGAP, N-TOOLBOX and Tried & Tested, in part because they help farmers to achieve an economic optimum yield in arable crops (RB209). However the actual field optimum rates may differ according to soil type and previous cropping (Goodlass et al., 2002).

Table 8.1 Summary of the recommendations for farmers to minimising nitrate leaching taken from COGAP, N-TOOLBOX and Tried and tested

Recommendations	Source	Applies to all crops	Applies to all soil types		Information in thesis
Fertiliser / manure rate					
Do not exceed crop nitrogen requirement.	COGAP, N-TOOLBOX, Tried & Tested	Yes	Yes	Rates are given for each crop in RB209. Information on soil type, time of application and crops are also provided by COGAP, N-TOOLBOX, and Tried & Tested.	Yes
You should not apply more than 250 kg of total nitrogen in organic manures to any given hectare in any 12 month period.	COGAP, RB209, Tried & Tested	Yes	Yes	Informations on spreading manure are given by COGAP and Tried & Tested.	Yes
Test manure for available N before use.	COGAP, N-TOOLBOX, Tried & Tested	Yes	Yes	Methods of measuring readily available N to crops in the manure are given by COGAP N-TOOLBOX, and Tried & Tested	No
Estimate release N from mineralisation of recently applied manure.	N-TOOLBOX, Tried & Tested	Yes	Yes	N-TOOLBOX and Tried & Tested recommend the use of methods (e.g. MANNER-NPK tool) to estimate N supply from recently applied manure.	No
Determine the supply of nutrients from the soil to guide fertiliser rate.	Tried & Tested	Yes	Yes	Methods of estimating of soil N supply are described in COGAP, N-TOOLBOX and Tried & Tested	No
Look up crop nutrient requirement at that level of soil supply.	COGAP, N-TOOLBOX, Tried & Tested	Yes	Yes	Managing soil nutrients are given by COGAP, N-TOOLBOX and Tried & Tested	No
Fertiliser type					
Use slow or controlled release fertiliser.	COGAP, N-TOOLBOX	Yes	Yes	Types of fertiliser are described by COGAP and N-TOOLBOX.	No

Recommendations	Source	Applies to all crops	Applies to all soil types		Information in thesis
Fertiliser / manure application timing					
Apply fertilisers at appropriate time ideally close to crop uptake periods	COGAP,	Yes	Yes	Timing of application is described by COGAP	Yes
Do not apply manure and nitrogen fertiliser when soil is waterlogged, soil has cracks or fissures or before heavy rain	COGAP, N-TOOLBOX, Tried & Tested		Yes		Yes
Apply manure in spring rather than autumn	N-TOOLBOX		Yes		Yes
Incorporate any other organic manure as soon as possible	Tried & Tested	Yes	Yes	Steps and incorporation methods are provided by Tried & Tested	No
Use split applications	COGAP, N-TOOLBOX	Yes	Especially in soils with rapid drainage	Rates and times are given by RB209 and N-TOOLBOX	No
Fertiliser / manure application location					
Do not apply manure to areas, where there is a significant risk of nitrogen getting into surface water, taking into account in particular the slope of the land, ground cover, proximity to surface waters, soil conditions and the presence of land drains.	COGAP, N-TOOLBOX	Yes	No	Some limited information is given in N-TOOLBOX	Yes

Recommendations	Source	Applies to all crops	Applies to all soil types		Information in thesis
Crop selection, rotation design					
Choose a high yielding variety to maximise the use of available N	N-TOOLBOX	Yes	Yes		Yes
Grow deep rooted crops following shallow rooted crops	N-TOOLBOX		Yes		No
Include N fixing green manure in the rotation as alternative to inorganic N fertiliser	N-TOOLBOX	Yes	Yes		No
Use catch crops	N-TOOLBOX	Before spring sown crops	Yes	Information on sowing date is provided by N-TOOLBOX	No
Crop management					
Plan to sow autumn sown crops as early as possible	COGAP, N-TOOLBOX	Yes	Yes	Crops types and timing is provided by COGAP, N-TOOLBOX	Yes
Use appropriate controls to minimise pest, disease and weed	N-TOOLBOX	Yes	Yes		Yes
Delay cultivation until just before the next crop	COGAP, N-TOOLBOX	Yes	Yes	Crop types and benefits of late cultivation are described COGAP, N-TOOLBOX	No
Incorporate crop residues that do not contain much nitrogen (high C:N promoting immobilisation)	COGAP, N-TOOLBOX,		Yes	More details on crop residues and C:N ratio are given by COGAP, N-TOOLBOX	No

In our study we investigated the possible effect of these recommended rates on the amount of nitrate at risk of leaching following potato and cereal crops in the NFSC trial (Chapter 5). Inorganic nitrogen fertiliser and composted cattle manure were applied at rates close to the recommended rates for all crops, and did not result in high PHSNi (means after potato (2010/2011) 33, spring wheat (2011) 17, winter wheat, (2012) 28, and spring barley (2012) 35 kg N ha⁻¹ at 0- 90 cm depth). The results also show that there is no significant difference in the level of PHSNi between the two fertility treatments (ammonium nitrate and composted cattle manure). The risk of nitrate losses via leaching was considered to be low (Section 5.4.1). However, a higher level of PHSNi was measured in some plots (up to 116 kg N ha⁻¹). None of the treatments studied, or the interactions between them, could explain these high levels of PHSNi (Section 5.3.3.3). As a result of unmanageable in-field variability, even where recommended rates of N fertilisers are applied, higher risk of nitrate losses via leaching in some areas is expected.

Our study supports these current recommendations to optimise N fertiliser use in order to reduce the level of PHSNi which is vulnerable to losses via leaching. This highlights the importance of applying N fertiliser at recommended rates in order to optimise profitability and to minimise the N residues at risk of loss after harvest (Chaney, 1990b).

8.3.2 *You should not apply more than 250 kg ha⁻¹ of total nitrogen in organic manures to any given hectare in any 12 month period.*

This recommendation is a legal requirement in NVZs and is included as a recommendation for all locations in COGAP, RB209, N-TOOLBOX and Tried & Tested.

In one of our experiments the rates of composted cattle manure applied to winter wheat in autumn were 85 and 170 kg total N ha⁻¹ per year. Measurements of mineral N in early spring (Section 4.3.3) showed that there was no significant difference in the amount of soil nitrate measured in the subsoil (30-90 cm) between the control plot (15.5 kg N ha⁻¹) and plots that had received composted cattle manure in autumn (13 and 14 kg N ha⁻¹ after 85 and 170 kg total N ha⁻¹ respectively). This suggests that application of composted cattle manure in autumn did not have significant effect on the soil nitrate that was lost via leaching.

In the main NFSC trials, the level of composted cattle manure applied to potatoes (2010 and 2011) and to cereals (2011 and 2012) in the organic fertility treatments was at or below 250 kg ha⁻¹ (Section 5.2.2, 5.2.3). The results show that there was no difference in the PHSNi which was vulnerable to losses via leaching over winter, between plots which had received composted cattle manure or recommended optimum rates of N fertiliser (Section 5.4.5). This suggests that composted cattle manure applied at or below the 250 kg ha⁻¹ limit did not increase the risk of nitrate losses via leaching compared with the use of mineral fertilisers.

Our study confirms that application of composted cattle manure at or below the 250 kg ha⁻¹ limit is not likely to increase the risk of nitrate losses via leaching over winter, and in our studies application of manures were able to provide N for crop growth under the restrictions of organic production.

8.3.3 Do not apply manure and nitrogen fertiliser when soil is waterlogged, soil has cracks or fissures or before heavy rain

These recommendations were included in COGAP, RB209, N-TOOLBOX and Tried & Tested.

Over one drainage season, measurements using bromide tracer showed that soluble compounds present at the soil surface in autumn could be lost from the rooting zone overwinter via leaching (Section 7.3.7). Up to 20% of the surface applied bromide moved quickly (after 71 mm of drainage) via preferential flow to 60 cm depth (Section 7.3.4). Bromide tracer also moved via leaching through the mesopores in the soil matrix but more slowly. Therefore in some soils, preferential flow within the soil may lead to losses from the rooting zone of soluble N compounds (including nitrate) in fertiliser and manure applied in early spring via preferential flow. This highlights the risk of early spring N application on some soils.

The results of our study therefore support the recommendation that applying nitrogen fertiliser to cracked soil or before heavy rain may increase the risk of nitrate losses via leaching. However, more guidance may be needed for farmers to support their understanding of water movement in and through the soil profile so that they can better

predict the local risk of losses of nitrate via preferential flow and adopt locally adapted management strategies.

8.3.4 Do not apply manure to areas, where there is a significant risk of nitrogen getting into surface water, taking into account in particular ... soil conditions and the presence of land drains.

These recommendations were included in COGAP and N-TOOLBOX.

Slowly permeable heavy soils are often thought to be at low risk of nitrate leaching losses (Castle *et al.*, 1984). However, such soils often have more permeable surface layers overlying less permeable subsoil layers as found at Nafferton (Section 6.3.9). In our study, bromide tracer clearly showed evidence of lateral movement within the soil profile of c. 20% of the surface-applied tracer (Section 7.3.7). This indicates that in such soils, a major proportion of added nitrate can move laterally through the more permeable surface horizons, even where gradients are small.

In the UK these types of soils often have subsurface drainage when under agricultural use (such as reported for the experimental field at Nafferton, (Section 3.2). Castle *et al.* (1984) reported a maximum depth of drainage pipes of 0.75 m. Where porous cups were installed in the bromide tracer experiment, nitrate leaching past the cups installed at 60 cm was 10.5 kg N ha⁻¹ over winter in 2011/12 (182 mm drainage; Section 7.3.5). 13.5% of the applied bromide tracer was recovered at 60-90 cm (Section 7.3.7). In our research soil mineral nitrogen at 60-90 cm depth was always below 12 kg N ha⁻¹ under both wheat and potato (Section 5.3.3 and 5.3.4); soil water content at this depth fluctuated little and overall there was no strong evidence of water movement to 90 cm; saturated hydraulic conductivity in the 60-90 cm horizon was v. low (0.04 cm day⁻¹ compared with 3 cm day⁻¹ in the topsoil, Section 6.3.9).

Where soils are drained then lateral migration can also move nitrate to permeable backfill laid above the drains, from which water will travel quickly through the pipes and be lost. In addition if the drainage system was installed at a shallower depth for instance 60cm in this profile, then a significant amount of nitrate and other soluble nutrients could also be lost from the soil profile as a result of preferential flow (Section 8.3.3).

The results of our study therefore support the recommendation that farmers need to take soil conditions and the presence of land drains into careful account when planning nitrogen fertiliser and manure applications. However, more guidance may be needed for farmers to support their understanding of the impacts of soil type (including characteristics of subsurface horizons) and drainage systems on water movement in and through the soil profile so that they can better identify high risk areas and adapt their management appropriately.

8.3.5 Apply manure in spring rather than autumn

This recommendation was included in COGAP and N-TOOLBOX.

As described above (Section 8.3.2) in our study there was no significant difference in the amount of soil nitrate measured in the subsoil (30-90 cm) between the control plot and plots that had received composted cattle manure in autumn at 85 and 170 kg total N ha⁻¹ respectively (Section 4.3.3). This suggests that application of composted cattle manure in autumn did not have a significant effect on the soil nitrate that was lost via leaching. COGAP distinguishes between manures with high (>30%) and low available N suggesting that composted manures (such as farmyard manure) can be “applied at any time, if field conditions are suitable to avoid causing run-off” (Section 8.21).

Therefore the experimental results support recommendations in COGAP which indicate that manures with low available N levels can be applied in mid/late autumn with little impact on losses of nitrate via leaching. However, care should be taken in communicating this information to farmers, as if manures have been applied regularly for a number of years or weather conditions are warm and dry following manure application then mineralisation of organic N will increase the risk of nitrate leaching ((Shepherd and Newell-Price, 2013).

8.3.6 Choose a high yielding variety to maximise the use of available N

This recommendation was included in N-TOOLBOX.

In our study different varieties of winter wheat (with a range of yield expectation) planted in mid-October had no impact on the amount of mineral N measured in the soil profile in early spring (Section 4.3.3). However, differences in yield potential (and

associated N uptake) were not expected in this very early crop growth period; later in the growing period significant effect of the interaction between fertility management and variety were observed (Cooper pers. comm.).

In the main NFSC trial, two potato varieties (Sante and Sarpo Mira) were compared in the 2010 and 2011 seasons (Section 5.2.2), Sarpo Mira (main crop) had higher yield than Sante (early) (Rempelos *et al.*, 2013). However, there was no significant difference in PHSNi (0-90 cm) between the varieties (Section 5.3.3.1, 5.3.3.2). However, analysis of the distribution of the PHSNi within the soil profile (Section 5.3.3.4) indicated that the nitrate content in the subsoil (30-90 cm) was slightly higher after the early variety (Sante) than following Sarpo Mira (Section 5.4.2). Increased N uptake has been found as a result of the difference in the length of the growing season of different potato varieties (Kristensen and Thorup-Kristensen, 2007; McPharlin and Lancaster, 2010).

Therefore the results of our study do not give clear evidence to either support or reject this recommendation. As here, where Sarpo Mira was included in the trial as a blight resistant variety (Rietman *et al.*, 2012), a range of factors will drive a farmer's selection of crop variety. Sowing date and other crop management decisions will also interact with the impact of variety selection on nitrate leaching risk.

8.3.7 Plan to sow autumn-sown crops as early as possible....crops sown in early September will take up more nitrate than later sown crops...

