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EVALUATION OF STABLE ISOTOPE ANALYSIS AS A TOOL TO DETERMINE NITRATE SOURCES IN IRISH GROUNDWATERS

Presented in fulfilment
of the requirements for the degree of
Doctor of Philosophy
April 2007

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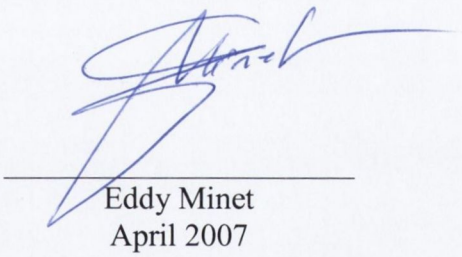
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SUMMARY

This project, which explores combined $\delta^{15}N$ and $\delta^{18}O$ analyses on soil-water and groundwater nitrate in conjunction with conventional chemical analysis of water constituents, primarily aims to give a critical evaluation of stable isotope analysis of nitrate as a tool to determine nitrate sources in Irish groundwaters. First, the unsaturated zone was investigated as nitrate leachate samples were collected under small-scale experiments of well-drained soils simulating different agricultural practices. The saturated zone investigations were mainly carried out in the Barrow Valley, south County Kildare and north County Carlow, where unsewered dwellings and farms are scattered in areas of intensive agricultural activities, a significant proportion of tillage land and relatively free-draining soils overlying shallow sand/gravel and Carboniferous limestone aquifers. Research work was also undertaken to a lesser extent at Moorepark Research Centre, north-east County Cork, where an intensive dairy farm and a thin free-draining soil cover overlie a karstified limestone bedrock aquifer. Nitrate was extracted from each water sample using an anion exchange resin technique (Silva *et al.*, 2000), and $\delta^{15}N$ and $\delta^{18}O$ values were both measured by Continuous-Flow Isotopic Ratio Mass Spectrometry.

The unsaturated zone investigations showed that soil-water nitrate poorly mirrored the ^{15}N content of applied nitrogenous sources (artificial fertilisers, dairy wastewater or slurry), which could be attributed to the interference of soil-water nitrate derived from the nitrification of soil organic matter. Notwithstanding this, $\delta^{15}N\text{-}NO_3^-$ was consistently lower where artificial fertiliser had been applied than in unfertilised controls and organic waste treatments. Soil-water nitrate showed $\delta^{18}O\text{-}NO_3^-$ values that were consistently in the range expected for nitrification, even where artificial fertiliser was applied, which could be attributed to the occurrence of Mineralisation-Immobilisation Turnover processes that tend to level all $\delta^{18}O\text{-}NO_3^-$ values. A positive correlation between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ was observed only where dairy wastewater was applied (regression slope of 0.63), which was attributed to the occurrence of denitrification. Distinctively, negative correlations between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were observed under artificial fertiliser treatments, which were related to the increasing influence synthetic fertiliser nitrate had during the leaching process.

The first step in the saturated zone investigation consisted of testing the use of groundwater chemistry and spatial characteristics as a tool to identify nitrate sources. The Barrow Valley sampling sites were classified according to i) hydrochemistry (based on the exceedance or non-exceedance of contamination thresholds), and ii) spatial characteristics based on the presence/absence of organic point sources (unsewered houses and farmyards) within 100 m and 300 m radius, each classification associating sites to either artificial diffuse or organic point source contamination. The comparison of both site classifications showed some contradictions. 100 % of high nitrate sites with no organic point source within 100 m and 300 m radius showed groundwater chemistry indicative of contamination by artificial diffuse sources (i.e. artificial fertilisers). But only 34 % of high nitrate sites with organic point sources (i.e. unsewered houses and/or farmyards) within 100 m and 300 m radius showed groundwater chemistry indicative of contamination by organic point N sources, whereas 64 % of sites with organic point sources within 100 m and 300 m radius had groundwater chemistry indicative of contamination by artificial diffuse sources.

The second step in the groundwater investigation consisted of analysing site mean δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values in relation to both site classifications. The results established that regardless of the site classification and the type of associated N source, most values lay within the 4 ‰ to 9 ‰ range reported in the literature for soil organic N-derived nitrate. In addition, all δ^{18}O-NO_3^- values were consistently low, overlapping with the 0 ‰ to 5 ‰ range reported for nitrification by Durka *et al.* (1994), which was attributed to the occurrence of Mineralisation-Immobilisation Turnover. Despite these limitations, important differences in δ^{15}N-NO_3^- values were observed between site classifications. When sites were classified according to spatial characteristics (i.e. presence/absence of organic point source within 100 m and 300 m radius), δ^{15}N-NO_3^- (log-transformed) values were significantly lower at the 0.05 level at sites associated with artificial diffuse than organic point source contamination. On the other hand, when sites were classified according to hydrochemistry (i.e. in regard of contamination thresholds), the significance of the difference between sites associated with artificial diffuse and organic point source contamination was improved to the 0.0005 level. The significance of this difference further improved to the 0.0001 level when comparing sites where hydrochemistry and spatial characteristics agreed. Finally, positive and significant correlations (at the 0.001 level) between δ^{15}N-NO_3^- and δ^{18}O-NO_3^- on five sampling occasions out of six, with regression slopes close to 0.5, were attributed to the occurrence of denitrification.

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UNITS, TERMINOLOGY AND ABBREVIATIONS

CHEMISTRY

NH_4^+	Ammonium
Ca^{2+}	Calcium
C	Carbon
Cl^-	Chloride
[X]	Concentration of a X ion in mg/l
µS/cm	Conductivity (microSiemens per centimetre)
DOC	Dissolved organic carbon
H	Hydrogen
Mg^{2+}	Magnesium
µmol	Micromole (1 mole × 10^{-6})
meq/l	Milliequivalent per litre (equal to millimoles of charge per litre)
mg/l	Milligram per litre (concentration)
M	Mole per litre (molarity)
NO_3^-	Nitrate
NO_3-N	Nitrate-nitrogen
NO_2^-	Nitrite
N	Nitrogen
O	Oxygen
PO_4^{3-}	Phosphate (or orthophosphate)
K^+	Potassium
Na^+	Sodium
SO_4^{2-}	Sulphate
SO_4-S	Sulphate-sulfur
TN	Total Nitrogen

ISOTOPES

δ	Difference in isotopic ratio R (ratio of the heavy to light stable isotope) between a sample and the standard it was measured against, and defined as follows: $\delta = \{(R_{sample}-R_{std}) / R_{std}\} \times 1000$
R	Isotopic ratio of one isotope to another for the same element (applies to $^{15}N/^{14}N$, $^{18}O/^{16}O$ and $^{2}H/^{1}H$ in this project)
‰	Parts per thousand (or permil)
AIR	Diatomic nitrogen in air (reference for ^{15}N analysis)
V-SMOW	Vienna – Standard Mean Ocean Water standard (reference for ^{18}O and ^{2}H analyses)
δ^{15}N-TN	Difference in stable nitrogen isotopic ratio ($R = ^{15}N/^{14}N$) in total nitrogen between a sample and a reference (AIR): $\delta = \{(R_{sample}-R_{AIR}) / R_{AIR}\} \times 1000$
δ^{15}N-NO_3^-	Difference in stable nitrogen isotopic ratio ($R = ^{15}N/^{14}N$) in nitrate between a sample and a reference (AIR): $\delta = \{(R_{sample}-R_{AIR}) / R_{AIR}\} \times 1000$
δ^{18}O-NO_3^-	Difference in stable oxygen isotopic ratio ($R = ^{18}O/^{16}O$) in nitrate between a sample and a reference (V-SMOW): $\delta = \{(R_{sample}-R_{V\text{-}SMOW}) / R_{V\text{-}SMOW}\} \times 1000$
δ^{18}O-H_2O	Difference in stable oxygen isotopic ratio ($R = ^{18}O/^{16}O$) in water between a sample and a reference (V-SMOW): $\delta = \{(R_{sample}-R_{V\text{-}SMOW}) / R_{V\text{-}SMOW}\} \times 1000$
δ^{2}H-H_2O	Difference in stable hydrogen isotopic ratio ($R = ^{2}H/^{1}H$) in water between a sample and a reference (V-SMOW): $\delta = \{(R_{sample}-R_{V\text{-}SMOW}) / R_{V\text{-}SMOW}\} \times 1000$
Δ	Apparent fractionation (also called "big delta") during an equilibrium or kinetic reaction
α	Fractionation factor
ϵ	Isotopic enrichment factor
MS	Mass Spectrometer
CF-IRMS	Continuous-Flow Isotopic Ratio Mass Spectrometry
EA	Elemental Analyser
GC	Gas Chromatography
D	Deuterium ^{2}H

WATER QUALITY AND LEGISLATION

AP	Action Programme in the Nitrate Directive
GL	Guide level, value set for nitrate at 25 mg/l NO_3^- in the Directive 80/778/EEC
NBL	Natural background level
NVZ	Nitrate Vulnerable Zone (Directive 91/676/EEC)
S.I.	Statutory Instruments
ZOC	Zone of contribution (around a well)

STATISTICAL/ANALYTICAL

ANOVA	Analysis of variance
r	Pearson product-moment correlation coefficient
QA	Quality Assurance
QC	Quality control
r_s	Spearman's rank coefficient

ORGANISATIONS

EPA	Environmental Protection Agency
CSO	Central Statistics Office
DAF	Department of Agriculture and Food
DELG	Department of the Environment and Local Government
DEHLG	Department of the Environment, Heritage and Local Government
GSI	Geological Survey of Ireland
IAEA	International Atomic Energy Agency
Moorepark RC	Moorepark Research Centre
Oak Park RC	Oak Park Research Centre
OSI	Ordnance Survey of Ireland
USGS	United States Geological Survey

OTHER

AOD	Above Ordnance Datum
bgl	Below ground level (depth given in metres)
CEC	Cation exchange capacity
ED	Electoral Division
LU	Livestock Unit (e.g. cattle over 2 years = 1 LU/ha)
MIT	Mineralisation-Immobilisation Turnover

CHAPTER 1: INTRODUCTION

1.1 Introduction to the nitrate issue and isotope analysis

Nitrate is one of the most common N-bearing contaminants in groundwater, whose presence has been an increasing cause of concern for many years because of potential detrimental effects on human health. In addition, groundwater may also discharge into surface water bodies to contribute, in association with phosphate, to eutrophication in lakes, rivers and more especially estuaries. In response to both of these concerns, several European Directives were implemented in the last fifteen years to tackle the problem. These concerns and related legislation are discussed in greater depth in sections 2.1.1 and 2.1.4 respectively.