This recommendation was included in COGAP and N-TOOLBOX.

As described above (Section 8.3.6.), different varieties of winter wheat (with a range of yield expectation) planted in mid-October had no impact on the amount of mineral N measured in the soil profile in early spring (section 4.3.3). No comparison was made in the study with an earlier sowing date, therefore the results of our study do not give clear evidence to either support or reject this recommendation. The results of our study are in line with other studies which have shown that later sowing dates (after early October) do not allow crop roots to develop sufficiently to mitigate losses of nitrate via leaching (Lord *et al.*, 1999; Webster *et al.*, 2003; Thorup-Kristensen *et al.*, 2009).

8.4 Conclusions

The existing recommendations that are available to farmers on minimising nitrate losses via leaching have been collated and summarised. Sources used to collate these recommendations are COGAP, RB209, N-TOOLBOX and Tried & Tested. The recommendations that linked to the PhD study were evaluated using the results obtained from field work done during the period of the study, the recommendations which the PhD study consistent with are:

- Do not exceed crop nitrogen requirement.
- You should not apply more than 250 kg of total nitrogen in organic manures to any given hectare in any 12 month period.
- Do not apply manure and nitrogen fertiliser when soil is waterlogged, soil has cracks, or fissures or before heavy rain.
- Do not apply manure to areas, where there is a significant risk of nitrogen getting into surface water, taking into account in particular ... soil conditions and the presence of land drains.
- Apply manure (with high available N) in spring rather than autumn.
- Plan to sow autumn-sown crops as early as possible

This study has shown that PHSNi at risk of losses via leaching could be minimised by following these recommendations.

Despite the effectiveness of these recommendations for minimising nitrate leaching, they are mostly focussed on the management of the agricultural nitrogen cycle. However, the effect of the soil type and/or the factors driving water movement in and through the soil profile are not described in detail. We have found that preferential flow through the soil profile could put fertiliser and manure applied in early spring at risk of losses by transporting nitrate below the rooting zone. In addition, our study emphasises the importance of soil properties, i.e. macroporosity and saturated hydraulic conductivity, which influence the movement of water and mobile nutrients (e.g. nitrate) laterally and vertically within the soil profile. These results show the need to manage agricultural cropping fields according to their unique properties. Therefore I would recommend that more guidance is needed for farmers to support their understanding of the impacts of soil type (including characteristics of subsurface horizons) and drainage systems on water movement in and through the soil profile so that they can better identify high risk areas and adapt their management appropriately.

The next step is to encourage farmers and land owners to adapt their practices and use the existing recommendations to minimise nitrate leaching. Farmers use particular agricultural methods within their production systems based on their knowledge of the local and site conditions and the economic benefits. Consequently it is easier to produce new recommendations rather than convince farmers to change their farm management. There is no one magic solution for reducing nitrate losses from all agricultural fields. Therefore farmers should have more recommendation options, so they can use their local knowledge and specialist skills to choose some recommendations that are suited to their financial circumstances and specific site conditions, rather than forcing them to accept one solution to minimise nitrate losses. For example, one option for farmers is to use a catch crop; a second option is to choose a high yielding variety for the main crop to maximise the use of available N. These two options both aim to reduce the amount of nitrate at risk of loss via leaching. However the economic impact of these two options could be quite different. Research results showing the economic costs and benefits of applying the recommendations will be a key factor to persuade farmers and land owners to adopt them.

More co-operation between government bodies, funded research and industry are needed. More investment should be made to develop and improve technologies such as decision support systems (including models) which allow farmers to use their local knowledge and specialist skills to adapt general recommendations into site specific practices. However, any systems should be simple and accessible. In addition, case studies should be published to share examples of successful farmer adoption of these recommendations and how they have both reduced nitrate losses as well as benefiting the farm system.

CHAPTER

9

9 Conclusion

This PhD study aimed to improve the recommendations that are available to farmers to minimise nitrate losses via leaching from arable rotations under UK conditions by investigating the impact of typical agricultural management practices (and their interactions) on the risks of nitrate leaching in crop rotations with potatoes and cereals. In general, we believe that the objectives of the thesis (Section 1.2) have largely been achieved.

The effect of autumn-applied composted cattle manure and winter wheat varieties on the amount of mineral N in the soil profile in early spring 2009/10 were measured in a field trial in 2010 (Chapter 4). This work has shown that autumn application of composted cattle manures with a low proportion of available N to winter wheat did not increase nitrate leaching losses compared with no input control plots in the season of study. There were no differences in the amount of mineral N recovered in the subsoil between the 8 winter wheat varieties suggesting that changing the variety of late autumn sown winter wheat will have no effect on the amount of NO_3^- -N lost via leaching over winter. We took the opportunity offered to us to make measurements of mineral N in this trial to test and validate our laboratory approaches. Therefore, further work is needed to study the effect of sowing date and a wider variety of cover crops. Yield and N uptake on these plots were monitored until harvest (as part of a separate study, data not available) therefore a more complete N balance should be compiled so that more complete advice to farmers on variety selection can be offered.

The effects of crop management practices (year, crop protection, fertility management, crop rotation and variety choice) on nitrate at risk of leaching were measured by measuring soil nitrate content in the soil profile (0-90 cm) after potato and cereal harvest (2010-2012; Chapter 5). Our study considered the effects of optimal crop management practices under either organic or conventional guidance. None of the crop management practices used in the Nafferton Factorial Systems Comparison trial (NFSC) markedly influenced the amount of post-harvest soil nitrate following potato and cereal crops in 2010, 2011 or 2012. The findings suggest that applying nitrogen inputs at recommended rates as either composted cattle manure or ammonium nitrate fertiliser to potato and cereals crops result in levels of post-harvest soil nitrate which are not expected to give a high risk of leaching.

The measurements carried out in the NFSC trial to underpin understanding of the N dynamics could be extended by quantification of N mineralisation, immobilisation and denitrification. Nitrogen tracer (^{15}N) could be used to label fertiliser or manure inputs to improve our understanding of the soil-plant N cycle in these arable rotations. Swain *et al.* (2014b) used our data in the calculation of the nitrogen use efficiency and N balance for potato crops in the NFSC and found that, in a rotation with a high proportion of N-fixing crops (organic rotation), the highest nitrogen use efficiency occurred where nitrogen efficient genotypes of potato were combined with conventional crop management (fertiliser and crop protection). However, longer term monitoring of these experiments is needed, together with nutrient balance and modelling studies at a rotational scale. Work is already underway to calibrate and validate the NDICEA model in the NFSC trial using the mineral N data collected as part of this study (Swain *et al.*, 2014a). This initial work highlights NDICEA's potential as a decision making tool for researchers and farmers to maximise nitrogen use efficiency and minimise losses of nitrate via leaching. However, further rigorous parameter optimisation for UK soils is required.

we measured soil physical properties (Chapter 6) and used bromide tracer (Chapter 7) to increase understanding of the hydrological pathways leading to nitrate leaching in the experimental field at Nafferton farm. Changes in soil texture were observed with depth and higher macroporosity and saturated hydraulic conductivity was measured in the topsoil compared with the subsoil (especially 60-90 cm). This indicated that these soils are likely to show some subsurface accumulation of water within the profile which may lead to lateral movement within the soil. The presence of this hydrological pathway was

confirmed where bromide tracers were applied, as it was shown that more than 12 % of bromide applied was transported laterally in these soils. Both piston and preferential flow were responsible for the transport of the surface applied bromide downward through the soil profile. These data showed that up to 20 % of the soluble compounds in surface-applied fertiliser (e.g. nitrate) were transported quickly into the subsoil by preferential flow, when soil was at or above field capacity, and therefore may be lost from the rooting zone. This work has highlighted that observations of the soil profile together with measurements of porosity (bulk density), ideally macroporosity, are needed before field studies of nitrate leaching are carried out so that the most appropriate monitoring strategy can be put into place.

The existing recommendations that are available to farmers in the UK on minimising nitrate losses via leaching were evaluated using the results obtained from the field studies (Chapter 8). In general, the findings are consistent with the recommendations on the management of the agricultural nitrogen cycle, e.g. matching N applications with crop N requirements; not applying N fertiliser when soil is waterlogged, has cracks or fissures or before heavy rain. However, the recommendations and supporting information do not fully describe the effect of the soil type and/or the factors driving water movement in and through the soil profile. Therefore we would recommend that more guidance is needed for farmers to support their understanding of the impacts of soil type (including characteristics of subsurface horizons) and drainage systems on water movement in and through the soil profile so that they can better identify areas with a high risk of nitrate losses via leaching and adapt their management appropriately. The findings of this work also suggest that the risk of early spring nitrate losses as a result of preferential flow following only small amounts of drainage currently may be underestimated. Therefore more advice is needed to help farmers optimise the timing of nitrate applications in the spring to reduce these losses.

Measurements of soil mineral N in these studies (Chapter 5) have shown that topsoil nitrate content (0-30 cm) after harvest is a good indicator of the nitrate content in the whole soil profile (0-90 cm), which is at risk of leaching overwinter. Hence we recommend that farmers are encouraged to make more measurements of topsoil nitrate rather than a small number of whole profile measurements, as this could be achieved at a similar cost but give much more useful information to guide practice. These season and site specific measurements of soil mineral N could be used by farmers to calibrate

decision support models, such as NDICEA, which may allow them to plan and adjust their management to minimise losses of nitrate via leaching.

There is no one magic solution for reducing nitrate losses from all agricultural fields. More detailed understanding of the amounts and locations of nitrate that is at risk of leaching would allow farmers to select between recommendations using their local knowledge and specialist skills and select approaches that are suited to their financial circumstances and specific site conditions. There is a need to develop and improve simple and accessible technologies such as decision support systems (including models) which allow farmers to use their local knowledge and specialist skills to adapt general recommendations into site specific practices to minimise nitrate leaching from arable rotations with potatoes and cereals.

References

- Aarts, H.F.M., Habekotté, B. and Van Keulen, H. (2000) 'Nitrogen (N) management in the 'De Marke'dairy farming system', *Nutrient Cycling in Agroecosystems*, 56(3), pp. 231-240.
- ADAS, B.C., Nick Nicholson and Ken Smith (2001) *Making better use of livestock manures on arable land* Available at: <http://www.nutrientmanagement.org/>.
- Addiscott, T. (2006) 'Is it nitrate that threatens life or the scare about nitrate?', *Journal of the Science of Food and Agriculture*, 86(13), pp. 2005-2009.
- Addiscott, T.M. (1990) 'measurement of nitrate leaching- a review of methods', Calvet, R. *Conference Inst Natl Recherche Agronomique*. Paris: Nitrates-Agriculture-Water: International Symp, pp. 157-168.
- Addiscott, T.M. (1993) 'Simulation modelling and soil behavior', *Geoderma*, 60(1-4), pp. 15-40.
- Addiscott, T.M. (1996a) 'Fertilizers and nitrate leaching', *Issues in environmental science and technology*, 5, pp. 1-26.
- Addiscott, T.M. (1996b) 'Measuring and modelling nitrogen leaching: Parallel problems', *Plant and Soil*, 181(1), pp. 1-6.
- Addiscott, T.M. (2005) *Nitrate, agriculture, and environment*. CABI Publishing., Wallingford, Oxfordshire, UK.
- Addiscott, T.M. and Benjamin, N. (2004) 'Nitrate and human health', *Soil Use and Management*, 20(2), pp. 98-104.
- Addiscott, T.M. and Wagenet, R.J. (1985) 'Concepts of solute leaching in soils: a review of modelling approaches', *Journal of Soil Science*, 36(3), pp. 411-424.
- Addiscott, T.M. and Whitmore, A.P. (1987) 'Computer- simulation of changes in soil mineral nitrogen and cop nitrogen during autumn, winter and spring. ', *Journal of Agricultural Science*, 109, pp. 141-157.
- Addiscott, T.M. and Whitmore, A.P. (1991) 'Simulation of solute leaching in soils of differing permeabilities', *Soil Use and Management*, 7(2), pp. 94-102.
- Addiscott, T.M., Whitmore, A.P. and Powlson, D.S. (1991) *Farming, fertilizers and the nitrate problem*. CAB International (CABI).
- Afyuni, M.M., Cassel, D.K. and Robarge, W.P. (1994) 'Lateral and vertical bromide ion transport in a Piedmont landscape', *Soil Science Society of America Journal*, 58(3), pp. 967-974.

- Al-Sibai, M., Adey, M.A. and Rose, D.A. (1997) 'Movement of solute through a porous medium under intermittent leaching', *European journal of soil science*, 48(4), pp. 711-725.
- Alkaeed, O., Flores, C., Jinno, K. and Tsutsumi, A. (2006) 'Comparison of several reference evapotranspiration methods for Itoshima Peninsula area, Fukuoka, Japan'.
- Allen, R.G., Pereira, L.S., Raes, D. and Smith, M. (1998) 'Crop evapotranspiration-Guidelines for computing crop water requirements-FAO Irrigation and drainage paper 56', *FAO, Rome*, 300, pp. 65-41.
- Alluvione, F., Bertora, C., Zavattaro, L. and Grignani, C. (2010) 'Nitrous oxide and carbon dioxide emissions following green manure and compost fertilization in corn', *Soil Science Society of America Journal*, 74(2), pp. 384-395.
- Amlinger, F., Götz, B., Dreher, P., Geszti, J. and Weissteiner, C. (2003) 'Nitrogen in biowaste and yard waste compost: dynamics of mobilisation and availability-a review', *European Journal of Soil Biology*, 39(3), pp. 107-116.
- Angus, J.F. (2001) 'Nitrogen supply and demand in Australian agriculture', *Animal Production Science*, 41(3), pp. 277-288.
- Aparicio, V. and Costa, J.L. (2007) 'Soil quality indicators under continuous cropping systems in the Argentinean Pampas', *Soil and Tillage Research*, 96(1), pp. 155-165.
- Askegaard, M., Olesen, J.E., Rasmussen, I.A. and Kristensen, K. (2011) 'Nitrate leaching from organic arable crop rotations is mostly determined by autumn field management', *Agriculture, Ecosystems & Environment*, 142(3), pp. 149-160.
- Avery, A.A. (1999) 'Infantile methemoglobinemia: Reexamining the role of drinking water nitrates', *Environmental Health Perspectives*, 107(7), pp. 583-586.
- Avery, B.W. (1980) *Soil classification for England and Wales (Higher Categories)*. Soil Survey Technical Monograph No.14 Harpenden.
- Avery, B.W. and Bascomb, C.L. (1982) *Soil survey laboratory methods*. Rothamsted Experimental Station Harpenden.
- Baeckstrom, G., Hanell, U. and Svensson, G. (2006) 'Nitrogen use efficiency in an 11-year study of conventional and organic wheat cultivation', *Communications in Soil Science and Plant Analysis*, 37(3-4), pp. 417-449.
- Bandaranayake, W.M. and Arshad, M.A. (2006) 'Soil profile distributions of water and solutes following frequent high water inputs', *Soil and Tillage Research*, 90(1), pp. 39-49.
- Barrett, J.H., Parslow, R.C., McKinney, P.A., Law, G.R. and Forman, D. (1998) 'Nitrate in drinking water and the incidence of gastric, esophageal, and brain cancer in Yorkshire, England', *Cancer Causes and Control*, 9(2), pp. 153-159.

- Bathke, G.R. and Cassel, D.K. (1991) 'Anisotropic variation of profile characteristics and saturated hydraulic conductivity in an Ultisol landscape', *Soil Science Society of America Journal*, 55(2), pp. 333-339.
- Bathke, G.R., Cassel, D.K. and McDaniel, P.A. (1992) 'Bromide movement at selected sites in a dissected piedmont landscape', *Journal of Environmental Quality*, 21(3), pp. 469-475.
- Bechmann, M., Eggestad, H.O. and Vagstad, N. (1998) 'Nitrogen balances and leaching in four agricultural catchments in southeastern Norway', *Environmental Pollution*, 102, pp. 493-499.
- Beckwith, C.P., Cooper, J., Smith, K.A. and Shepherd, M.A. (1998) 'Nitrate leaching loss following application of organic manures to sandy soils in arable cropping. I. Effects of application time, manure type, overwinter crop cover and nitrification inhibition', *Soil Use and Management*, 14(3), pp. 123-130.
- Belanger, G., Richards, J.E., Milburn, P. and Walker, D. (1998) 'Influence of previous cropping practices on the response of spring wheat to applied N', *Canadian Journal of Soil Science*, 78(2), pp. 267-273.
- Belanger, G., Ziadi, N., Walsh, J.R., Richards, J.E. and Milburn, P.H. (2003) 'Residual soil nitrate after potato harvest', *Journal of Environmental Quality*, 32(2), pp. 607-612.
- Bergström, L. and Jarvis, N.J. (1991) 'Prediction of nitrate leaching losses from arable land under different fertilization intensities using the SOIL-SOILN models', *Soil Use and Management*, 7(2), pp. 79-84.
- Berry, P.M., Stockdale, E.A., Sylvester-Bradley, R., Philipps, L., Smith, K.A., Lord, E.I., Watson, C.A. and Fortune, S. (2003) 'N, P and K budgets for crop rotations on nine organic farms in the UK', *Soil Use and Management*, 19(2), pp. 112-118.
- Berry, P.M., Sylvester-Bradley, R., Philipps, L., Hatch, D.J., Cuttle, S.P., Rayns, F.W. and Gosling, P. (2002) 'Is the productivity of organic farms restricted by the supply of available nitrogen?', *Soil Use and Management*, 18(s1), pp. 248-255.
- Berryman, C., Davies, D., Evans, C., Harrod, M., Hughes, A., Skinner, R., Swain, R. and Soane, D. (1982) 'Techniques for measuring soil physical properties', *Techniques for measuring soil physical properties*, 18.
- Bittelli, M. and Flury, M. (2009) 'Errors in water retention curves determined with pressure plates', *Soil Science Society of America Journal*, 73(5), pp. 1453-1460.
- Blankenau, K. and Kuhlmann, H. (2000) 'Effect of N supply on apparent recovery of fertilizer N as crop N and N_{min} in soil during and after cultivation of winter cereals', *Journal of Plant Nutrition and Soil Science*, 163(1), pp. 91-100.
- Blight, G.E. (2005) 'Desiccation of a clay by grass, bushes and trees', *Geotechnical and Geological Engineering*, 23(6), pp. 697-720.

Boehm, C., Landgraf, D. and Makeschin, F. (2009) 'Effects of two contrasting agricultural land-use practices on nitrogen leaching in a sandy soil of Middle Germany', *Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde*, 172(3), pp. 408-417.

Bouraoui, F. and Grizzetti, B. (2014) 'Modelling mitigation options to reduce diffuse nitrogen water pollution from agriculture', *The Science of the total environment*, 468-469, pp. 1267-77.

Bouwman, A.F., Boumans, L.J.M. and Batjes, N.H. (2002) 'Estimation of global NH₃ volatilization loss from synthetic fertilizers and animal manure applied to arable lands and grasslands', *Global Biogeochemical Cycles*, 16(2).

Brady, N.C. (1990) *Nature and Properties of Soils*. Macmillan Publishing Company. New York.

Brisson, N., Mary, B., Ripoche, D., Jeuffroy, M.H., Ruget, F., Nicoullaud, B., Gate, P., Devienne-Barret, F., Antonioletti, R. and Durr, C. (1998) 'STICS: a generic model for the simulation of crops and their water and nitrogen balances. I. Theory and parameterization applied to wheat and corn', *Agronomie*, 18(5-6), pp. 311-346.

Bruce, R.R., Leonard, R.A., Thomas, A.W. and Jackson, W.A. (1985) 'Redistribution of bromide by rainfall infiltration into a Cecil sandy loam landscape', *Journal of environmental quality*, 14(3), pp. 439-445.

Bullock, P.R., Whetter, D.A. and Fuller, L.G. (2008) 'Bromide redistribution as influenced by landscape morphology and pedogenic properties in a variable glacial till landscape: A quantitative examination', *Canadian Journal of Soil Science*, 88(4), pp. 491-499.

Bundy, L.G. and Andraski, T.W. (2005) 'Recovery of fertilizer nitrogen in crop residues and cover crops on an irrigated sandy soil', *Soil Science Society of America Journal*, 69(3), pp. 640-648.

Burt, Heathwaite.A.L and Trudgill.S.T (1993) *Nitrate Processes ,Patterns and Management*. Chichester: John Wiley & Sons, Chichester.

Camargo, J.A. and Alonso, Á. (2006) 'Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment', *Environment International*, 32(6), pp. 831-849.

Cameron, K.C., Di, H.J. and Moir, J.L. (2013) 'Nitrogen losses from the soil/plant system: a review', *Annals of Applied Biology*.

Cameron, K.C., Rate, A.W., Noonan, M.J., Moore, S., Smith, N.P. and Kerr, L.E. (1996) 'Lysimeter study of the fate of nutrients following subsurface injection and surface application of dairy pond sludge to pasture', *Agriculture, Ecosystems & Environment*, 58(2-3), pp. 187-197.

- Campbell, C.A., Zentner, R.P., Selles, F. and Akinremi, O.O. (1993) 'Nitrate leaching as influenced by fertilization in the brown soil zone', *Canadian Journal of Soil Science*, 73(4), pp. 387-397.
- Campiglia, E., Mancinelli, R., Radicetti, E. and Marinari, S. (2011) 'Legume cover crops and mulches: effects on nitrate leaching and nitrogen input in a pepper crop (*Capsicum annuum* L.)', *Nutrient Cycling in Agroecosystems*, 89(3), pp. 399-412.
- Canali, S., Ciaccia, C., Antichi, D., Barberi, P., Montemurro, F. and Tittarelli, F. (2010) 'Interactions between green manure and amendment type and rate: Effects on organic potato and soil mineral N dynamic', *Journal of Food Agriculture & Environment*, 8(2), pp. 537-543.
- Carter, M.R. (1993) *Soil sampling and methods of analysis*. Lewis Publishers. Boca Raton.
- Castle, D.A., McCunnall, J. and Tring, I.M. (1984) *Field drainage: principles and practices*. BT Batsford Ltd.
- Chambers, B.J., Smith, K.A. and Pain, B.F. (2000) 'Strategies to encourage better use of nitrogen in animal manures', *Soil Use and Management*, 16, pp. 157-161.
- Chaney, K. (1990a) 'Effect of nitrogen-fertiliser rate on soil nitrogen-content after harvesting winter-wheat', *Journal of Agricultural Science*, 114, pp. 171-176.
- Chaney, K. (1990b) 'Effect of nitrogen fertilizer rate on soil nitrate nitrogen content after harvesting winter wheat', *Journal of Agricultural Science, Cambridge*, 114, pp. 171-176.
- Chen, X. and Hu, Q. (2004) 'Groundwater influences on soil moisture and surface evaporation', *Journal of Hydrology*, 297(1), pp. 285-300.
- Cherry, K.A., Shepherd, M., Withers, P.J.A. and Mooney, S.J. (2008) 'Assessing the effectiveness of actions to mitigate nutrient loss from agriculture: A review of methods', *Science of The Total Environment*, 406(1-2), pp. 1-23.
- Chien, S.H., Prochnow, L.I. and Cantarella, H. (2009) 'Recent developments of fertiliser production and use to improve nutrient efficiency and minimise environmental impacts', in Sparks, D.L. (ed.) *Advances in Agronomy, Vol 102*. pp. 267-322.
- Christensen, B.T., Rasmussen, J., Eriksen, J. and Hansen, E.M. (2009) 'Soil carbon storage and yields of spring barley following grass leys of different age', *European Journal of Agronomy*, 31(1), pp. 29-35.
- Cichota, R., Snow, V.O. and Vogeler, I. (2013) 'Modelling nitrogen leaching from overlapping urine patches', *Environmental Modelling & Software*, 41(0), pp. 15-26.
- Close, M.E., Magesan, G.N., Lee, R., Stewart, M.K. and Hadfield, J.C. (2003) 'Field study of pesticide leaching in an allophanic soil in New Zealand. 1: Experimental results', *Australian Journal of Soil Research*, 41(5), pp. 809-824.

COGAP (2009) 'A Code of Good Agricultural Practice for farmers, growers and land managers. Surry'.

Collins, R., Jenkins, A. and Harrow, M. (2000) 'The contribution of old and new water to a storm hydrograph determined by tracer addition to a whole catchment', *Hydrological processes*, 14(4), pp. 701-711.

Comly, H.H. (1945) 'Cyanosis in infants caused by nitrates in well water ', *Reprinted in JAMA*, 1987.20:2788-2792.

Correa, P., Cuello, C., Duque, E., Burbano, L.C., Garcia, F.T., Bolanos, O., Brown, C. and Haenszel, W. (1976) 'Gastric cancer in Colombia.3. Natural-history of precursor lesions', *Journal of the National Cancer Institute*, 57(5), pp. 1027-1035.

Craig, R.F. (2004) *Soil mechanics (Fifth Edition)*. Chapman & Hall, London.

Cruz, C. and Loução, M.A.M. (2002) 'Comparison of methodologies for nitrate determination in plants and soils', *Journal of plant nutrition*, 25(6), pp. 1185-1211.

Cullum, R.F. (2009) 'Macropore flow estimations under no-till and till systems', *Catena*, 78(1), pp. 87-91.

Curley, E.M., O'Flynn, M.G. and McDonnell, K.P. (2010) 'Porous ceramic cups: Preparation and installation of samplers for measuring nitrate leaching', *International Journal of Soil Science*, 5(1), pp. 19-25.

Curley, E.M., O'Flynn, M.G. and McDonnell, K.P. (2011) 'The use of porous ceramic cups for sampling soil pore water from the unsaturated zone', *International Journal of Soil Science*, 6(1), pp. 1-11.

Cuttle, S., Macleod, C., Chadwick, D., Scholefield, D., Haygarth, P., Newell-Price, P., Harris, D., Shepherd, M., Chambers, B. and Humphrey, R (2007) 'An Inventory of Methods to Control Diffuse Water Pollution from Agriculture – User Manual' *Final Report for Defra project ES0203*.

Dampney, P.M.R., Lord, E.I. and Chambers, B.J. (2000) 'Development of improved advice for farmers and advisers', *Soil Use and Management*, 16, pp. 162-166.

Dane, J.H., Topp, C., Campbell, G.S., Horton, R., Jury, W.A., Nielsen, D.R., van Es, H.M., Wierenga, P.J. and Topp, G.C. (2002) 'Part 4-Physical methods', *Methods of Soil Analysis*.

Davidson, K., Gowen, R.J., Tett, P., Bresnan, E., Harrison, P.J., McKinney, A., Milligan, S., Mills, D.K., Silke, J. and Crooks, A.-M. (2012) 'Harmful algal blooms: How strong is the evidence that nutrient ratios and forms influence their occurrence?', *Estuarine Coastal and Shelf Science*, 115, pp. 399-413.