In Ireland, although nitrate contamination is not as widespread a problem as in many European Union countries, there are nonetheless some regions where concentrations approach or exceed the drinking water limit set out at 50 mg/l NO_3^- (Council of the European Communities, 1998). Early investigations stressed that these problems were due to localised organic point sources (e.g. stored farmyard wastes and septic tank systems). However, in recent years research has indicated that while the highest nitrate values are generally associated with localised sources of organic contamination, diffuse fertiliser sources appear to have caused a significant increase above background levels in some areas.

Although conventional chemical analyses, in conjunction with a good knowledge of the area under study, can help to determine the origin of nitrate, groundwater contamination sources often cannot be fully elucidated in this way. This is especially true where multiple potential sources coexist within a small perimeter, as is often seen in rural areas. Early work on the nitrogen stable isotope ^{15}N in nitrate in the 1970's, and further developments since, brought a new field of promising experiments that aimed to answer questions left by conventional chemical analysis. It appeared in many studies that the natural abundance of ^{15}N in nitrate (measured as ^{15}N to ^{14}N ratio, and referred to as $\delta^{15}N\text{-}NO_3^-$ in this thesis) was somewhat related to the source of contamination. Nitrate derived from artificial fertilisers

has often been found to be display lower $\delta^{15}N\text{-}NO_3^-$ values than nitrate derived from an organic source such as animal or human wastes.

In the 1980's, work progressed on using analysis of the oxygen stable isotope ^{18}O within the nitrate ion to determine the origin of contamination. The great potential of $\delta^{18}O$ analysis lay in the fact that the difference in ^{18}O natural abundance (measured as ^{18}O to ^{16}O ratio, and referred to as $\delta^{18}O\text{-}NO_3^-$ in this thesis) between synthetic nitrate from artificial fertilisers and organic waste-derived nitrate was greater than for ^{15}N. It was not until the early 1990's that combined analysis of nitrogen and oxygen stable isotopes ^{15}N and ^{18}O in nitrate were really put together with the aim of creating a more powerful tool than $\delta^{15}N\text{-}NO_3^-$ alone for identifying sources of nitrate in groundwater. This is discussed in greater depth in section 2.6.

1.2 Study aims and specific objectives

This project, which explores combined $\delta^{15}N$ and $\delta^{18}O$ analyses on groundwater nitrate in conjunction with conventional chemical analysis of water constituents, primarily aimed to give a critical evaluation of stable isotope analysis of nitrate as a tool to determine nitrate sources in Irish groundwaters. Under this primary aim, several objectives were developed:

- Analyse soil-water and groundwater nitrate isotopic composition under different types of land use (grass and tillage) and N inputs (artificial diffuse or point/diffuse organic N sources), and compare with the isotopic composition of artificial fertilisers and animal organic wastes.
- Analyse groundwater nitrate isotopic composition in relation to hydrochemistry.
- Identify microbial processes likely to affect groundwater nitrate original isotopic composition.

This work was mainly carried out in the Barrow Valley, south County Kildare and north County Carlow, where unsewered dwellings and farms are scattered in areas of intensive agricultural activities. Here, a significant proportion of tillage land and relatively free-draining soils overlie shallow sand/gravel and Carboniferous limestone aquifers. Research work was also undertaken to a lesser extent at Moorepark Research Centre, north-east County Cork, where an intensive dairy farm and a thin free-draining soil cover overlie a karstified limestone bedrock aquifer.

The potential sources of groundwater nitrate identified in the study areas were linked with the diffuse application of artificial N fertiliser to tillage and grassland fields, but also with the point discharge of organic waste nitrogen originating from farmyard and septic tank effluents. Organic wastes were also a major diffuse N source at Moorepark RC, but not in the Barrow Valley sampling areas where little livestock was present. The situation was complicated by the fact that, in many sampling wells, groundwater nitrate probably arose from mixed sources, i.e. from both artificial diffuse and organic sources. Previous research in the Barrow Valley carried out in the 1980's (Daly and Daly, 1982; Coxon and Thorn, 1991) had demonstrated a nitrate problem, but the relative importance of diffuse agricultural sources (i.e. inorganic fertiliser application) and organic point sources (i.e. farmyards, septic, manure pits, etc) remained unresolved.

A secondary aim of this research work was then to investigate nitrate sources and N transformations in the Barrow Valley and the Cork study areas, with the following objectives to be reached:

- To determine the origin of nitrate in the groundwater sampling areas, and assess the important of diffuse fertiliser nitrate sources.
- To obtain information on denitrification processes in Irish soils and aquifer materials.

1.3 Thesis layout

This section intends to outline and explain the organisation of this thesis, which consists of a literature review, followed by the description of the study areas, the methods, three results chapters and discussions, and finally a general conclusion.

Chapter 2 presents the nitrogen cycle from the nitrate perspective, in order to provide the basis for later discussions in the results chapters. Potential nitrogen sources at the origin of nitrate leaching are introduced and discussed along with microbial and physico-chemical processes that can affect nitrate directly or indirectly. Both N sources and processes are described in relation to the chemistry, before moving on to stable isotopes.

Chapter 3 identifies potential sources of nitrogen in the groundwater sampling areas, and classifies sampling sites according to these spatial characteristics. This information is used

in groundwater analyses and discussion presented throughout chapters 6 and 7. A description of soil-water experimental plots and land management is also given to facilitate results interpretation in chapter 5. In addition, reference is also made to geological and hydrogeological characteristics of the study areas.

Experimental and analytical methods are explained in chapter 4, in relation to conventional chemical analyses on water samples (e.g. measurement of major ions concentrations), and also stable isotope analyses on nitrate and water. In this chapter, the reliability of the analyses is also tested; crucial in assessing the validity of the approach presented here.

Chapter 5 discusses the chemical and isotopic results for the soil-water investigation, which was mainly carried out on the Moorepark RC unsaturated zone, and to a lesser extent on soils from the Barrow Valley. In chapter 6, groundwater chemistry is analysed in relation to site spatial characteristics discussed in chapter 3. Chapter 7 furthers groundwater analyses and discussion initiated in chapter 6, focussing on the isotopic composition of groundwater nitrate in relation to both groundwater chemistry and site spatial characteristics. It should be noted that chapters 6 and 7 deal primarily with groundwater samples from the Barrow Valley sampling area, Moorepark RC groundwater samples accounting for only a small fraction of the whole groundwater dataset. Finally, chapter 8 links soil-water and groundwater results.

CHAPTER 2: LITERATURE REVIEW ON NITRATE LEACHING AND STABLE ISOTOPES

2.1 Introduction to the nitrate problem

2.1.1 Why groundwater contamination by nitrate is a concern

- Health

The impact of high nitrate concentration in drinking water on human health has been studied for several decades now. The reason for such concern is that, although itself harmless to humans, nitrate is a precursor of potentially hazardous substances once ingested. Ingestion of nitrate has been linked to methaemoglobinemia, also called "blue baby disease" (Bryson, 1984; Addiscott *et al.*, 1991; Fan and Steinberg, 1996) when present in drinking water at concentrations above 50 mg/l NO_3^-. After ingestion, nitrate is transformed into nitrite by bacteria in the digestive system. Nitrite can then oxidize iron in the haemoglobin of red blood cells to form methaemoglobin, which lacks the ability to carry sufficient oxygen to cells. While most humans have the ability to convert methaemoglobin back to "oxyhaemoglobin", the risk of cyanosis after ingestion exists for infants under six months whose digestive and enzyme systems are underdeveloped to cope with this task. Older people with gastrointestinal system disorder, individuals with genetically impaired enzyme system and foetuses (through breast milk feeding) are also at greater risk than the general population (Kross *et al.*, 1992; Jasa *et al.*, 1999). Because of these health concerns, the World Health Organisation has recommended a limit of 50 mg/l NO_3^- in drinking water (WHO, 1998), and in the European Union, this limit has been set in successive drinking water directives (Council of the European Communities, 1980; Council of the European Communities, 1998). As for animals and especially livestock, concentrations of 180 - 450 mg/l NO_3^- are considered risky (Freeze and Cherry, 1979; Di and Cameron, 2002).

Nitrate may also react with amines or amides in the body to form N-nitroso compounds (particularly nitrosamine), which are known to cause cancer in animals (Bryson, 1984). Hence high ingestion of nitrate could elevate the risk of gastric and stomach cancers in humans. Nevertheless, most studies trying to correlate high nitrate concentration in

drinking water and high occurrence of gastric cancer presented mixed results (Gilli *et al.*, 1984; Rademaher *et al.*, 1992). Ingestion of large quantities of nitrate is also believed to increase the risk of Non-Hodgkins Lymphoma, which affects the cells of the lymphatic system with lymphocytes starting to behave like cancerous cells and multiplying uncontrollably (Weisenburger, 1991; Ward *et al.*, 1996; Freedman *et al.*, 2000).

Finally, ingestion of water highly loaded in nitrate may be the cause of recurrent diarrhoea, which can prove quite damaging in developing countries such as India. Gupta *et al.* (2001) observed a strong correlation between the occurrence of diarrhoea and the nitrate levels measured in ingested water that ranged from 26 to 460 mg/l NO_3^-.

- Nitrate and environment

As described by Iversen *et al.* (1998), the natural N cycle has been increasingly disturbed in Europe over the last fifty years by human activity and anthropogenic inputs coming mainly from increased fossil fuel combustion and burning of biomass, increased production and discharge of waste and sewage, but also intensification of agriculture and production of artificial fertiliser. The extensive use of nitrogen in intensive farming systems represents an established threat to the environment in general (Vitousek *et al.*, 1997) and the water resources in particular (Reisenhofer *et al.*, 1995).

The over-enrichment in nutrients of surface water bodies is a phenomenon known as eutrophication (EC, 2002a). When nitrate is present in excess, the balance in the N cycle is disrupted and this can lead to the disproportionate growth of algae (e.g. toxic cyanobacteria on the surface) or higher plants (e.g. reeds), which can deplete oxygen in the system - coupled with aerobic bacterial degradation of organic matter, potentially resulting in anoxia, and shade other plants from necessary sunlight. The consequence is the death of less tolerant species (flora and fauna) and an impoverishment of the biodiversity, especially during summer when higher temperatures favour growth. The contamination of surface water by nitrate is usually caused by surface run-off (fertiliser application followed by heavy precipitation) or atmospheric deposition. Through discharge into lakes, streams and estuaries, groundwater containing high levels of nitrate can also contribute to algal blooms and surface water clouding. Eutrophication also depends on the levels of phosphorus present in water. In surface water and marine areas, both nitrogen and phosphorus can be the first limiting nutrient. Generally, plant growth in rivers and lakes is

limited by the availability of phosphorus, whereas nitrogen is frequently the limiting nutrient for plant growth in estuarine and marine aquatic systems (Howarth, 1988; Iversen *et al.*, 1998).

An indirect effect of intensive farming and high levels of nitrate is the emission of nitrous oxide N_2O, which is an intermediate or a final product of denitrification, and is a potent greenhouse gas in the atmosphere also involved in the destruction of ozone. Depending on a combination of soil factors (see section 2.4.3), denitrification can produce N_2O rather than N_2, and thus elevate atmospheric N_2O concentrations. Nitrous oxide is 180 times more efficient than carbon dioxide as a greenhouse gas, and accounted for 5-10 % in the potential increase in global warming at the end of the 1980's (Addiscott *et al.*, 1991). Jenkinson (1990) assessed that, on a global scale, soil produced twice the amount of N_2O emitted by burning fossil fuels.

- Nitrate and economy

The environmental and health damages caused by nitrate contamination of groundwater have a monetary cost. Scott (2005) exposed some financial implications by taking into account the treatment or prevention costs, but also the administration and monitoring costs in the case of damage caused by overuse of fertilisers, which impacts the economy negatively as demonstrated by the following examples. Any groundwater scheme that is deemed unfit for human consumption is usually abandoned. A new well must then be installed, or else an existing well could be drilled deeper, but both will have high costs. As an alternative option, a nitrate removal system could be installed on a private or municipal water supply, which would prove costly. Besides installation costs, households pay annual operation and maintenance costs. In addition, the Nitrates Directive (see section 2.1.4) requires action to be taken wherever nitrate levels are above 50 mg/l NO_3^-, whether groundwater is currently being used as a water supply or not, which can induce pricey solutions.

From the farmer viewpoint, the key concern is to maintain high yields. A reduction of fertiliser application may result in lower yields, and therefore lower incomes. This is especially true for nutrient-demanding crops such as potatoes, which take up soil nutrients inefficiently in comparison with other crops (Addiscott *et al.*, 1991), and require high fertiliser application rates. Some farmers believe they cannot afford the extra costs

associated with nitrate reducing decisions and practices whereas others believe those decisions and practices will save them money. Implementation of the Nitrates Directive in Ireland will impose limits on N application.

2.1.2 Extent of the nitrate problem in European and Irish groundwaters

Although groundwater contamination by nitrate may not be as widespread a problem in Ireland as it is in other parts of Europe, it is nonetheless an issue that should be addressed appropriately as many Irish aquifers are vulnerable to contamination, as reported in section 2.1.5. Elsewhere in Europe, the nitrate levels measured seem to have globally stabilised throughout the 1990's after decades of increase, but the situation in many regions is still worrying.

- Nitrate in groundwater across Europe and trends over time

A compilation of data provided by twenty-eight European countries to the European Environment Agency revealed groundwater quality records from the 1990's throughout the European Union and peripheral areas (Scheidleder *et al.*, 1999a & 1999b). Seventeen countries made available national-level information (i.e. for no specific area), whereas twenty-two countries released figures specific to smaller geographical areas (numbering 96 regions in total). These data confirmed that nitrate in groundwater was a significant problem in some parts of Europe. The trend in nitrate concentrations, from the 1950's until recent years, including throughout the 1990's, was also discussed for several countries.

National studies revealed that in seven countries (Austria, Czech Republic, France, Germany, Romania, Slovakia, Slovenia), the guide level of 25 mg/l NO_3^- was exceeded at more than a quarter of the groundwater sampling sites. In Romania for instance, about 35 % of 1000 sampling sites exceeded even the drinking water limit (50 mg/l NO_3^-). In comparison, Scandinavian and Baltic countries recorded relatively low nitrate concentrations at their sampling sites. The latest report from the European Commission (EC, 2002b), which accounted for groundwater nitrate records for the period 1996-1998 across fifteen EU member states at the time, also revealed the extent of the nitrate problem. 20 % of the EU monitoring stations exhibited nitrate concentrations above 50 mg/l NO_3^-, and 40 % above 25 mg/l NO_3^-.

A study involving ninety-six European regions was necessary to identify problem areas or 'hot spots'. It revealed that fifty regions had nitrate levels exceeding 25 mg/l NO_3^- in at least 25 % of their sampling sites, whereas 12 regions had nitrate levels in excess of the drinking water limit of 50 mg/l NO_3^- in at least 25 % of their sampling sites. France, Netherlands and Slovenia each had one region where the situation was critical to the point that up to 67 % of their sampling sites exceeded the drinking water limit.

The temporal trend in groundwater contamination by nitrate for aquifers and regions is more difficult to assess because of a lack of long-term data for single sampling sites. In this context, only a few countries provided enough information to evaluate the temporal trend in a few aquifers. These data may not necessarily represent typical temporal trends experienced on a national level. For instance, a survey carried out in the UK over the period 1945-1996 revealed a general increase in nitrate levels in some aquifers since World War II by almost 0.4 mg/l NO_3^-/year for fifty years. This contrasts with the early 1990's, where nitrate concentrations in many European aquifers appeared overall quite stable. Nevertheless, this trend is quite variable within each country. South and eastern of France for instance showed some important decreases, whereas nitrate levels in the north and west of France were increasing. In countries like Germany, Netherlands and Greece, results seem to be equally variable.

- Groundwater quality in Ireland

In 1995, the EPA commenced a systematic survey of Irish groundwater quality based on a representative network of about three hundred monitoring stations that forms part of the EPA's National Groundwater Quality Monitoring Programme. The aim was to detect trends in groundwater quality and to determine the causes of any changes. To meet these objectives, sampling was generally carried out twice per year, to coincide with groundwater levels being at their lowest and highest, and important physico-chemical and microbial parameters were analysed.

Table 2.1 summarises results of the three successive sampling programmes operated between 1995 and 2003, and reported successively by Lucey *et al.* (1999), McGarrigle *et al.* (2002) and Toner *et al.* (2005). Results, which only take into account stations that were sampled between four and six times during each three-year monitoring period, are presented in terms of the percentage of stations where averaged parametric values (e.g.

mean nitrate concentration between 2001 and 2003) complied with the corresponding drinking water limits (see Drinking Water Directive's standards in section 2.1.4) as set out in the old EC drinking water Regulations (Statutory Instruments 81 of 1988). It should be noted that some parametric values are higher under the new Regulations (S.I. 439 of 2000), namely conductivity and pH, but such changes would not have influenced the results displayed in table 2.1.

Table 2.1: Percentage of EPA groundwater quality monitoring stations with mean parametric values complying with drinking water limits as set in the European Communities (Quality of Water Intended for Human Consumption) Regulation, 1988 (S.I. 81 of 1988) for a number of physico-chemical and microbial parameters. (Adapted from Lucey *et al.*, 1999; McGarrigle *et al.*, 2002 and Toner *et al.*, 2005).