Dawson, J.C., Murphy, K.M., Huggins, D.R. and Jones, S.S. (2011) 'Evaluation of winter wheat breeding lines for traits related to nitrogen use under organic management', *Organic Agriculture*, 1(2), pp. 65-80.

DEFRA (2010) 'fertiliser Manual (RB209), 8th Edition'. United Kingdom.

Defra (2013) *Farming Statistics, Final Land Use, Livestock Populations and Agricultural Workforce*. [Online]. Available at: <https://www.gov.uk/government> (Accessed: 0.5 March 2014).

Delogu, G., Cattivelli, L., Pecchioni, N., De Falcis, D., Maggiore, T. and Stanca, A.M. (1998) 'Uptake and agronomic efficiency of nitrogen in winter barley and winter wheat', *European Journal of Agronomy*, 9(1), pp. 11-20.

Deugd, M., Roling, N. and Smaling, E.M.A. (1998) 'A new praxeology for integrated nutrient management, facilitating innovation with and by farmers', *Agriculture Ecosystems & Environment*, 71(1-3), pp. 269-+.

Di, H.J. and Cameron, K.C. (2002) 'The use of a nitrification inhibitor, dicyandiamide (DCD), to decrease nitrate leaching and nitrous oxide emissions in a simulated grazed and irrigated grassland', *Soil use and management*, 18(4), pp. 395-403.

Diacono, M. and Montemurro, F. (2010) 'Long-term effects of organic amendments on soil fertility. A review', *Agronomy for Sustainable Development*, 30(2), pp. 401-422.

Dilz, K. (1988) 'Efficiency of uptake and utilization of fertilizer nitrogen by plants', *Nitrogen efficiency in agricultural soils*, pp. 1-26.

Djurhuus, J. and Jacobsen, O.K. (1995) 'Comparison of ceramic suction cups and KC1 extraction for the determination of nitrate in soil', *European Journal of Soil Science*, 46(3), pp. 387-395.

Dobriyal, P., Qureshi, A., Badola, R. and Hussain, S.A. (2012) 'A review of the methods available for estimating soil moisture and its implications for water resource management', *Journal of Hydrology*, 458-459(0), pp. 110-117.

Droogers, P. and Allen, R. (2002) 'Estimating Reference Evapotranspiration Under Inaccurate Data Conditions', *Irrigation and Drainage Systems*, 16(1), pp. 33-45.

Drury, C.F., Yang, J.Y., De Jong, R., Yang, X.M., Huffman, E.C., Kirkwood, V. and Reid, K. (2007) 'Residual soil nitrogen indicator for agricultural land in Canada', *Canadian journal of soil science*, 87(Special Issue), pp. 167-177.

Dungait, J.A.J., Cardenas, L.M., Blackwell, M.S.A., Wu, L., Withers, P.J.A., Chadwick, D.R., Bol, R., Murray, P.J., Macdonald, A.J., Whitmore, A.P. and Goulding, K.W.T. (2012) 'Advances in the understanding of nutrient dynamics and management in UK agriculture', *Science of The Total Environment*, 434(0), pp. 39-50.

Eghball, B. (2000) 'Nitrogen mineralization from field-applied beef cattle feedlot manure or compost', *Soil Science Society of America Journal*, 64(6), pp. 2024-2030.

El-Hendawy, S.E., Hokam, E.M. and Schmidhalter, U. (2008) 'Drip irrigation frequency: The effects and their interaction with nitrogen fertilization on sandy soil water distribution, maize yield and water use efficiency under Egyptian conditions', *Journal of Agronomy and Crop Science*, 194(3), pp. 180-192.

- Entekhabi, D. and Eagleson, P.S. (1989) *Landsurface hydrology parameterization for atmospheric general circulation models: inclusion of subgrid scale spatial variability and screening with a simple climate model*. Ralph M. Parsons Laboratory Hydrology and Water Resource Systems, Massachusetts Institute of Technology.
- Erhart, E., Feichtinger, F. and Hartl, W. (2007) 'Nitrogen leaching losses under crops fertilized with biowaste compost compared with mineral fertilization', *Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde*, 170(5), pp. 608-614.
- Eriksen, J., Askegaard, M. and Sjøgaard, K. (2008) 'Residual effect and nitrate leaching in grass-arable rotations: effect of grassland proportion, sward type and fertilizer history', *Soil Use and Management*, 24(4), pp. 373-382.
- Errebhi, M., Rosen, C.J., Gupta, S.C. and Birong, D.E. (1998) 'Potato yield response and nitrate leaching as influenced by nitrogen management', *Agronomy Journal*, 90(1), pp. 10-15.
- Ersahin, S. and Rüstü Karaman, M. (2001) 'Estimating potential nitrate leaching in nitrogen fertilized and irrigated tomato using the computer model NLEAP', *Agricultural Water Management*, 51(1), pp. 1-12.
- Escudero, A., González-Arias, A., del Hierro, O., Pinto, M. and Gartzia-Bengoetxea, N. (2012) 'Nitrogen dynamics in soil amended with manures composted in dynamic and static systems', *Journal of Environmental Management*, 108(0), pp. 66-72.
- Evans, C.D., Norris, D., Ostle, N., Grant, H., Rowe, E.C., Curtis, C.J. and Reynolds, B. (2008) 'Rapid immobilisation and leaching of wet-deposited nitrate in upland organic soils', *Environmental Pollution*, 156(3), pp. 636-643.
- Everts, C.J. and Kanwar, R.S. (1990) 'Estimating preferential flow to a subsurface drain with tracers', *Transactions of the ASAE*, 33(2), pp. 451-457.
- Faurès, J.M., Goodrich, D.C., Woolhiser, D.A. and Sorooshian, S. (1995) 'Impact of small-scale spatial rainfall variability on runoff modeling', *Journal of Hydrology*, 173(1), pp. 309-326.
- Fewtrell, L. (2004) 'Drinking-water nitrate, methemoglobinemia, and global burden of disease: a discussion', *Environmental health perspectives*, 112(14), pp. 1371-1374.
- Fiener, P., Auerswald, K. and Van Oost, K. (2011) 'Spatio-temporal patterns in land use and management affecting surface runoff response of agricultural catchments-A review', *Earth-Science Reviews*, 106(1-2), pp. 92-104.
- Follett, R.F. (2008) 'Transformation and transport processes of nitrogen in agricultural systems', *Nitrogen in The Environment: Sources, Problems and Management*, Elsevier, The Netherlands, pp. 19-50.
- Foulkes, M.J., Sylvester-Bradley, R. and Scott, R.K. (1998) 'Evidence for differences between winter wheat cultivars in acquisition of soil mineral nitrogen and uptake and

utilization of applied fertilizer nitrogen', *The Journal of Agricultural Science*, 130(1), pp. 29-44.

Francis, G.S., Bartley, K.M. and Tabley, F.J. (1998) 'The effect of winter cover crop management on nitrate leaching losses and crop growth', *The Journal of Agricultural Science*, 131(3), pp. 299-308.

Fraser, P. and Chilvers, C. (1981) 'Health aspects of nitrate in drinking water', *Science of The Total Environment*, Vol. 18, pp. 103-116.

Fraser, P.M., Curtin, D., Harrison-Kirk, T., Meenken, E.D., Beare, M.H., Tabley, F., Gillespie, R.N. and Francis, G.S. (2013) 'Winter Nitrate Leaching under Different Tillage and Winter Cover Crop Management Practices', *Soil Science Society of America Journal*, 77(4), pp. 1391-1401.

Garforth, C., Angell, B., Archer, J. and Green, K. (2003) 'Fragmentation or creative diversity? Options in the provision of land management advisory services', *Land Use Policy*, 20(4), pp. 323-333.

Gebregiorgis, M.F. and Savage, M.J. (2007) 'Field, laboratory and estimated soil-water content limits', *Water SA*, 32(2), pp. 155-162.

Giddins, J. (2004) *readily available water* Available at: www.agric.nsw.gov.au/water (Accessed: March 2014).

Glass, A.D.M. (2003) 'Nitrogen use efficiency of crop plants: physiological constraints upon nitrogen absorption', *Critical Reviews in Plant Sciences*, 22(5), pp. 453-470.

Glendining, M.J., Powelson, D.S., Poulton, P.R., Bradbury, N.J., Palazzo, D. and Li, X. (1996) 'The effects of long-term applications of inorganic nitrogen fertilizer on soil nitrogen in the Broadbalk Wheat Experiment', *The Journal of Agricultural Science*, 127(03), pp. 347-363.

Goodrich, D.C., Faurès, J.-M., Woolhiser, D.A., Lane, L.J. and Sorooshian, S. (1995) 'Measurement and analysis of small-scale convective storm rainfall variability', *Journal of Hydrology*, 173(1-4), pp. 283-308.

Goss, M.J. and Goorahoo, D. (1995) 'Nitrate contamination of groundwater: Measurement and prediction', *Nutrient Cycling in Agroecosystems*, 42(1), pp. 331-338.

Goulding, K. (2000) 'Nitrate leaching from arable and horticultural land', *Soil Use and Management*, 16, pp. 145-151.

Goulding, K., Jarvis, S. and Whitmore, A. (2008) 'Optimizing nutrient management for farm systems', *Philosophical Transactions of the Royal Society B: Biological Sciences*, 363(1491), pp. 667-680.

Goulding, K.W.T., Poulton, P.R., Webster, C.P. and Howe, M.T. (2000) 'Nitrate leaching from the Broadbalk Wheat Experiment, Rothamsted, UK, as influenced by fertilizer and manure inputs and the weather', *Soil Use and Management*, 16(4), pp. 244-250.

- Griffin, G., Jokela, W., Ross, D., Pettinelli, D., Morris, T. and Wolf, A. (2010) 'Recommended Soil Nitrate Tests'.
- Grinsven, H.J.M.v., Berge, H.F.M.t., Dalgaard, T., Fraters, B., Durand, P., Hart, A., Hofman, G., Jacobsen, B.H., Lalor, S.T.J. and Lesschen, J.P. (2012) 'Management, regulation and environmental impacts of nitrogen fertilization in Northwestern Europe under the Nitrates Directive; a benchmark study', *Biogeosciences Discussions*, 9(6), pp. 7353-7404.
- Grismer, M.E. (2013) 'Estimating agricultural deep drainage lag times to groundwater: application to Antelope Valley, California, USA', *Hydrological Processes*, 27(3), pp. 378-393.
- Grizzetti, B., Bouraoui, F., Billen, G., van Grinsven, H., Cardoso, A.C., Thieu, V., Garnier, J., Curtis, C., Howarth, R. and Johnes, P. (2011) 'Nitrogen as a threat to European water quality', *The European Nitrogen Assessment*, pp. 379-404.
- Grossmann, J. and Udluft, P. (1991) 'The extraction of soil water by suction cup method - A review', *Journal of Soil Science*, 42(1), pp. 83-93.
- Grylls, J.P., Webb, J. and Dyer, C.J. (1997) 'Seasonal variation in response of winter cereals to nitrogen fertilizer and apparent recovery of fertilizer nitrogen on chalk soils in southern England', *The Journal of Agricultural Science*, 128(3), pp. 251-262.
- Gupta, S. and Larson, W.E. (1979) 'Estimating soil water retention characteristics from particle size distribution, organic matter percent, and bulk density', *Water Resources Research*, 15(6), pp. 1633-1635.
- Gupta, S.K., Gupta, R.C., Seth, A.K., Gupta, A.B., Bassin, J.K. and Gupta, A. (1999) 'Adaptation of cytochrome-b5 reductase activity and methaemoglobinaemia in areas with a high nitrate concentration in drinking-water', *Bulletin of the World Health Organization*, 77(9), pp. 749-753.
- Haase, T., Schüler, C. and Heß, J. (2007) 'The effect of different N and K sources on tuber nutrient uptake, total and graded yield of potatoes (*Solanum tuberosum* L.) for processing', *European Journal of Agronomy*, 26(3), pp. 187-197.
- Habteselassie, M.Y., Miller, B.E., Thacker, S.G., Stark, J.M. and Norton, J.M. (2006) 'Soil nitrogen and nutrient dynamics after repeated application of treated dairy-waste', *Soil Science Society of America Journal*, 70(4), pp. 1328-1337.
- Hall, D.G.M., Reeve, M.J., Thomasson, A.J. and Wright, V.F. (1977) *Water retention, porosity and density of field soils*. Rothamsted Experimental Station Harpenden, Herts, UK.
- Hansen, S., Jensen, H.E., Nielsen, N.E. and Svendsen, H. (1991) 'Simulation of nitrogen dynamics and biomass production in winter wheat using the Danish simulation model DAISY', *Nutrient Cycling in Agroecosystems*, 27(2), pp. 245-259.

Hardie, M.A., Doyle, R.B., Cotching, W.E. and Lisson, S. (2012) 'Subsurface Lateral Flow in Texture-Contrast (Duplex) Soils and Catchments with Shallow Bedrock', *Applied and Environmental Soil Science*, 2012.

Hart, P.B.S., Powlson, D.S., Poulton, P.R., Johnston, A.E. and Jenkinson, D.S. (1993) 'The availability of the nitrogen in the crop residues of winter wheat to subsequent crops', *The Journal of Agricultural Science*, 121(3), pp. 355-362.

Hartl, W. and Erhart, E. (2005) 'Crop nitrogen recovery and soil nitrogen dynamics in a 10-year field experiment with biowaste compost', *Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde*, 168(6), pp. 781-788.

Hatano, R., Shinano, T., Taigen, Z., Okubo, M. and Zuowei, L. (2002) 'Nitrogen budgets and environmental capacity in farm systems in a large-scale karst region, southern China', *Nutrient Cycling in Agroecosystems*, 63(2), pp. 139-149.

Hatch, D.J., Jarvis, S.C., Rook, A.J. and Bristow, A.W. (1997) 'Ionic contents of leachate from grassland soils: a comparison between ceramic suction cup samples and drainage', *Soil use and management*, 13(2), pp. 68-74.

Hati, K.M., Swarup, A., Singh, D., Misra, A.K. and Ghosh, P.K. (2006) 'Long-term continuous cropping, fertilisation, and manuring effects on physical properties and organic carbon content of a sandy loam soil', *Soil Research*, 44(5), pp. 487-495.

Hegesh, E. and Shiloah, J. (1982) 'Blood nitrates and infantile methemoglobinemia', *Clinica Chimica Acta*, 125(2), pp. 107-115.

Heinrich, A.L. and Pettygrove, G.S. (2012) 'Influence of Dissolved Carbon and Nitrogen on Mineralization of Dilute Liquid Dairy Manure', *Soil Science Society of America Journal*, 76(2), pp. 700-709.

Hillel, D. (1998) *Environmental soil physics*. Academic press. New York, USA.

Honeycutt, C.W., Clapham, W.M. and Leach, S.S. (1995) 'Influence of crop rotation on selected chemical and physical soil properties in potato cropping systems', *American potato journal*, 72(12), pp. 721-735.

Hossain, M.F., Elahi, S.F., White, S.K., Alam, Q.K., Rother, J.A. and Gaunt, J.L. (2012) 'Nitrogen budgets for Boro rice (*Oryza sativa* L.) fields in Bangladesh', *Field Crops Research*, 131(0), pp. 97-109.

Howard, P.J.A. and Howard, D.M. (1990) 'Use of organic carbon and loss-on-ignition to estimate soil organic matter in different soil types and horizons', *Biology and Fertility of Soils*, 9(4), pp. 306-310.

Howarth, R.W. (2008) 'Coastal nitrogen pollution: A review of sources and trends globally and regionally', *Harmful Algae*, 8(1), pp. 14-20.

Howden, N.J.K., Burt, T.P., Mathias, S.A., Worrall, F. and Whelan, M.J. (2011) 'Modelling long-term diffuse nitrate pollution at the catchment-scale: Data, parameter and epistemic uncertainty', *Journal of Hydrology*, 403(3-4), pp. 337-351.

Hu, B., Fan, M.-S., Hao, Y.-F. and Zhang, J.-H. (2012a) 'Potato-Cabbage Double Cropping Effect on Nitrate Leaching and Resource-Use Efficiencies in an Irrigated Area', *Pedosphere*, 22(6), pp. 842-847.

Hu, W., Shao, M.A. and Si, B.C. (2012b) 'Seasonal changes in surface bulk density and saturated hydraulic conductivity of natural landscapes', *European Journal of Soil Science*, 63(6), pp. 820-830.

Iragavarapu, T.K., Posner, J.L. and Bubenzer, G.D. (1998) 'The effect of various crops on bromide leaching to shallow groundwater under natural rainfall conditions', *Journal of Soil and Water Conservation*, 53(2), pp. 146-151.

Islam, M.R., Mao, S., Xue, X., Eneji, A.E., Zhao, X. and Hu, Y. (2011) 'A lysimeter study of nitrate leaching, optimum fertilisation rate and growth responses of corn (*Zea mays* L.) following soil amendment with water-saving super-absorbent polymer', *Journal of the Science of Food and Agriculture*, 91(11), pp. 1990-1997.

Izadi, B., King, B., Westermann, D. and McCann, I. (1993) 'Field scale transport of bromide under variable condition observed in a furrow irrigated field', *Transactions of the Asae*, 36(6), pp. 1679-1685.

Jackson, D.R. and Smith, K.A. (1997) 'Animal manure slurries as a source of nitrogen for cereals; effect of application time on efficiency', *Soil use and management*, 13(2), pp. 75-81.

Jahangir, M.M.R., Khalil, M.I., Johnston, P., Cardenas, L.M., Hatch, D.J., Butler, M., Barrett, M., O'Flaherty, V. and Richards, K.G. (2012) 'Denitrification potential in subsoils: A mechanism to reduce nitrate leaching to groundwater', *Agriculture Ecosystems & Environment*, 147, pp. 13-23.

Jang, C.-S., Chen, S.-K. and Kuo, Y.-M. (2013) 'Applying indicator-based geostatistical approaches to determine potential zones of groundwater recharge based on borehole data', *CATENA*, 101(0), pp. 178-187.

Jégo, G., Sánchez-Pérez, J.M. and Justes, E. (2012) 'Predicting soil water and mineral nitrogen contents with the STICS model for estimating nitrate leaching under agricultural fields', *Agricultural Water Management*, 107(0), pp. 54-65.

Jemison, J.M., Jabro, J.D. and Fox, R.H. (1994) 'Evaluation of LEACHM.2. Simulation of nitrate leaching from nitrogen -fertilised and manured corn', *Agronomy Journal*, 86(5), pp. 852-859.

Jenkinson, D.S. (2001) 'The impact of humans on the nitrogen cycle, with focus on temperate arable agriculture', *Plant and Soil*, 228(1), pp. 3-15.

Jenkinson, D.S., Fox, R.H. and Rayner, J.H. (1985) 'Interaction between fertilizer nitrogen and soil-nitrogen-the so -called priming effect', *Journal of Soil Science*, 36(3), pp. 425-444.

Johnston, A.E., McEwen, J., Lane, P.W., Hewitt, M.V., Poulton, P.R. and Yeoman, D.P. (1994) 'Effects of one to six year old ryegrass-clover leys on soil nitrogen and on the

subsequent yields and fertilizer nitrogen requirements of the arable sequence winter wheat, potatoes, winter wheat, winter beans (*Vicia faba*) grown on a sandy loam soil', *The Journal of Agricultural Science*, 122(01), pp. 73-89.

Johnston, A.E., Poulton, P.R. and Coleman, K. (2009) 'Chapter 1 Soil Organic Matter: Its Importance in Sustainable Agriculture and Carbon Dioxide Fluxes', in Donald, L.S. (ed.) *Advances in Agronomy*. Academic Press, pp. 1-57.

Julia Cooper, H.L.K., Miguel Quemada, Geert-Jan van der Burgt (2012) *Strategies to reduce nitrate leaching The N-TOOLBOX*. Available at: <http://research.ncl.ac.uk/nefg/ntoolbox/> (Accessed: March 2014).

Kampf, S.K. and Burges, S.J. (2010) 'Quantifying the water balance in a planar hillslope plot: Effects of measurement errors on flow prediction', *Journal of Hydrology*, 380(1-2), pp. 191-202.

Kargas, G., Kerkides, P. and Poulouvasilis, A. (2012) 'Infiltration of rain water in semi-arid areas under three land surface treatments', *Soil & Tillage Research*, 120, pp. 15-24.

Kay, P., Edwards, A.C. and Foulger, M. (2009) 'A review of the efficacy of contemporary agricultural stewardship measures for ameliorating water pollution problems of key concern to the UK water industry', *Agricultural Systems*, 99(2), pp. 67-75.

Kayser, M., Mueller, J. and Isselstein, J. (2010) 'Nitrogen management in organic farming: comparison of crop rotation residual effects on yields, N leaching and soil conditions', *Nutrient Cycling in Agroecosystems*, 87(1), pp. 21-31.

Kemmitt, S.J., Lanyon, C.V., Waite, I.S., Wen, Q., Addiscott, T.M., Bird, N.R.A., O'Donnell, A.G. and Brookes, P.C. (2008) 'Mineralization of native soil organic matter is not regulated by the size, activity or composition of the soil microbial biomass - a new perspective', *Soil Biology & Biochemistry*, 40(1), pp. 61-73.

Kersebaum, K., Hecker, J.M., Mirschel, W. and Wegehenkel, M. (2007) 'Modelling water and nutrient dynamics in soil-crop systems: a comparison of simulation models applied on common data sets', *Modelling water and nutrient dynamics in soil-crop systems*, pp. 1-17.

Kessavalou, A., Doran, J.W., Powers, W.L., Kettler, T.A. and Qian, J.H. (1996) 'Bromide and nitrogen-15 tracers of nitrate leaching under irrigated corn in Central Nebraska', *Journal of Environmental Quality*, 25(5), pp. 1008-1014.

Kirchmann, H. and Bergstrom, L. (2001) 'Do organic farming practices reduce nitrate leaching?', *Communications in Soil Science and Plant Analysis*, 32(7-8), pp. 997-1028.

Knobeloch, L., Salna, B., Hogan, A., Postle, J. and Anderson, H. (2000) 'Blue babies and nitrate-contaminated well water', *Environmental Health Perspectives*, 108(7), pp. 675-678.

Kool, D.M., Wrage, N., Zechmeister-Boltenstern, S., Pfeffer, M., Brus, D., Oenema, O. and Van Groenigen, J.W. (2010) 'Nitrifier denitrification can be a source of N₂O from

soil: a revised approach to the dual-isotope labelling method', *European Journal of Soil Science*, 61(5), pp. 759-772.

Koopmans, C.J. and Bokhorst, J. (2002) 'Nitrogen mineralisation in organic farming systems: a test of the NDICEA model', *Agronomie*, 22(7-8), pp. 855-862.

Kristensen, H.L. and Thorup-Kristensen, K. (2007) 'Effects of vertical distribution of soil inorganic nitrogen on root growth and subsequent nitrogen uptake by field vegetable crops', *Soil Use and Management*, 23(4), pp. 338-347.

Lado, M., Paz, A. and Ben-Hur, M. (2004) 'Organic matter and aggregate-size interactions in saturated hydraulic conductivity', *Soil Science Society of America Journal*, 68(1), pp. 234-242.

Lange, B., Germann, P.F. and Lüscher, P. (2011) 'Runoff-generating processes in hydromorphic soils on a plot scale: free gravity-driven versus pressure-controlled flow', *Hydrological Processes*, 25(6), pp. 873-885.

Léonard, J., Ancelin, O., Ludwig, B. and Richard, G. (2006) 'Analysis of the dynamics of soil infiltrability of agricultural soils from continuous rainfall-runoff measurements on small plots', *Journal of Hydrology*, 326(1-4), pp. 122-134.

Lewis, J. and Sjöström, J. (2010) 'Optimizing the experimental design of soil columns in saturated and unsaturated transport experiments', *Journal of contaminant hydrology*, 115(1), pp. 1-13.

Li, K.-y., Zhao, Y.-y., Yuan, X.-l., Zhao, H.-b., Wang, Z.-h., Li, S.-x. and Malhi, S.S. (2012) 'Comparison of Factors Affecting Soil Nitrate Nitrogen and Ammonium Nitrogen Extraction', *Communications in Soil Science and Plant Analysis*, 43(3), pp. 571-588.

Lim, S.-S., Kwak, J.-H., Lee, S.-I., Lee, D.-S., Park, H.-J., Hao, X. and Choi, W.-J. (2010) 'Compost type effects on nitrogen leaching from Inceptisol, Ultisol, and Andisol in a column experiment', *Journal of Soils and Sediments*, 10(8), pp. 1517-1526.

Litaor, M.I. (1988) 'Review of soil solution samplers', *Water Resources Research*, 24(5), pp. 727-733.

Liu, H., Lei, T.W., Zhao, J., Yuan, C.P., Fan, Y.T. and Qu, L.Q. (2011) 'Effects of rainfall intensity and antecedent soil water content on soil infiltrability under rainfall conditions using the run off-on-out method', *Journal of Hydrology*, 396(1), pp. 24-32.

Logsdon, S.D. (2007) 'Subsurface lateral transport in glacial till soils', *Trans. ASAE*, 50, pp. 875-883.

Lord, E.I. and Anthony, S.G. (2000) 'MAGPIE: A modelling framework for evaluating nitrate losses at national and catchment scales', *Soil Use and Management*, 16, pp. 167-174.

- Lord, E.I., Johnson, P.A. and Archer, J.R. (1999) 'Nitrate Sensitive Areas: a study of large scale control of nitrate loss in England', *Soil Use and Management*, 15(4), pp. 201-207.
- Lord, E.I. and Shepherd, M.A. (1993) 'Developments in the use of porous ceramic cups for measuring nitrate leaching', *Journal of Soil Science*, 44(3), pp. 435-449.
- Lynch, D.H., Zheng, Z., Zebarth, B.J. and Martin, R.C. (2008) 'Organic amendment effects on tuber yield, plant N uptake and soil mineral N under organic potato production', *Renewable Agriculture and Food Systems*, 23(3), pp. 250-259.
- Macdonald, A.J. and Gutteridge, R.J. (2012) 'Effects of take-all (*Gaeumannomyces graminis* var. *tritici*) on crop N uptake and residual mineral N in soil at harvest of winter wheat', *Plant and Soil*, 350(1-2), pp. 253-260.
- Macdonald, A.J., Poulton, P.R., Powlson, D.S. and Jenkinson, D.S. (1997) 'Effects of season, soil type and cropping on recoveries, residues and losses of N-15-labelled fertilizer applied to arable crops in spring', *Journal of Agricultural Science*, 129, pp. 125-154.
- Macdonald, A.J., Powlson, D.S., Poulton, P.R. and Jenkinson, D.S. (1989) 'Unused fertilizer nitrogen in arable soils—its contribution to nitrate leaching', *Journal of the Science of Food and Agriculture*, 46(4), pp. 407-419.
- Macgregor, C.J. and Warren, C.R. (2006) 'Adopting sustainable farm management practices within a Nitrate Vulnerable Zone in Scotland: The view from the farm', *Agriculture Ecosystems & Environment*, 113(1-4), pp. 108-119.
- Madsen, H.B., Jensen, C.R. and Boysen, T. (1986) 'A comparison of the thermocouple psychrometer and the pressure plate methods for determination of soil water characteristic curves', *Journal of Soil Science*, 37(3), pp. 357-362.
- Magesan, G.N., White, R.E., Scotter, D.R. and Bolan, N.S. (2007) 'Estimating leaching losses from sub-surface drained soils', *Soil Use and Management*, 10(2), pp. 87-93.
- Mallory, E.B. and Griffin, T.S. (2007) 'Impacts of soil amendment history on nitrogen availability from manure and fertilizer', *Soil Science Society of America Journal*, 71(3), pp. 964-973.
- Manassaram, D.M., Backer, L.C., Messing, R., Fleming, L.E., Luke, B. and Monteilh, C.P. (2010) 'Nitrates in drinking water and methemoglobin levels in pregnancy: a longitudinal study', *Environmental Health*, 9.
- Marley, C.L., Fychan, R., Theobald, V.J., Cuttle, S.P. and Sanderson, R. (2013) 'Effects of a winter or spring sowing date on soil nitrogen utilisation and yield of barley following a forage crop of red clover, lucerne or hybrid ryegrass', *Agriculture Ecosystems & Environment*, 181, pp. 213-222.
- Martin, R.C. (1993) 'Soil sampling and methods of analysis', *Canadian Society of Soil Science, Florida*.