Parameters measured & units	Drinking water limits [1]	% compliance for 1995-1997	% compliance for 1998-2000	% compliance for 2001-2003
pH	6.0 – 9.0	ND	ND	98.7
Conductivity (µS/cm)	1500	ND	ND	99
Ammonium (mg/l NH_4^+)	0.3	95	93.5	93.4
Nitrate (mg/l NO_3^-)	50	97.4	98.5	98.3
Chloride (mg/l Cl^-)	250	100	100	100
Orthophosphate (mg/l P)	0.03 [2]	77	77.3	69
Iron (mg/l Fe^{2+})	0.2	78	82	83.6
Manganese (mg/l Mn^{2+})	0.05	78	80	82.5
Faecal coliform (units/100 ml)	0	66	62	78

ND Not Determined

1) Drinking water limits under the European Communities (Quality of Water Intended for Human Consumption) Regulations, 1988 (S.I. 81 of 1988) (orthophosphate excluded)

2) Drinking water limit under the Water Pollution Act, 1977 (Quality Standards for Phosphorus) Regulations, 1998 (S.I. 258 of 1998) if groundwater discharges into a river (limit of 0.02 mg/l P if groundwater feed a lake)

From the nitrate perspective, results revealed a generally acceptable condition as most sampling sites complied with the drinking water nitrate limit of 50 mg/l NO_3^-. Between 1995 and 2003, the percentage of stations in compliance with the drinking water limit was never below 97 %. But what table 2.1 does not show is that between 20 and 23 % of sites had nitrate levels above 25 mg/l NO_3^- between 1995 and 2003, which may indicate some contamination. In addition, nitrate 'hot spots' tended to occur mainly in the east and south of Ireland. During 1995-1997 for instance, over 80 % of sites above nitrate guide levels were located in east Munster and Leinster, which are regions largely dedicated to intensive agriculture. Similar distributions and conclusions were drawn by surveys carried out in the mid 1990's and reviewed by Wright (1997), who did not report any nitrate-related problem in northern and western counties such as like Leitrim, Mayo and Sligo.

The monitoring programme also raised other sources of concern. Firstly, relatively high levels of orthophosphate were measured at almost half of the sites. In conjunction with high nitrate concentration, this can lead to serious eutrophication in surface water bodies.

Secondly, and more seriously from a human-health perspective, was the extent of measured faecal coliform contamination. Despite a recent improvement for the period 2001-2003 with 'only' 22 % of all stations not complying with EC Regulations, faecal coliforms were found at almost one third of all sites between 1995 and 2000. This indicates persistent organic contamination that may be the result of sampling wells being poorly located (e.g. too close to a septic tank or farmyard), badly constructed (e.g. run-off water entering the well) or weakly protected, together with inadequate animal waste management on nearby farms.

2.1.3 Importance of groundwater as drinking water supply in Ireland

Groundwater is an important resource that needs to be looked after. In Ireland, it accounts for at least 11 % of all drinking water distributed either by public or group water schemes in the country (Page *et al.*, 2004). If one includes private wells, one quarter of all water abstracted for public or private drinking water supply comes from groundwater, and this percentage may reach 86 % in rural areas (McGarrigle *et al.*, 2002). According to Wright (1999), there are at least 200,000 water supply wells in Ireland - either private wells, public or group water schemes. In most cases, water abstracted does not undergo any sort of chemical treatment.

2.1.4 Legislation to control groundwater contamination by nitrate

Many EU Directives are related to groundwater quality, setting standards and objectives to acquire a good status. In the context of this project, which investigates groundwater nitrate in an agricultural rural area of Ireland, attention is focused on agricultural N diffuse sources, but also on agricultural N point sources and septic tank discharge (section 2.3) as these N sources are thought to participate to nitrate contamination. Several EU Directives, which are implemented in Ireland by the EPA and local authorities, aimed to protect groundwaters and prevent any further pollution. Although the Nitrates Directive addresses specifically nitrate losses related to agriculture (diffuse sources and management of organic wastes), other Directives deal with any potential threat to groundwater quality, which includes contamination by septic tanks among others. Limits related to nitrate referred to in this thesis are in mg/l NO_3^-, whereas some authors in the literature may use mg/l NO_3-N, which involves the division of the former by a factor of 4.43.

- The Nitrate Directive and its implementation in Ireland

The Nitrates Directive (Council of the European Communities, 1991), introduced in 1991, focuses on nitrate losses from agriculture to water bodies, its objective being to reduce water pollution caused or induced by nitrates from agricultural sources and prevent further such pollution. Among others, it addresses groundwaters which contain or could contain, if preventative action is not taken, nitrate concentrations greater than 50 mg/l NO_3^-. It was transposed into Irish law in May 2003 as European Communities (Protection of Waters against Pollution from Agricultural Sources) Regulations, 2003 (S.I. 213 of 2003). The various steps of implementation of the directive involved:

1) Detection of polluted or threatened waters.
2) Designation of Nitrate Vulnerable Zones NVZs (areas with known or potential nitrate levels in water that exceed guide values specified in the Directive) by 1993.
3) Establishing by 1993 Code(s) of Good Agricultural Practice on all member state territories, the implementation of which is mandatory within NVZs, but not outside where it is voluntary. In NVZs, the Code of Good Practice is applied through what is called Action Programmes (APs).
4) Development of Action Programmes (for NVZs), i.e. a list of measures to be implemented by farmers that will achieve the Directive's objectives.
5) Establishing national monitoring (200-2000 points per member state) by 2005 and reporting to the European Commission every 4 years on nitrate concentrations and eutrophication.

In order to limit the losses of N linked to agricultural activities, the main types of actions that concern APs are (EC, 2002b):

- Crop rotations, soil winter cover, catch crops, in order to limit leaching during the wet seasons.
- Use of fertilisers and manure with a balance between crop needs, N inputs and soil supply; frequent manure and soil analysis; mandatory fertilisation plans and general limitations per crop for both mineral and organic N fertilisation.
- Appropriate N spreading calendars and sufficient manure storage, for availability only when the crop needs nutrients, and good spreading practices.
- 'Buffer' effect of non-fertilised grass strips and hedges along watercourses and ditches.

- Good management and restriction of cultivation on steeply sloping soils, and of irrigation; good farmyard management and organic wastes storage requirements.

In Ireland, the Code of Agricultural Good Practice was issued in July 1996 by the Department of the Environment and Department of Agriculture, Food and Forestry (DE and DAFF, 1996). After failing to designate any NVZs and receiving warnings from the European Commission over several issues breaching the Directive, the Minister for the Environment, Heritage and Local Government devised on May 2003 the Regulations (S.I. 213 of 2003) that formally identified the national territory of Ireland as the area to which an AP will be applied. It was not until December 2003 that a draft AP was issued for public consultation, jointly by the Department of the Environment, Heritage and Local Government and the Department of Agriculture and Food (DEHLG and DAF, 2003). This was followed by a revised draft AP issued on October 2004 and submitted to the European Commission, to which it responded unfavourably on the grounds that this AP was not complete and did not comply with the requirements of the Nitrates Directive. It was not until 28 July 2005 that a newly revised AP (DEHLG and DAF, 2005) was submitted again to the European Commission, whose decision was not known at the time of the writing.

In addition, the Irish government's revised AP, which contains a limit of 170 kg organic N ha/year application, is contested by the Irish Farmers Association which argues that there is no scientific basis for such measures, which would eventually force Irish farmers to cut down their livestock and then their incomes. In its latest statement issued on 24th May 2005 on its website, the IFA urges that the Government 'must now move quickly to secure a workable derogation from the organic nitrogen limit of 250 kg N. per hectare'.

- The Drinking Water Directive

The new Drinking Water Directive (Council of the European Communities, 1998), which replaced the old Directive (Council of the European Communities, 1980), aims to ensure good quality drinking water for consumers throughout the EU by imposing standards for nitrate concentration and forty seven other parameters that should not be exceeded in waters intended for human consumption. It was transposed into Irish law on December 2000 as the European Communities (Quality of Water Intended for Human Consumption) Regulations, 2000 (Statutory Instruments No. 439 of 2000), which revoked the European Communities (Quality of Water Intended for Human Consumption) Regulations, 1988

(Statutory Instruments No. 81 of 1988) and came into force on 1st January 2004. Although drinking water standards apply only to waters intended for human consumption at the point of use, and not in the groundwater body itself, these standards are used for the assessment of groundwater quality in many studies, including this project.

One task of the new Drinking Water Directive was to streamline drinking water regulations. In Directive 80/778/EEC (Council of the European Communities, 1980), most of the sixty six parameters covered, which were divided between six categories, were associated with two different parametric values: i) a maximum admissible concentration (MAC) or value that should not be exceeded; ii) a guide level (GL) that was used as a warning indicator of contamination. In the new Directive 98/83/EC (Council of the European Communities, 1998), the number of parameters was reduced to forty eight, divided into three groups (microbial, chemical and indicator parameters), and guide levels were abandoned. In addition, drinking water limits (formerly referred to as MACs in the 1980 Drinking Water Directive) were reviewed and strengthened in accordance with the latest available scientific knowledge, but this did not bring any change for nitrate, the MAC in drinking water remaining at 50 mg/l NO_3^-. Another improvement brought by the new Directive was to increase transparency in member states by obliging them to report on drinking water quality to the Commission and consumers, and also to inform these bodies of measures that may be taken to comply with the requirements of the Directive.

Table 2.2 reviews GLs from the old Directive 80/778/EEC along with drinking water limits from the new Directive 98/83/EC for a selection of physico-chemical and microbial parameters that were either measured during this project or referred to in the literature review. It should be noted that for a few parameters, both old and new Regulations were actually less lenient than the Directives themselves. For instance, the drinking water limit for ammonia is set at 0.5 mg/l as NH_4^+ in the new Directive, but the drinking water Regulations (S.I. 439 of 2000) brought this limit down to 0.3 mg/l as NH_4^+.
Under the new drinking water Regulations (S.I. 439 of 2000), parametric values for microbial and chemical parameters, which includes nitrate, are mandatory and should not be exceeded. In case of exceedance, local authorities must investigate as soon as the case has been reported and identify the cause of such failure. Remedial action must then be taken to restore drinking water quality. Parametric values for indicator parameters are not mandatory, and the local authorities are left to decide of any action after the risk for human health has been assessed.

Table 2.2: Guide Levels (GLs) of some chemical and microbial parameters as specified in the old Drinking Water Directive 80/778/EEC, and corresponding drinking water limit under the new Drinking Water Directive 98/83/EC.

Parameters & units (as set in Directive 98/83/EC)	GL (Directive 80/778/EEC)	Drinking water limits (Directive 98/83/EC)
MICROBIAL PARAMETERS		
Total Coliform (number/100 ml)	N/A	N/A [1]
Faecal Coliform (number/100 ml)	N/A	0
CHEMICAL PARAMETERS		
Nitrate (mg/l NO_3^-)	25	50
INDICATOR PARAMETERS		
Ammonium (mg/l NH_4^+)	0.05	0.5 [3]
Chloride (mg/l Cl^-)	25	250
Sulphate (mg/l SO_4^{2-})	25	250
Potassium (mg/l K^+)	10	N/A [1]
Sodium (mg/l Na^+)	20	200
Magnesium (mg/l Mg^{2+})	30	N/A [1]
Calcium (mg/l Ca^{2+})	100	N/A [2]
pH	6.5 - 8.5	6.0 - 9.5
Conductivity (μS/cm) at 20°C	400	2500

N/A Not Applicable

1) drinking water limit for total coliform, potassium and magnesium set at 0/100 ml, 12 mg/l K^+ and 50 mg/l Mg^{2+} respectively, under the Drinking Water Directive 80/778/EEC

2) drinking water limit for calcium set at 200 mg/l Ca^{2+} under the European Communities (Quality of Water Intended for Human Consumption) Regulations, 1988 (S.I. 81 of 1988)

3) Drinking water limit for ammonium set at 0.3 in mg/l NH_4^+ under both European Communities (Quality of Water Intended for Human Consumption) Regulations, 1988 (S.I. 81 of 1988) and 2000 (S.I. 439 of 2000)

- The Water Framework Directive

The Water Framework Directive (Council of the European Communities, 2000), which came into force in 2000, was transposed into Irish law on December 2003 as the European Communities (Water Policy) Regulation, 2003 (Statutory Instruments No. 722 of 2003). It establishes a framework for the protection of all water resources - groundwater, surface water and coastal waters. The objectives are:

- To prevent further deterioration, protecting and enhancing the status of aquatic ecosystems,
- To promote sustainable water use based on long-term protection of available water resources,
- To enhance protection and improvement of the aquatic environment,
- To ensure the progressive reduction of pollution of groundwater and prevent its further pollution,
- To contribute to mitigating the effects of flooding and pollution.

These objectives are to be achieved by designating river basin districts (RBD) for all waters covered by the Directive. Seven districts have already been selected for Irish waters. Within each RBD, monitoring programmes (volume, flow rate, ecological and chemical status) must be put in place. Subsequently, a programme of measures must be put in place to achieve the water quality objectives. The development and implementation of these measures will have to involve the active participation of the agricultural stakeholders including tillage farmers. In addition, the Water Framework Directive requires identification of all waters to be used for human consumption, above a specified volume, and the measures that will be put in place to achieve compliance with the Drinking Water Directive. Finally, the principle of recovery of the costs of water services, including environmental and resource cost, has to be applied.

2.1.5 Aquifers at risk in Ireland

- General features of risk assessment

To maintain or improve the quality of groundwater resources, prevent pollution and help implement EU legislation (section 2.1.4), the GSI, the DELG and the EPA have developed a national methodology for Groundwater Protection Schemes. These schemes aim to 'provide guidelines for the planning and licensing authorities in carrying out their functions, and a framework to assist in decision-making on the location, nature and control of developments and activities in order to protect groundwater' (GSI/DELG/EPA, 1999). Among many components of the Groundwater Protection Schemes are the groundwater vulnerability maps, which classify soils and sediments according to the ease with which contaminants can move downwards to contaminate underlying groundwater (Daly, 2001). This classification is used for regional scale vulnerability mapping, but also for site vulnerability assessment. Unfortunately, not all the counties have been covered at the time of writing, and little information is available for some areas studied in this project, including Co. Carlow. Within Ireland, there are four classes of vulnerability: Extreme, High, Moderate and Low. Table 2.3 shows how these categories relate to subsoil characteristics (subsoil defined by GSI as all unconsolidated material between the topsoil and the bedrock) and the type of recharge.

Table 2.3: Geological and hydrogeological conditions governing vulnerability mapping, adapted from GSI/DELG/EPA (1999) and Daly (2001).

Thickness of overlying subsoil [1]	Hydrogeological conditions				
	Diffuse recharge				Point recharge
	Subsoil [2] permeability (and type)			Unsaturated zone [1]	Karst features
	High permeability *(sand/gravel)*	Moderate permeability *(sandy subsoil)*	Low permeability *(clayey subsoil, clay, peat)*	*(unconfined sand & gravel aquifers only)*	*(swallow holes, losing streams)*
0 - 3 m	Extreme	Extreme	Extreme	Extreme	Extreme (30 m radius)
3 - 5 m	High	High	High	High	N/A
5 - 10 m	High	High	Moderate	High	N/A
> 10 m	High	Moderate	Low	High	N/A

N/A Not Applicable

1) Depth ranges refer to subsoil thickness (i.e. thickness of unconsolidated material above the bedrock), except in the Unsaturated zone column where it refers to thickness of the unsaturated zone above an unconfined sand & gravel aquifer

2) Subsoil is defined by GSI as all unconsolidated material between bedrock and 1 to 2 m thick topsoil

The topsoil is not taken into account in the vulnerability mapping because the point of release of contaminants is assumed to be 1 - 2 m below ground level. What is taken into account, in the case of a bedrock aquifer, is the thickness and the permeability of all unconsolidated material above the bedrock (and below the topsoil). For unconfined sand and gravel aquifers, it is the thickness of the unsaturated zone that is taken into consideration. If confined, i.e. overlain by material with low permeability such as till, the sand and gravel aquifer is then treated like a bedrock aquifer and it is then the thickness and the permeability of all unconsolidated material above the sand and gravel that is considered (Daly, 2001).

- Extreme to high vulnerability of sand/gravel or bedrock aquifers to nitrogen inputs

It appears clear from table 2.3 that under the Irish hydrogeological context, shallow and unconfined sand and gravel aquifers are as vulnerable to contamination as bedrock aquifers overlain by a thin layer of soil. Under the above classification, an unconfined sand and gravel aquifer overlain by more than three meters of unsaturated zone qualifies as highly vulnerable, whereas if the overlying unsaturated zone is less than three meters thick it is considered to be extremely vulnerable. In the case of a bedrock aquifer subjected to a diffuse recharge process, if there is less than three meters of subsoil above the bedrock then the aquifer is classified as extremely vulnerable, no matter the permeability of the overlying unconsolidated materials. Such vulnerability to contaminants, such as nitrate, is found in the groundwater sampling areas of the Barrow Valley and at Moorepark RC, for which detailed descriptions are given in chapter 3.

High transmitivity within the aquifer also plays an important role in groundwater contamination since it favours the transportation of contaminants over long distances. This situation prevails in sand and gravel or karstic aquifers where the impact of nitrate leaching may be manifested far from the nitrate source. In addition, some studies have shown that many sand and gravel aquifers do not have appreciative contaminant dilution potential (Sudicky *et al.*, 1983; Freyberg, 1986; Moltyaner and Killey, 1988a & 1988b). Attenuation by dilution is likely to be more important in karstic aquifers where mixing of water can be important.