Mary, B., Beaudoin, N., Justes, E. and Machet, J.M. (1999) 'Calculation of nitrogen mineralization and leaching in fallow soil using a simple dynamic model', *European Journal of Soil Science*, 50(4), pp. 549-566.

Masclaux-Daubresse, C., Daniel-Vedele, F., Dechorgnat, J., Chardon, F., Gaufichon, L. and Suzuki, A. (2010) 'Nitrogen uptake, assimilation and remobilization in plants: challenges for sustainable and productive agriculture', *Annals of Botany*, 105(7), pp. 1141-1157.

McEwen, J., Darby, R.J., Hewitt, M.V. and Yeoman, D.P. (1990) 'Effect of field beans, fallow, lupins, oats, oilseed rape, peas, ryegrass, sunflowers and wheat on nitrogen residues in the soil and on the growth of a subsequent wheat crop', *Journal of Agricultural Science*, 115, pp. 209-219.

McKnight, G.M., Duncan, C.W., Leifert, C. and Golden, M.H. (1999) 'Dietary nitrate in man: friend or foe?', *British Journal of Nutrition*, 81(05), pp. 349-358.

McPharlin, I.R. and Lancaster, R.A. (2010) 'Yield and quality of crisping potatoes (*Solanum Tuberosum*) to applied nitrogen', *Journal of Plant Nutrition*, 33(8), pp. 1195-1215.

McTaggart, I.P. and Smith, K.A. (1993) 'Estimation of potentially mineralisable nitrogen in soil by KCL extraction.2. comparison with soil N uptake in the field', *Plant and Soil*, 157(2), pp. 175-184.

Milne, A.E., Haskard, K.A., Webster, C.P., Truan, I.A., Goulding, K.W.T. and Lark, R.M. (2011) 'Wavelet analysis of the correlations between soil properties and potential nitrous oxide emission at farm and landscape scales', *European Journal of Soil Science*, 62(3), pp. 467-478.

Mineral, R. (2010) *Serving industry and agriculture*. Available at: www.rsminerals.co.uk (Accessed: 2010).

Minschew, H., Selker, J., Hemphill, D. and Dick, R.P. (2002) 'NLEAP computer model and multiple linear regression prediction of nitrate leaching in vegetable systems', *HortTechnology*, 12(2), pp. 250-256.

Mitchell, R., Webb, J. and Harrison, R. (2001) 'Crop residues can affect N leaching over at least two winters', *European Journal of Agronomy*, 15(1), pp. 17-29.

Mitchell, R.D.J., Harrison, R., Russell, K.J. and Webb, J. (2000) 'The effect of crop residue incorporation date on soil inorganic nitrogen, nitrate leaching and nitrogen mineralization', *Biology and Fertility of Soils*, 32(4), pp. 294-301.

Mohanty, B.P., Kanwar, R.S. and Everts, C.J. (1994) 'Comparison of saturated hydraulic conductivity measurement methods for a glacial-till soil', *Soil Science Society of America Journal*, 58(3), pp. 672-677.

Moreau, P., Ruiz, L., Raimbault, T., Vertès, F., Cordier, M.O., Gascuel-Oudou, C., Masson, V., Salmon-Monviola, J. and Durand, P. (2012) 'Modeling the potential

benefits of catch-crop introduction in fodder crop rotations in a Western Europe landscape', *Science of The Total Environment*, 437(0), pp. 276-284.

Mostaghimi, S., McMahon, P.C. and Lembke, W.D. (1989) 'Surface and subsurface drainage simulations for a claypan soil', *Agricultural Water Management*, 15(3), pp. 211-222.

Munoz, F., Mylavarapu, R.S. and Hutchinson, C.M. (2005) 'Environmentally responsible potato production systems: a review', *Journal of plant nutrition*, 28(8), pp. 1287-1309.

Nachabe, M.H., Ahuja, L.R. and Butters, G. (1999) 'Bromide transport under sprinkler and flood irrigation for no-till soil condition', *Journal of Hydrology*, 214(1-4), pp. 8-17.

Nascimento, A.F., Mendonça, E.S., Leite, L.F.C., Scholberg, J. and Neves, J.C.L. (2012) 'Calibration and validation of models for short-term decomposition and N mineralization of plant residues in the tropics', *Scientia Agricola*, 69(6), pp. 393-401.

Nevens, F. and Reheul, D. (2003) 'The application of vegetable, fruit and garden waste (VFG) compost in addition to cattle slurry in a silage maize monoculture: nitrogen availability and use', *European Journal of Agronomy*, 19(2), pp. 189-203.

Nielsen, D.R., Van Genuchten, M.T. and Biggar, J.W. (1986) 'Water flow and solute transport processes in the unsaturated zone', *Water Resour. Res.*, 22(9), pp. 89S-108S.

Nyiraneza, J. and Snapp, S. (2007) 'Integrated management of inorganic and organic nitrogen and efficiency in potato systems', *Soil Science Society of America Journal*, 71(5), pp. 1508-1515.

O'Connell, P.E., Ewen, J., O'Donnell, G. and Quinn, P. (2007) 'Is there a link between agricultural land-use management and flooding?', *Hydrology and Earth System Sciences Discussions*, 11(1), pp. 96-107.

Olatuyi, S.O., Akinremi, O.O., Flaten, D.N. and Lobb, D.A. (2012a) 'Solute transport in a hummocky landscape: I. Two-dimensional redistribution of bromide', *Canadian Journal of Soil Science*, 92(4), pp. 609-629.

Olatuyi, S.O., Akinremi, O.O. and Hao, X. (2012b) 'Solute transport in a hummocky landscape: II. Vertical and seasonal redistribution of bromide and N-15-labelled nitrate', *Canadian Journal of Soil Science*, 92(4), pp. 631-643.

Olfs, H.W., Blankenau, K., Brentrup, F., Jasper, J., Link, A. and Lammel, J. (2005) 'Soil- and plant-based nitrogen-fertilizer recommendations in arable farming', *Journal of Plant Nutrition and Soil Science*, 168(4), pp. 414-431.

Palmer, M.W., Cooper, J., Tetard-Jones, C., Srednicka-Tober, D., Baranski, M., Eyre, M., Shotton, P.N., Volakakis, N., Cakmak, I., Ozturk, L., Leifert, C., Wilcockson, S.J. and Bilsborrow, P.E. (2013) 'The influence of organic and conventional fertilisation and crop protection practices, preceding crop, harvest year and weather conditions on yield and quality of potato (*Solanum tuberosum*) in a long-term management trial', *European Journal of Agronomy*, 49, pp. 83-92.

- Paramasivam, S., Alva, A.K., Fares, A. and Sajwan, K.S. (2002) 'Fate of nitrate and bromide in an unsaturated zone of a sandy soil under citrus production', *Journal of Environmental Quality*, 31(2), pp. 671-681.
- Patra, A.K. and Rego, T.J. (1997) 'Measurement of nitrate leaching potential of a vertisol using bromide as a tracer under rainfed conditions of the Indian semi-arid tropics', *Soil science*, 162(9), pp. 656-665.
- Payton, R.W. and Palmer, R.C. (1990) *Soils of the Alnwick and Rothbury District*. Soil Survey and Land Research Centre.
- Peralta, J.M.a. and Stockle, C.O. (2002) 'Dynamics of nitrate leaching under irrigated potato rotation in Washington State: a long-term simulation study', *Agriculture, ecosystems & environment*, 88(1), pp. 23-34.
- Perkins, K.S., Nimmo, J.R., Rose, C.E. and Coupe, R.H. (2011) 'Field tracer investigation of unsaturated zone flow paths and mechanisms in agricultural soils of northwestern Mississippi, USA', *Journal of Hydrology*, 396(1-2), pp. 1-11.
- Phillips, R.L. (2008) 'Denitrification in cropping systems at sub-zero soil temperatures. A review', *Agronomy for Sustainable Development*, 28(1), pp. 87-93.
- Pinheiro, J., Bates, D., DebRoy, S. and Sarkar, D. (2011) 'R Development Core Team. 2010. nlme: linear and nonlinear mixed effects models. R package version 3.1-97', *R Foundation for Statistical Computing, Vienna*.
- Pinheiro, J.C. and Bates, D.M. (2000) *Mixed effects models in S and S-PLUS*. Springer. New York.
- Pollacco, J.A.P. (2008) 'A generally applicable pedotransfer function that estimates field capacity and permanent wilting point from soil texture and bulk density', *Canadian Journal of Soil Science*, 88(5), pp. 761-774.
- Poss, R., Noble, A.D., Dunin, F.X. and Reyenga, W. (1995) 'Evaluation of ceramic cup samplers to measure nitrate leaching in the field', *European journal of soil science*, 46(4), pp. 667-674.
- Potato Council (2011) *The ndustry potato council* www.potato.org.uk (Accessed: 04 March 2014).
- Power, I.L., Ledgard, S.F., Monaghan, R. and Policy, M.A.F. (2002) *Nutrient budgets for three mixed farming catchments in New Zealand*. Ministry of Agriculture and Forestry.
- Powelson, D.S. (1993) 'Understanding the soil nitrogen cycle', *Soil Use and Management*, 9(3), pp. 86-93.
- Powelson, D.S., Addisott, T.M., Benjamin, N., Cassman, K.G., de Kok, T.M., van Grinsven, H., L'Hirondel, J.L., Avery, A.A. and van Kessel, C. (2008) 'When does nitrate become a risk for humans?', *Journal of Environmental Quality*, 37(2), pp. 291-295.

- Powelson, D.S., Pruden, T.L.G., Johnston, A.E. and Jenkinson, D.S. (1986) 'The nitrogen cycle in the Broadbalk Wheat Experiment: recovery and losses of ¹⁵N-labelled fertilizer applied in spring and inputs of nitrogen from the atmosphere', *The Journal of Agricultural Science*, 107(03), pp. 591-609.
- Premrov, A., Coxon, C.E., Hackett, R., Kirwan, L. and Richards, K.G. (2012) 'Effects of over-winter green cover on groundwater nitrate and dissolved organic carbon concentrations beneath tillage land', *Science of The Total Environment*, 438(0), pp. 144-153.
- Qiu, S., Ju, X., Lu, X., Li, L., Ingwersen, J., Streck, T., Christie, P. and Zhang, F. (2012) 'Improved Nitrogen Management for an Intensive Winter Wheat/Summer Maize Double-cropping System', *Soil Science Society of America Journal*, 76(1), pp. 286-297.
- Rab, M.A., Chandra, S., Fisher, P.D., Robinson, N.J., Kitching, M., Aumann, C.D. and Imhof, M. (2011) 'Modelling and prediction of soil water contents at field capacity and permanent wilting point of dryland cropping soils', *Soil Research*, 49(5), pp. 389-407.
- Rabalais, N.N. and Nixon, W. (2002) 'Dedicated issue. Nutrient over-enrichment in coastal waters: Global patterns of cause and effect. ', *Estuaries*, 25.
- Ramos, C. and Carbonell, E.A. (1991) 'Nitrate leaching and soil moisture prediction with the LEACHM model ', *Fertilizer Research*, 27(2-3), pp. 171-180.
- Rashid, M.I., de Goede, R.G.M., Brussaard, L. and Lantinga, E.A. (2013) 'Home field advantage of cattle manure decomposition affects the apparent nitrogen recovery in production grasslands', *Soil Biology and Biochemistry*, 57(0), pp. 320-326.
- Rawls, W.J., Brakensiek, D.L. and Saxton, K.E. (1982) 'Estimation of soil water properties', *Trans. Asae*, 25(5), pp. 1316-1320.
- Rawls, W.J., Pachepsky, Y.A., Ritchie, J.C., Sobecki, T.M. and Bloodworth, H. (2003) 'Effect of soil organic carbon on soil water retention', *Geoderma*, 116(1), pp. 61-76.
- Rayns, F., Rosenfeld, A., Schmutz, U. and Rahn, C. (2009) 'A comparison of two models to predict nitrogen dynamics in organic agricultural systems', *Aspects of Applied Biology*, 93, pp. 219-222.
- Rempelos, L., Cooper, J., Wilcockson, S., Eyre, M., Shotton, P., Volakakis, N., Orr, C.H., Leifert, C., Gatehouse, A.M.R. and Tetard-Jones, C. (2013) 'Quantitative proteomics to study the response of potato to contrasting fertilisation regimes', *Molecular Breeding*, 31(2), pp. 363-378.
- Rice, R.C., Bowman, R.S. and Jaynes, D.B. (1986) 'Percolation of water below an irrigated field', *Soil Science Society of America Journal*, 50(4), pp. 855-859.
- Richards, I.R., Wallace, P.A. and Paulson, G.A. (1996) 'Effects of applied nitrogen on soil nitrate-nitrogen content after harvest of winter barley', *Fertilizer Research*, 45(1), pp. 61-67.