2.2 Nitrate dynamics in terrestrial systems of agricultural areas

2.2.1 What is nitrate?

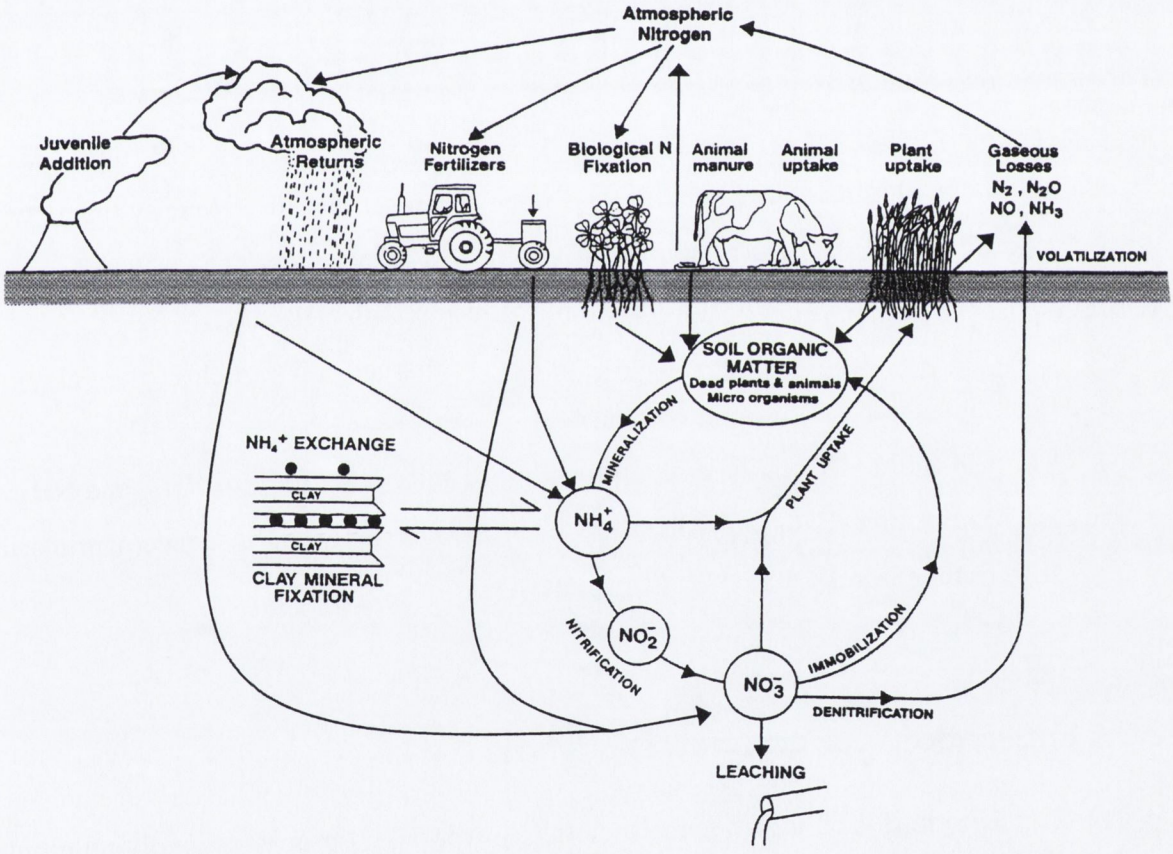
Nitrate is a common ion on Earth that humans ingest on a daily basis. According to the World Health Organization, most adults consume 20 - 70 milligrams of nitrate-nitrogen per day with most of this coming from foods like lettuce, celery, beets, and spinach. It is a natural constituent of plants and vegetables, and it is also present in soils in different ways. It occurs as a mining resource in the form of salts (e.g. Chile saltpetre $NaNO_3$), and it naturally appears in soil water, surface and groundwater bodies in low concentrations, typically in the range 5-9 mg/l NO_3^- in Ireland (McGarrigle *et al.*, 2002). But nitrate is also artificially synthesised from the atmospheric reservoir of N_2 and O_2 for the needs of the fertiliser industry, which involves huge quantities of artificial fixation every year that are added to terrestrial systems by farmers (Vitousek *et al.*, 1997).

From a chemical point of view, nitrate, chemical formula NO_3^-, is a small inorganic anion with a high diffusion coefficient of 10^{-6} cm^2/s, which means that it can move easily in soil water for instance. It is made up of three atoms of oxygen bound to one atom of nitrogen, which represents the most oxidized chemical form of N to be found in natural systems (oxidation state of +5). From the isotopic point of view, nitrogen and oxygen have two main stable isotopes, ^{15}N and ^{14}N for nitrogen, ^{18}O and ^{16}O for oxygen, which are found in nitrate in proportions that vary and depend on the system nitrate samples are collected from.

2.2.2 Nitrate in the Nitrogen cycle

Nitrogen is an essential element to living organisms that is abundantly present on Earth in many chemical forms. It is found in inorganic forms as a gas (N_2, N_2O, NO, NO_2, NH_3, etc) or an ion (NH_4^+, NO_2^-, NO_3^-), but also in organic compounds such as amino acids and proteins of organic matter. Present in the atmosphere, the biosphere, the geosphere, and the hydrosphere, N-bearing species undergo an ongoing succession of complex physical and biochemical reactions at the global scale. In terrestrial systems though, the N cycle is restricted to a few processes, which are closely associated with nitrate as seen in figure 2.1 and described in detail in sections 2.4 and 2.5.

Figure 2.1: Terrestrial N cycle in agricultural soils (McLaren and Cameron, 1990).



First, nitrate occurs in soils following input from three sources:

- By nitrification, which is the process that transforms NH_4^+/NH_3 from various origins (e.g. artificial fertilisers, urine, etc) into NO_3^-.
- By field applications of artificial nitrate fertilisers by farmers.
- By wet and dry atmospheric deposition, which is considered marginal in Ireland or UK in comparison with quantities involved above.

At the same time, nitrate found in soil is used up in three different ways involving biochemical and microbial activity:

- By plant uptake through the rooting system, which results in the incorporation of nitrate nitrogen into plant tissues and genetic material (synthesis of amino-acids and proteins).
- By microbial immobilisation, which results in the incorporation of nitrogen into bacterial tissues and genetic materials.
- By denitrification, which refers to the bacterial reduction of NO_3^- into nitrous oxide N_2O and/or diazote N_2.

Once in soil, nitrate can also be subjected to leaching, which is a conservative physical process that consists of the transportation of nitrate with percolating waters through the unsaturated zone and potentially to the water table, which is the cause of the groundwater contamination problem.

In addition to the aforementioned processes, some other reactions are indirectly linked with nitrate because they affect its precursors:

- Volatilisation of NH_3 (in equilibrium in soil-water with NH_4^+).
- Clay mineral adsorption of NH_4^+ on negatively charged soil particles (often clay).
- Plant uptake of NH_4^+ (along with nitrate).
- Mineralisation (also called ammonification) of soil organic N into NH_4^+ and NH_3.
- Microbial immobilisation, which has been thought for years to concern primarily NH_4^+ rather than NO_3^-.

2.2.3 Implications for groundwater nitrate

With the exception of leaching and clay mineral adsorption, all processes involving nitrate directly or indirectly take place in the upper part of soils. NH_3 volatilisation happens on soil-surface, plant uptake occurs around the rooting zone, and other microbial processes (i.e. mineralisation, nitrification, immobilisation, and denitrification) arise only where bacteria are present and where there is enough carbon (i.e. energy) available to them, which is mainly within the top metre of soil, as described in section 2.4 (although denitrification can also take place a greater depth). The nitrate leaching process appears to be very different from other processes in that it takes place through the whole profile of

soil and subsoil that stands between the soil-surface and the water-table, and not only in its upper part. Consequently, the pool of nitrate that leaches downward and the fraction that reaches groundwater has potentially been subjected to some of the other processes described above, some of these reactions being favoured to the detriment of others depending on the local context (geology, weather conditions and land management).

Because any N input that is not already in the form of nitrate can be subjected to mineralisation and/or nitrification in terrestrial systems, as seen in figure 2.1, leaching of nitrate towards groundwater concerns any source of N present in the study area under consideration (types of N sources are discussed in section 2.3). As explained in section 2.6.2, the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ isotopic ratios in nitrate are initially highly dependent on the type of source. Because all the biochemical or physical processes described above can take place and affect nitrate during leaching (or at least during its early stage), and because some of these processes involve some isotopic fractionation, the original composition of nitrate can be altered to various extents (section 2.6.3). In other words, nitrate that has reached the water-table may have a very different isotopic composition to that of the nitrate prior to leaching. Therefore, isotopic interpretation must take into account not only the source of N that generates nitrate but also the fact that some biochemical and physical processes may have taken place in the unsaturated zone.

In addition, many N inputs to soils also contain, and contribute to the leaching of, other non N-bearing ions such as chloride, potassium and sodium among others. In fact, each nitrate source-type is associated with specific ions, which will influence the chemical composition of percolating water, and consequently groundwater. Expected values for groundwater chemistry and groundwater nitrate isotopic composition are compiled in sections 2.5.4 and 2.6.6 respectively, in accordance with the occurrence of different types of N sources and microbial processes that can affect nitrate.

2.3 Sources of nitrogen, nitrate and other contaminants in soils

2.3.1 Types of nitrogen and nitrate sources associated with groundwater contamination

A wide variety of sources contributing to soil N are reviewed in table 2.4. As explained previously, this soil N can be subjected to mineralisation and nitrification, and thus can

potentially lead to the leaching of nitrate towards water bodies, including groundwater. For this reason, any nitrogen source should also be seen as a potential source of groundwater contamination by nitrate.

The type of N source is commonly distinguished in two main ways:

- Organic N versus inorganic N.
- Point sources versus diffuse sources (i.e. localised point of release versus non-localised point of release).

Table 2.4: Nitrogen sources in soils, adapted from Fitzsimons *et al.* (2000). (Most likely sources to be found in the study areas are underlined).

	POINT SOURCES	DIFFUSE SOURCES
Organic N	▪ Sewage (with industry process water): - On-site wastewater treatment systems (i.e. septic tanks) -Sewage lagoons -Leaky Sewers ▪ Farmyard: - Manures and slurries - Silage effluent - Soiled water ▪ Waste disposal sites ▪ Contaminated surface water	▪ Organic wastes spread on land: - Manure - Slurry - Soiled water, silage effluent, etc - Sewage sludge, etc ▪ Artificial organic fertilisers (e.g. synthetic urea) ▪ Soil organic matter ▪ Urban areas (agglomeration of point sources) ▪ Geological sources ▪ Atmospheric deposit (wet, dry)
Inorganic N	▪ Waste disposal sites ▪ Industry	▪ Artificial inorganic fertilisers spread on land (e.g. synthetic ammonium nitrate) ▪ Rainfall

Each of these N sources has intrinsic characteristics when it comes to the forms of N and other nutrients they hold and release into soils. But in general, all farmyard wastes and human effluents contain little inorganic N and are dominated by organic N, whereas artificial N fertilisers usually contain either inorganic (e.g. ammonium nitrate NH_4NO_3) or organic N (e.g. urea $CO(NH_2)_2$)). These chemical features are discussed in section 2.3.2 to 2.3.7, which also refers to contaminants other than nitrogenous compounds (discussed in relation to groundwater contamination in section 2.5.4). Isotopic characteristics in relation to N-bearing species are discussed in section 2.6.

In the study areas, only a few types of N sources, underlined in table 2.4, are likely to contribute to soil N, and hence groundwater contamination. Early investigations suggested that groundwater contamination by nitrate in the Barrow Valley was due to localised organic point sources (Daly, 1981; Daly and Daly, 1982). This may be consistent with the

Irish rural situation. Ireland's countryside is in fact characterised by a high proportion of scattered dwellings with individual on-site wastewater treatment systems, and farms equipped with storage facilities for animal wastes (manure, slurry soiled water) and/or the products of harvests (silage, grains, etc). Although septic tank systems treat domestic effluents, large quantities of nitrogen are discharged into subsoil where it will nitrify. As for storage facilities, they are often leaky and can release large quantities of highly N-concentrated effluents into soils.

Other studies pointed out that diffuse fertiliser sources could cause a significant increase above background levels in some areas (Coxon and Thorn, 1991). As described in chapter 3, the study areas in the Barrow Valley and in Moorepark RC are dedicated to tillage and grassland. In this context, on-land applications of artificial N fertilisers and organic wastes represent the main diffuse sources of inorganic and organic N, and hence a likely source of nitrate diffuse pollution to groundwater. Generally speaking, soil organic matter represents another diffuse source of organic N, which consists of a heterogeneous build up of organic material ranging from plant residues prior to decomposition to humus. This includes bacteria, enzymes and any micro- and macro-living organisms in general.

2.3.2 Artificial fertilisers

Although some inorganic N fertilisers are extracted from mines (e.g. saltpetre), the vast majority are industrially produced by fixation of atmospheric N_2, followed with oxidation by atmospheric O_2 in case of nitrate production. These N fertilisers are referred to in the literature as artificial, synthetic or manufactured fertilisers. Many types are available to farmers, and the use of a specific one is usually dependent on the type of crop grown, the climate and soil characteristics. The N fraction contained in artificial fertilisers comes in different forms, either ammoniacal (NH_4^+), nitric (NO_3^-) or organic, hence the following categories of fertiliser (Indiaagronet, 2006):

- Nitrate fertilisers where all the nitrogen being in nitrate form, such as sodium nitrate $NaNO_3$, calcium nitrate $Ca(NO_3)_2$.
- Ammonium fertilisers where all the nitrogen is in ammonium form (or ammonia), such as ammonium sulphate $(NH_4)_2SO_4$, ammonium chloride NH_4Cl, ammonium phosphate $NH_4(H_2PO_4)$, ammonia NH_3 anhydrous or in solution.

- Nitrate and ammonium fertilisers where both ammonium and nitrate are present, such as ammonium nitrate NH_4NO_3, calcium ammonium nitrate $Ca(NO_3)_2NH_4NO_3$.
- Artificial organic nitrogenous fertilisers, such as amide fertilisers like artificial urea $CO(NH_2)_2$ or calcium cyanamide $CaCN_2$, or recently developed slow release organic fertilisers (e.g. oximade, isobutylidine diurea, etc).

With the exception of slow release organic fertilisers, artificial N, regardless of the particular chemical formula, is readily available for plants because it is water soluble and does not need much transformation, if any, to enable plant uptake. Pre-formed nitrate can be directly assimilated by roots, whereas ammonium is quickly nitrified once in soil or can even be assimilated as such. As for urea, it is quickly hydrolysed into ammonium once in soil, followed by an equally quick nitrification.

The total nitrogen (TN) and nitrate contents, in percentage by net weight, vary from one type of fertiliser to another. Table 2.5 summarises the chemical composition of a selection of artificial fertilisers commonly used by Teagasc in Oak Park RC over the last fifteen years. Most of these fertilisers were also reported by Coulter *et al.* (2002) during their national survey of fertiliser use for grassland and arable crops in 2000.

Table 2.5: Chemical composition of some artificial fertilisers used in Ireland, with values reported in mass percentage may vary by a few percents depending on the manufacturer (John Hogan, Teagasc Oak Park RC, personal communication).

Fertilisers (or trade names)	% TN	% NO3-N	% P	% K	% Other
ORGANIC NITROGENOUS FERTILISERS					
Artificial Urea	47	0	0	0	0
NITRATE & AMMONIUM FERTILISERS					
Sugar beet Compound No.1	13	?	4	14	5 % Na^+, 3 % S
Sugar beet Compound No.2	8	?	5	18	6 % Na^+, 3 % S
CAN	27.5	20.6	0	0	20 % Ca^{2+}
Sul CAN	27.5	11.1	0	0	5% S
Super Net	27.5	13.5	0	0	3.7 % S
Nitro Sulfur	?	?	0	0	
Ammonium nitrate	35	17.5	0	0	
N-P-K COMPOUNDS					
10-10-20 compound	10	?	10	20	
16-5-20 compound	16	?	5	20	
20-0-15 compound	20	?	0	15	
24-2.5-10 compound	24	11	2.5	10	
18-6-12 compound	18	6.3	6	12	
NON-NITROGENOUS FERTILISERS					
Potash	0	0	0	52	48 % Cl^-
0-7-30 compound	0	0	7	30	
0-10-20 compound	0	0	10	20	

These fertilisers are quite diverse in their N and nitrate contents. Urea shows the highest nitrogenous content in table 2.5, with 47 % of net weight, whereas most other fertilisers have generally less than 30 % N. The most widely used fertiliser in Ireland, according to the national farm surveys between 2000 and 2003 (Coulter *et al.*, 2002, 2005), is calcium ammonium nitrate, which contains 27.5 % N, nitrate accounting for three quarters of that (20.6 % NO_3-N of net weight).

But artificial N fertilisers contain more than just N. Varying amounts of phosphorus and potassium are found in N-P-K compounds, 10 % P and 30 % K^+ at most . Potash, which was often used in Oak Park RC, is extremely rich in potassium, which accounts for half of its net weight, and also in chloride. Other minor nutrients such as calcium, magnesium and sulphate may also be present. Last, sodium appears to be present only in sugar beet compounds.

2.3.3 Animal wastes

Animal wastes represent a valuable source of N that can be used as natural organic fertilisers for grassland and crops, hence their association with diffuse nitrate contamination. They originate from livestock excretion and are stored in farmyards in different forms before being applied on fields. The storage facilities (i.e. tanks or open pits) and the livestock shelters can prove quite leaky depending on the quality of the installation. Highly N-concentrated effluents can then end up in soils, which is why animal wastes are also associated with point source nitrate contamination. Furthermore, animal wastes are also directly deposited on fields from livestock excretion in grazed pastures.

Prior to being spread by farmers, animal wastes are stored in different forms:

- Solid manure, which contains dung, urine and bedding materials (straw, wooden shavings) from where the livestock has been housed.
- Slurry, which consists of a diluted mixture of dung and urine.
- Farmyard wastewater (also called soiled water, dirty water, or dairy wastewater in dairy farms), which contains dung, urine, milk residues (in dairy farms only), rainwater and soil, produced as a result of the washing of farm installations.

At the origin of manure, slurry and wastewater are animal excretions. The concentration of N in cattle, pig or sheep faeces is usually in the range of 0.2-0.5 % fresh weight (Whitehead, 1995 / p.76; Chambers *et al.*, 2001), more than 90 % of it in organic forms, and more than 70 % in insoluble forms (Kirchmann and Witter, 1992 - cited by Whitehead, 1995 / p.77). In contrast, most N in urine is soluble and its concentration varies widely with diet. It ranges on average between 8,000-10,000 mg/l TN (Whitehead, 1995 / p.73), with 70-90 % of it in the form of urea (Haynes and Williams, 1993). In solid manures stored for few months, typical N concentrations are within the range of 0.4-0.8 % fresh weight (Whitehead, 1995 / p.81), almost all of it being in organic materials. In slurries, the N concentration depends on the level of dilution and ranges typically between 0.3-0.6 % fresh weight (Whitehead, 1995 / p.79), which corresponds to more than 3,000 mg/l TN. Mineral N is mostly found as NH_4^+, which derives from the hydrolysis of urea and accounts for 10-70 % of total nitrogen (MAFF, 1995), 50 % on average (Whitehead, 1995 / p.80), the remainder being contained in organic particles.

Soiled water is far less concentrated in N than manures and slurries due to dilution, but it induces more drainage because of its high water content. Importantly, all these farmyard organic wastes generally contain very little nitrate in comparison with ammonium and organic N owing to their anaerobic condition that inhibits nitrification. For instance, Richards (1999) tested dairy wastewater over a period of thirteen months and found seasonal variations, the highest NH_4-N value being 365 mg/l NH_4^+ in mid-August while the lowest value was observed in February at a concentration of 1 mg/l NH_4^+. These findings are supported by a few studies reported in table 2.6, where it appears that slurries are extremely enriched in nitrogen. Milk, which is part of soiled water in dairy farms, shows the highest nitrogen content with 5000 mg/l TN.