Rietman, H., Bijsterbosch, G., Cano, L.M., Lee, H.-R., Vossen, J.H., Jacobsen, E., Visser, R.G.F., Kamoun, S. and Vleeshouwers, V.G.A.A. (2012) 'Qualitative and quantitative late blight resistance in the potato cultivar Sarpo Mira is determined by the perception of five distinct RXLR effectors', *Molecular Plant-Microbe Interactions*, 25(7), pp. 910-919.

Robertson, G.P. and Groffman, P.M. (2007) 'Nitrogen transformations', *Soil microbiology, ecology, and biochemistry*, 3rd edn. Academic/Elsevier, New York, pp. 341-364.

Rose, C.W., Chichester, F.W., Williams, J.R. and Ritchie, J.T. (1982) 'Application of an approximate analytic method of computing solute profiles with dispersion in soils', *Journal of Environmental Quality*, 11(1), pp. 151-155.

Roth, K., Jury, W.A., Flühler, H. and Attinger, W. (1991) 'Transport of chloride through an unsaturated field soil', *Water Resources Research*, 27(10), pp. 2533-2541.

Rowell, D.L. (1994) *Soil science: methods and applications*. Longman Group Limited, Longman Scientific & Technical.

Sánchez-Monedero, M.A., Roig, A., Paredes, C. and Bernal, M.P. (2001) 'Nitrogen transformation during organic waste composting by the Rutgers system and its effects on pH, EC and maturity of the composting mixtures', *Bioresource Technology*, 78(3), pp. 301-308.

Sands, G. (2001) *Soil water concepts*. Agricultuer Drainage Publication series. University of Minnesota. USA.

Sapkota, T.B., Askegaard, M., Laegdsmand, M. and Olesen, J.E. (2012) 'Effects of catch crop type and root depth on nitrogen leaching and yield of spring barley', *Field Crops Research*, 125, pp. 129-138.

Scanlon, B.R., Healy, R.W. and Cook, P.G. (2002) 'Choosing appropriate techniques for quantifying groundwater recharge', *Hydrogeology Journal*, 10(1), pp. 18-39.

Schröder, J.J., Aarts, H.F.M., Ten Berge, H.F.M., Van Keulen, H. and Neeteson, J.J. (2003) 'An evaluation of whole-farm nitrogen balances and related indices for efficient nitrogen use', *European Journal of Agronomy*, 20(1), pp. 33-44.

Shaffer, M.J., Halvorson, A.D. and Pierce, F.J. (1991) *Nitrate leaching and economic analysis package (NLEAP) model description and application*.

Shantharam, S. and Mattoo, A.K. (1997) 'Enhancing biological nitrogen fixation: an appraisal of current and alternative technologies for N input into plants', *Plant and Soil*, 194(1-2), pp. 205-216.

Sharon Skipton, D.H. (1986) 'G98-1369 Drinking Water: Nitrate and Methemoglobinemia ("Blue Babay" Syndrome)'. University of Nebraska, Institute of Agriculture and Natural Resources.

- Shepherd, M. and Newell-Price, P. (2013) 'Manure management practices applied to a seven-course rotation on a sandy soil: effects on nitrate leaching', *Soil Use and Management*, 29(2), pp. 210-219.
- Shepherd, M.A. (1993a) 'Measurement of soil mineral nitrogen to predict the response of winter wheat to fertilizer nitrogen after applications of organic manures or after ploughed-out grass', *Journal of Agricultural Science -Cambridge*, 121, pp. 223-223.
- Shepherd, M.A. (1993b) 'Poultry manure and nitrate leaching', *Worlds Poultry Science Journal*, 49(2), pp. 171-172.
- Shepherd, M.A. and Lord, E.I. (1996) 'Nitrate leaching from a sandy soil: The effect of previous crop and post-harvest soil management in an arable rotation', *Journal of Agricultural Science*, 127(2), pp. 215-229.
- Shepherd, M.A., Stockdale, E.A., Powelson, D.S. and Jarvis, S.C. (1996) 'The influence of organic nitrogen mineralization on the management of agricultural systems in the UK', *Soil Use and Management*, 12(2), pp. 76-85.
- Shepherd, M.A. and Webb, J. (1999) 'Effects of overwinter cover on nitrate loss and drainage from a sandy soil: consequences for water management?', *Soil use and management*, 15(2), pp. 109-116.
- Shrestha, R.K., Cooperband, L.R. and MacGuidwin, A.E. (2010) 'Strategies to Reduce Nitrate Leaching into Groundwater in Potato Grown in Sandy Soils: Case Study from North Central USA', *American Journal of Potato Research*, 87(3), pp. 229-244.
- Siddique, K.H.M., Belford, R.K. and Tennant, D. (1990) 'Root: shoot ratios of old and modern, tall and semi-dwarf wheats in a Mediterranean environment', *Plant and Soil*, 121(1), pp. 89-98.
- Simmelsgaard, S.E. and Djurhuus, J. (1998) 'An empirical model for estimating nitrate leaching as affected by crop type and the long-term N fertilizer rate', *Soil Use and Management*, 14(1), pp. 37-43.
- Smith, J.U., Bradbury, N.J. and Addiscott, T.M. (1996) 'SUNDIAL: A PC-based system for simulating nitrogen dynamics in arable land', *Agronomy Journal*, 88(1), pp. 38-43.
- Smith, K.A. and Conen, F. (2004) 'Impacts of land management on fluxes of trace greenhouse gases', *Soil Use and Management*, 20(2), pp. 255-263.
- Smith, S.J. and Davis, R.J. (1974) 'Relative movement of bromide and nitrate through soil', *Journal of Environmental Quality*, 3(2), pp. 152-155.
- Soon, Y.K. and Clayton, G.W. (2003) 'Effects of eight years of crop rotation and tillage on nitrogen availability and budget of a sandy loam soil', *Canadian journal of soil science*, 83(5), pp. 475-481.
- Soon, Y.K., Clayton, G.W. and Rice, W.A. (2001) 'Tillage and previous crop effects on dynamics of nitrogen in a wheat–soil system', *Agronomy Journal*, 93(4), pp. 842-849.

Sorensen, P. and Rubaek, G.H. (2012) 'Leaching of nitrate and phosphorus after autumn and spring application of separated solid animal manures to winter wheat', *Soil Use and Management*, 28(1), pp. 1-11.

Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T. and Sumner, M.E. (1996) *Methods of soil analysis. Part 3-Chemical methods*. Soil Science Society of America Inc.

Stark, J.M. and Firestone, M.K. (1995) 'Mechanisms for soil-moisture effects on activity of nitrifying bacteria', *Applied and Environmental Microbiology*, 61(1), pp. 218-221.

Stockdale, E.A. (1999) 'Predicting nitrate losses from agricultural systems', in Wilson W, S., Ball, A.S. (ed.) *Managing Risks of Nitrates to Humans and the Environment*. Cornwall, UK: The Royal Society of Chemistry, pp. 21-34.

Stockdale, E.A. and Brookes, P.C. (2006) 'Detection and quantification of the soil microbial biomass - impacts on the management of agricultural soils', *Journal of Agricultural Science*, 144, pp. 285-302.

Stockdale, E.A., Gaunt, J.L. and Vos, J. (1997) 'Soil-plant nitrogen dynamics: what concepts are required?', *European Journal of Agronomy*, 7(1-3), pp. 145-159.

Stockdale, E.A., Hatch, D.J., Murphy, D.V., Ledgard, S.F. and Watson, C.J. (2002) 'Verifying the nitrification to immobilisation ratio (N/I) as a key determinant of potential nitrate loss in grassland and arable soils', *Agronomie*, 22(7-8), pp. 831-838.

Stockdale, E.A., Lampkin, N.H., Hovi, M., Keatinge, R., Lennartsson, E.K.M., Macdonald, D.W., Padel, S., Tattersall, F.H., Wolfe, M.S. and Watson, C.A. (2001) 'Agronomic and environmental implications of organic farming systems', *Advances in Agronomy*, 70, pp. 261-327.

Stone, L.R., Klocke, N.L., Schlegel, A.J., Lamm, F.R. and Tomsicek, D.J. (2011) 'Equations for drainage component of the field water balance', *Applied Engineering in Agriculture*, 27(3), p. 345.

Sullivan, J.B. and Krieger, G.R. (2001) *Clinical environmental health and toxic exposures*. Lippincott Williams & Wilkins.

Swain, E.Y., M. Almadni., Hall, G., Chapman, R., Leifert, C., Stockdale, E.A. and Cooper, J.M. (2014a) 'NDICEA Calibration and Validation on a Northern UK Soil', *To be submitted to Organic Agriculture*.

Swain, E.Y., Rempelos, L., Orr, C.H., Hall, G., Chapman, R., Almadni, M., Stockdale, E.A., Kidd, J., Leifert, C. and Cooper, J.M. (2014b) 'Optimizing nitrogen use efficiency in wheat and potatoes: interactions between genotypes and agronomic practices', *Euphytica*, 199(1-2), pp. 119-136.

Temesgen, B., Eching, S., Davidoff, B. and Frame, K. (2005) 'Comparison of some reference evapotranspiration equations for California', *Journal of irrigation and drainage engineering*, 131(1), pp. 73-84.

Thibodeau, J., Chanasyk, D.S. and Fuller, L.G. (2008) 'Variability of vertical bromide redistribution within hummocky landscape', *Canadian Journal of Soil Science*, 88(3), pp. 349-363.

Thomsen, I.K., Kjellerup, V. and Christensen, B.T. (2001) 'Leaching and plant offtake of N in field pea/cereal cropping sequences with incorporation of ¹⁵N-labelled pea harvest residues', *Soil use and management*, 17(4), pp. 209-216.

Thorup-Kristensen, K. (2006) 'Effect of deep and shallow root systems on the dynamics of soil inorganic N during 3-year crop rotations', *Plant and soil*, 288(1-2), pp. 233-248.

Thorup-Kristensen, K., Cortasa, M.S. and Loges, R. (2009) 'Winter wheat roots grow twice as deep as spring wheat roots, is this important for N uptake and N leaching losses?', *Plant and Soil*, 322(1-2), pp. 101-114.

Tilahun, K., J.F. B. and .T, B.A. (2005) 'Transport of Bromide in the Bainsvlei soil: Filed experiment and deterministic/stochastic model simulation', *Australian Journal of Soil Research*, 43(1), pp. 73-80.

Trebs, I., Lara, L.L., Zeri, L.M.M., Gatti, L.V., Artaxo, P., Dlugi, R., Slanina, J., Andreae, M.O. and Meixner, F.X. (2006) 'Dry and wet deposition of inorganic nitrogen compounds to a tropical pasture site (Rondônia, Brazil)', *Atmospheric Chemistry and Physics*, 6(2), pp. 447-469.

Tried&Tested (2014) *Professional nutrient management plan* Available at: <http://www.nutrientmanagement.org> (Accessed: March 2014).

Van der Burgt, G., Oomen, G.J.M. and Rossing, W.A.H. (2006a) 'The NDICEA model as a learning tool: experiences in 2005'.

van der Burgt, G. and Timmermans, B.G.H. (2009) 'The NDICEA model: a supporting tool for nitrogen management in arable farming', *Bioacademy 2009-Proceedings*, pp. 4-8.

van der Burgt, G.J.H.M., Oomen, G.J.M., Habets, A.S.J. and Rossing, W.A.H. (2006b) 'The NDICEA model, a tool to improve nitrogen use efficiency in cropping systems', *Nutrient Cycling in Agroecosystems*, 74, pp. 275-294.

van Grinsven, H.J.M., ten Berge, H.F.M., Dalgaard, T., Fraters, B., Durand, P., Hart, A., Hofman, G., Jacobsen, B.H., Lalor, S.T.J., Lesschen, J.P., Osterburg, B., Richards, K.G., Techen, A.K., Vertes, F., Webb, J. and Willems, W.J. (2012) 'Management, regulation and environmental impacts of nitrogen fertilization in northwestern Europe under the Nitrates Directive; a benchmark study', *Biogeosciences*, 9(12), pp. 5143-5160.

Venterea, R.T., Hyatt, C.R. and Rosen, C.J. (2011) 'Fertilizer management effects on nitrate leaching and indirect nitrous oxide emissions in irrigated potato production', *Journal of Environmental Quality*, 40(4), pp. 1103-1112.

Vilain, G., Garnier, J., Tallec, G. and Tournebize, J. (2012) 'Indirect N₂O emissions from shallow groundwater in an agricultural catchment (Seine Basin, France)', *Biogeochemistry*, 111(1-3), pp. 253-271.

- Vincent, C.D. and Gregory, P.J. (1989) 'Effect of temperature on the development and growth of winter - wheat roots.2.2 field studies of temperature, nitrogen and irradiance', *Plant and Soil*, 119(1), pp. 99-110.
- Vos, J. (1999) 'Split nitrogen application in potato: effects on accumulation of nitrogen and dry matter in the crop and on the soil nitrogen budget', *The Journal of Agricultural Science*, 133(3), pp. 263-274.
- Waddell, J.T. and Weil, R.R. (2006) 'Effects of fertilizer placement on solute leaching under ridge tillage and no tillage', *Soil and Tillage Research*, 90(1-2), pp. 194-204.
- Wagenet, R.J. and Hutson, J.L. (1991) *Modelling pesticide transport and transformation in the soil plant system*.
- Walt, V. (2010) *Soil solution, ceramic cups samplers*. Available at: www.vanwalt.com (Accessed: 2010).
- Wang, H., Ju, X., Wei, Y., Li, B., Zhao, L. and Hu, K. (2010) 'Simulation of bromide and nitrate leaching under heavy rainfall and high-intensity irrigation rates in North China Plain', *Agricultural Water Management*, 97(10), pp. 1646-1654.
- Wang, Q., Cameron, K., Buchan, G., Zhao, L., Zhang, E.H., Smith, N. and Carrick, S. (2012) 'Comparison of lysimeters and porous ceramic cups for measuring nitrate leaching in different soil types'.
- Ward, M.H., deKok, T.M., Levallois, P., Brender, J., Gulis, G., Nolan, B.T. and VanDerslice, J. (2005) 'Workgroup report: Drinking-water nitrate and health-recent findings and research needs', *Environmental Health Perspectives*, 113(11), pp. 1607-1614.
- Warwick, C., Guerreiro, A. and Soares, A. (2013) 'Sensing and analysis of soluble phosphates in environmental samples: A review', *Biosensors and Bioelectronics*, 41(0), pp. 1-11.
- Watson, C.A. and Atkinson, D. (1999) 'Using nitrogen budgets to indicate nitrogen use efficiency and losses from whole farm systems: a comparison of three methodological approaches', *Nutrient cycling in agroecosystems*, 53(3), pp. 259-267.
- Watson, C.A., Atkinson, D., Gosling, P., Jackson, L.R. and Rayns, F.W. (2002a) 'Managing soil fertility in organic farming systems', *Soil Use and Management*, 18(s1), pp. 239-247.
- Watson, C.A., Bengtsson, H., Ebbesvik, M., Løes, A.K., Myrbeck, A., Salomon, E., Schroder, J. and Stockdale, E.A. (2002b) 'A review of farm-scale nutrient budgets for organic farms as a tool for management of soil fertility', *Soil Use and Management*, 18, pp. 264-273.
- Watson, K.W. and Luxmoore, R.J. (1986) 'Estimating macroporosity in a forest watershed by use of a tension infiltrometer', *Soil Science Society of America Journal*, 50(3), pp. 578-582.

Webb, J., Ellis, S., Harrison, R. and Thorman, R. (2004) 'Measurement of N fluxes and soil N in two arable soils in the UK', *Plant and Soil*, 260(1-2), pp. 253-270.

Webb, J., Harrison, R. and Ellis, S. (2000a) 'Nitrogen fluxes in three arable soils in the UK', *European Journal of Agronomy*, 13(2), pp. 207-223.

Webb, J., Menzi, H., Pain, B.F., Misselbrook, T.H., Dammgen, U., Hendriks, H. and Dohler, H. (2005) 'Managing ammonia emissions from livestock production in Europe', *Environmental Pollution*, 135(3), pp. 399-406.

Webb, J., Ryan, M., Anthony, S.G., Brewer, A., Laws, J., Aller, M.F. and Misselbrook, T.H. (2006) 'Cost-effective means of reducing ammonia emissions from UK agriculture using the NARSES model', *Atmospheric Environment*, 40(37), pp. 7222-7233.

Webb, J., Seeney, F.M. and Sylvester-Bradley, R. (1998) 'The response to fertilizer nitrogen of cereals grown on sandy soils', *The Journal of Agricultural Science*, 130(3), pp. 271-286.

Webb, J., Sylvester-Bradley, R. and Seeney, F.M. (1997) 'Responses of cereals to residual fertiliser nitrogen applied to the preceding potato crop', *Journal of the Science of Food and Agriculture*, 73(1), pp. 63-80.

Webb, J., Sylvester-Bradley, R. and Seeney, F.M. (2000b) 'The fertiliser nitrogen requirement of cereals grown on sandy soils', *Journal of the Science of Food and Agriculture*, 80(2), pp. 263-274.

Webster, C.P., Conway, J.S., Crew, A.P. and Goulding, K.W.T. (2003) 'Nitrogen leaching losses under a less intensive farming and environment (LIFE) integrated system', *Soil Use and Management*, 19(1), pp. 36-44.

Webster, C.P., Shepherd, M.A., Goulding, K.W.T. and Lord, E. (1993) 'Comparisons of methods for measuring the leaching of mineral nitrogen from arable land', *Journal of Soil Science*, 44(1), pp. 49-62.

Westerman, R.L., Boman, R.K., Raun, W.R. and Johnson, G.V. (1994) 'Ammonium and nitrate-nitrogen in soil profile of long-term winter-wheat fertilization experiments', *Agronomy Journal*, 86(1), pp. 94-99.

Whetter, D.A., Bullock, P.R. and Fuller, L.G. (2008) 'Bromide redistribution as influenced by landscape morphology and pedogenic properties in a variable glacial till landscape: A qualitative examination', *Canadian Journal of Soil Science*, 88(4), pp. 477-490.

Widdowson, F.V., Penny, A., Darby, R.J., Bird, E. and Hewitt, M.V. (1987) 'Amounts of NO₃-N and NH₄-N in soil, from autumn to spring, under winter-wheat and their relationship to soil type, sowing date, previous crop and N uptake at Rothamsted, Woburn and Saxmundham, 1979-85', *Journal of Agricultural Science*, 108, pp. 73-95.

Wierenga, P.J., Hills, R.G. and Hudson, D.B. (1991) 'The Las Cruces Trench Site: Characterization, Experimental Results, and One-Dimensional Flow Predictions', *Water Resources Research*, 27(10), pp. 2695-2705.

Williams, J.R. and Lord, E.I. (1997) 'The use of porous ceramic cup water samplers to measure solute leaching on chalk soils', *Soil Use and Management*, 13(3), pp. 156-162.

Wilson, W., S and Ball, A., S (1999) *Managing Risks of Nitrates to Humans and the Environment*. The Royal Society of Chemistry.

Wilson, W.S. and Hinton, R. (1999) *Managing risks of nitrates to humans and the environment*. Woodhead Publishing.

Worrall, F., Spencer, E. and Burt, T.P. (2009) 'The effectiveness of nitrate vulnerable zones for limiting surface water nitrate concentrations', *Journal of Hydrology*, 370(1-4), pp. 21-28.

Wright, J.L., Westermann, D.T. and Lehrsch, G.A. (1998) 'Studying nitrate-N leaching with a bromide tracer in an irrigated silt loam soil'.

Xu, L., Zhang, Q. and Huang, L. (2010) 'Nitrogen leaching in a typical agricultural extensively cropped catchment, China: experiments and modelling', *Water and Environment Journal*, 24(2), pp. 97-106.

Xu, Q., Liu, S., Wan, X., Jiang, C., Song, X. and Wang, J. (2011) 'Effects of rainfall on soil moisture and water movement in a subalpine dark coniferous forest in southwestern China', *Hydrological Processes*.

Yamaguchi, J. and Tanaka, A. (1990) 'Quantitative observation on the root system of various crops growing in the field', *Soil Science and Plant Nutrition*, 36(3), pp. 483-493.

Yang, J.Y., Huffman, E.C., De Jong, R., Kirkwood, V., MacDonald, K.B. and Drury, C.F. (2007) 'Residual soil nitrogen in soil landscapes of Canada as affected by land use practices and agricultural policy scenarios', *Land Use Policy*, 24(1), pp. 89-99.

Zebarth, B.J., Leclerc, Y., Moreau, G., Gareau, R. and Milburn, P.H. (2003) 'Soil inorganic nitrogen content in commercial potato fields in New Brunswick', *Canadian Journal of Soil Science*, 83(4), pp. 425-429.

Zeegers, M.P., Selen, R.F.M., Kleinjans, J.C.S., Goldbohm, R.A. and van den Brandt, P.A. (2006) 'Nitrate intake does not influence bladder cancer risk: The Netherlands Cohort Study', *Environmental Health Perspectives*, 114(10), pp. 1527-1531.

Zotarelli, L., Scholberg, J.M., Dukes, M.D. and Muñoz-Carpena, R. (2007) 'Monitoring of nitrate leaching in sandy soils: Comparison of three methods', *Journal of Environmental Quality*, 36(4), pp. 953-962.

Zvomuya, F., Rosen, C.J., Russelle, M.P. and Gupta, S.C. (2003) 'Nitrate leaching and nitrogen recovery following application of polyolefin-coated urea to potato', *Journal of Environmental Quality*, 32(2), pp. 480-489.

APPENDIX 1

Profile: Plot 1

Soil classification: Stagnogleyic Brown Earth, Nercwys Series

Location: Nafferton farm /Northumbria 15 miles West of Newcastle Upon Tyne.

Date: 14/09/2012

Elevation: 116m

Slope: 2-3° degrees.

Geology: Greyish till derived from Carboniferous shale and sandstone (Payton 1990).

Soil surface: flat.

Land use: Grass Clover.

Erosion/Deposition: None evident.

Horizons:

0-31 cm Ap

Dark brown (10YR 3/3); sandy clay loam; with a few medium stones of fine-grained sandstone; moderately sticky and moderately plastic when wet; many fine fibrous roots; clear sharp boundary.

31-52 cm Bw (g)

Yellowish brown (10YR 5/4) sandy clay loam with common ochreous mottls; sandstone fragments; medium subangular structure; moderately sticky and moderately plastic when wet; common fine fibrous roots.

52-90cm Bg

Grayish brown (10YR 5/2) clay loam with common mottles medium stony with medium sized hard sandstone fragment; medium subangular blocky structure; moderately sticky; moderately plastic when wet.

Properties of soil horizons from plot 1. Mean values given.

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Bulk density (g cm ⁻³)	pH	% Organic matter (LOI)	Estimated t C ha ⁻¹	Texture
0-32	60.09	20.82	19.09	1.47	6.53	3.62	145.04	Sandy clay loam
33-49	58.30	22.02	19.68	1.61	6.54	2.72	135.73	Sandy clay loam
50-90	41.87	34.11	24.02	1.67	6.71	2.36	112.93	Clay loam

Profile: Plot 2

Soil classification: Stagnogleyic Brown Earth, Nerewys Series

Location: Nafferton farm /Northumbria 15 miles West of Newcastle Upon Tyne.

Date: 14/09/2012

Elevation: 113 m

Slope: 2-3° degrees.

Geology: Greyish till derived from Carboniferous shale and sandstone (Payton 1990)

Soil surface: flat.

Erosion/Deposition: None evident.

Land use: Grass Clover.

Horizons:

0-32cm Ap

Dark brown (10YR 3/3) sandy clay loam; a few medium sandstones; moderately sticky and moderately plastic when wet; many fine fibrous roots; clear sharp boundary.

32-49 cm Bw(g)

Yellowish brown (10YR 5/4) sandy clay loam with common ochreous mottles; moderately sticky and very plastic when wet; common fine fibrous roots; clear wavy boundary.

49-90 cm Btg

Dark grey (10YR 4/1) Sandy clay loam with common mottles abundant, light sticky and very plastic; medium sandstone fragments; medium subangular blocky: few fine fibrous roots.

Properties of soil horizons from plot 2. Mean values given, with \pm SE.

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Bulk density (g cm ⁻³)	pH	% Organic matter (LOI)	Estimated t C ha ⁻¹	Texture
0-32	62.46	20.08	17.46	1.33	6.15	2.93	130.43	Sandy clay loam
33-49	56.42	24.97	18.62	1.51	6.30	2.21	111.79	Sandy clay loam
50-90	56.53	24.44	19.03	1.66	6.83	2.14	107.35	Sandy clay loam

Profile: Plot 3

Soil classification: Cambic Stagnogley, Brickfield Series

Location: Nafferton farm /Northumbria 15 miles West of Newcastle Upon Tyne

Date: 14/09/2012

Elevation: 111 m

Slope: 2-3° degrees.

Geology: parent material is greyish till derived from Carboniferous shale and sandstone (Payton 1990).

Soil surface: Grass Clover.

Erosion/Deposition: None evident.

Horizons:

0-28 cm Ap

Dark brown (10YR 3/3) sandy clay loam, slightly stony; moderately sticky; plastic when wet; very common fine fibrous roots; fine clear wavy boundary; common earthworm burrows; clear sharp boundary.

28-48 cm Bg

Yellowish brown (10YR 5/4) clay loam with abundant dark grey mottles and common ochreous mottles, medium stony with common medium hard sandstone; common fibrous fine roots; moderately sticky and moderately plastic when wet; wavy boundary.

48-90 cm Bg

Grey (10YR 5/1); clay loam with ochreous mottles; Very stony with common medium hard sandstones fragments, moderately sticky and very plastic when wet; medium subangular blocky.

Properties of soil horizons from plot 3. Mean values given, with \pm SE.

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Bulk density (g cm ⁻³)	pH	% Organic matter (LOI)	Estimated t C ha ⁻¹	Texture
0-31	59.68	19.96	20.36	1.47	6.58	3.31	146.61	Sandy clay loam
32-52	41.7	34.3	24.0	1.66	6.62	2.75	133.63	Clay loam
53-90	38.19	32.83	29.0	1.68	6.79	1.73	87.11	Clay loam