The type of storage system influences the final composition of manure, slurry or wastewater. In normal storage systems, volatilisation of ammonia usually results in large quantities of nitrogen loss, and therefore in a decrease of ammonium content. Alternative storage systems can regulate N content, aeration resulting in much more ammonia volatilised, and hence far less inorganic N present, and anaerobic digestion resulting in an increase in ammonium content and low ammonia losses (Vetter *et al.*, 1987 – cited in Whitehead, 1995 / p.81). N content is also dependent on the animal species the wastes come from and their diet. Archer (1988) compared N contents between cattle, pig and poultry. It was found that poultry wastes have more dry matter and available N than both

cattle and pig wastes, although are of considerably lesser volume. In addition, 40-60 % N in poultry wastes is usually in inorganic soluble form (MAFF, 1995) whereas cattle, pig and sheep faeces contain mostly insoluble organic nitrogen.

Table 2.6: Chemical composition of cattle and pig slurry, soil water, milk and clean water (adapted from Mulqueen *et al.* (1999) and EPA (2001)).

Parameters	Cattle slurry	Pig Slurry	Soiled water	Milk	Clean water
Dry matter (g/kg)	85	65	ND	ND	-
Total nitrogen (mg/l TN)	3,820	3,700	300	5,000	< 1
Phosphorus (mg/l P)	743	1,700	30	1,000	0.005
Potassium (mg/l K^+)	4,461	1,650	ND	ND	ND
Magnesium (mg/l Mg^{2+})	410	850	ND	ND	ND
Sodium (mg/l Na^+)	743	300	ND	ND	ND
Calcium (mg/l Ca^{2+})	1871	2,800	ND	ND	ND
Nitrate-nitrogen (mg/l NO_3-N)	82	37	ND	ND	ND
Ammonium-nitrogen (mg/l NH_4-N)	1,140	1,887	ND	ND	ND
BOD [1] (mg/l)	17,500	15,200	1,500	100,000	< 4
COD [2] (mg/l)	62,500	55,000	ND	ND	ND
pH	ND	ND	ND	ND	ND

ND Not Determined
1) Biological oxygen demand
2) Chemical oxygen demand

Farmyard manures, slurries and wastewaters do not only bring in N, but also other nutrients, some of them in large quantities together with different types of faecal microorganisms. Table 2.6 shows that high levels of phosphorus, potassium, sodium and calcium are present in slurries. In his description of pig manure, Krapac *et al.* (2002), who reported a TN concentration similar to those in table 2.6, measured chloride and sulphate concentrations of 1748 and 90 mg/l respectively.

2.3.4 Septic tank effluents

In rural areas where no house is connected to public sewerage, human wastes and domestic wastewater are channelled into small individual septic tank systems that represent many potential point sources of nitrate contamination to groundwater. Septic tank systems consist of a septic tank and a percolation area or filter. The septic tank functions as a primary sedimentation tank, removing most of the suspended solids from wastewater with limited amount of anaerobic digestion, whereas it is in the percolation area or filter that the wastewater is mainly purified, undergoing surface filtration, straining and physico-chemical reactions and microbial breakdowns. After flowing through the percolation area, the effluents eventually percolate towards groundwater (Rodgers *et al.*, 1998).

The concentration of TN in septic tank effluent varies with the number of people living in the house, the volume of effluent released, the design of the septic tank system and the maintenance. Typically, it ranges from 25 to 60 mg/l TN (Wakida and Lerner, 2005), up to 80 % of it being inorganic N, mostly NH_4^+/NH_3 whereas nitrate is marginal (Robertson *et al.*, 1991; Gerritse *et al.*, 1995; Rodgers *et al.*, 1998). In comparison with farmyard waste sources, there is far less organic matter carried by septic tank effluents, the Biological Oxygen Demand (BOD) recorded by Rodgers *et al.* (1998) being below 20 mg/l and Dissolved Organic Carbon levels recorded by Robertson *et al.* (1991) being not higher than 50 mg/l. In addition, some studies showed that septic tank effluents also have very high concentrations of other contaminants that can reach groundwater, some of them reflecting our diet. In his description of septic tank effluents, Robertson *et al.* (1991) reported very high sodium concentrations between 90 and 98 mg/l, whereas potassium was between 12 and 21 mg/l and chloride ranged from 45 to 55 mg/l. A similar study by Close (1989) showed lower chloride concentrations (around 25 mg/l), but potassium and sodium levels in discharging effluents that were still elevated (around 6.7 and 28.2 mg/l respectively). Gill *et al.* (2005), who analysed wastewater from several types of septic tank systems before it discharges into soils, recorded chloride concentrations that ranged between 56 and 118 mg/l. Close (1989), Robertson *et al.* (1991) or Gill *et al.* (2005) also reported high levels of phosphorus, and occasionally high levels of sulphate. Septic tank effluents also carry traces of species characteristic of our diet that would not be found in natural systems, such as caffeine (Seiler, 1996; Winkley, 2001). But the most dangerous contaminants for human health concerns are undoubtedly faecal coliforms and pathogenic organisms (Pang *et al.*, 2004).

2.3.5 Silage effluents

Silage effluent is about 95 % water, but it is a highly contaminated substance farmers have to deal with. Liquid effluents from silage are typically highly acidic and rich in organic matter, nutrients, and salts. Furthermore, silage effluent, especially when mixed with manure, can produce hydrogen sulphide and other poisonous gases. Mulqueen *et al.* (1999) reported that silage effluent contained a TN concentration of 1833 mg/l, which is about half that of slurries (see table 2.6). Ammonia concentration was measured at 471 mg/l NH_4^+, and nitrate-nitrogen concentration at 37 mg/l NO_3-N (i.e. 164 mg/l NO_3^-). BOD and Chemical Oxygen Demand (COD) values of the silage effluent were 55,000 and 75,000

mg/l respectively which were higher than those of cow slurry reported in the same experiments in table 2.6. Acidity was moderate, with pH measured at 4.6, which was linked by Daly (2000) to reducing conditions in the ground that cause the mobilisation of iron, and particularly manganese.

2.3.6 Soil organic matter

Nitrogen is present in soil organic matter at a concentration of about 5 % of dry weight, and the amount of soil TN is therefore driven by the amount of organic matter present in soil (Whitehead, 1995 / p.82). In most soils, more than 95 % of TN is in insoluble organic matter, the remainder being in inorganic forms, i.e. mainly ammonium and nitrate. The actual amount of organic matter in a soil depends on a wide range of factors: the type of vegetation, the climate, the soil characteristics, the land use and the land management over the years. N content in long-term grassland soil is usually found to be much higher than in arable soils, total soil N amounting to 5000 to 15000 kg/ha for the former while amounting to 2000 to 4000 kg/ha for the latter (Whitehead, 1995 / p.82-83). Soil organic matter consists of various heterogeneous pools with different rates of decomposition (Schnitzer, 2000), and is found in a multitude of materials: humus that comes from generations of organic residues that have been decomposed, any dead organic matter in decay, and living micro and macro-organisms (bacteria, enzymes, earthworms, etc). In most soils, the content of organic matter and organic soil N is at its maximum in the first 5 cm, and then declines with depth to become often negligible below 30-40 cm.

Every year, only a small fraction of this organic N is mineralised, becoming available for plant uptake and nitrification, among other processes. But this can still result in high nitrate concentrations in percolating water and later groundwater if large amounts of N have accumulated in soil and if mineralisation is important. This is typical in farming systems, whilst, in comparison, net rates of mineralisation and nitrification are quite low in natural systems.

2.3.7 Atmospheric deposits

N inputs can involve wet and dry deposition from the atmosphere in different forms of inorganic N (Whitehead, 1995 / p.87). Roughly one third of atmospheric N inputs are in

the form of dissolved NH_3 or NH_4^+, mostly of agricultural origin. The remainder is of non-agricultural origin, derived primarily from the burning of fossil fuels and from lightning, and is mainly a mixture of dissolved nitrogen oxides and nitrate (MAFF, 1995). This source of N is not deemed to contribute to a large extent to the total N inputs in countries like Ireland and UK when compared with other sources, although it should be considered. In fact, Goulding (1990) reported TN deposited by wet and dry atmospheric deposition amounting to between 30 and 35 kg N/ha/yr on arable land in south and east of England, of which around 30 % was leached during winter (MAFF, 1995). Campbell *et al.* (1990) estimated such deposition at about 15 kg N/ha/yr in areas remote from intensive agriculture and urban centres, whereas Wakida and Lerner (2005) refer to the highest deposition ranging between 10 and 20 kg N/ha/yr in areas of the UK with the highest rainfall.

2.4 Processes affecting nitrate during leaching

2.4.1 Mineralisation, nitrification and immobilisation: the MIT concept

- Overview

Mineralisation, also called ammonification, is a multi-step bacterial process that oxidises organic nitrogen into soluble inorganic nitrogen NH_4^+ (equation 2.1). In soils, it is followed by nitrification (also bacterial process), where ammonium is oxidised into nitrite and then nitrate (equation 2.2). Simultaneously, mineralisation and nitrification are both in balance with the reverse process called immobilisation, which is the assimilation of inorganic N by soil bacteria (equation 2.3 and figure 2.2).

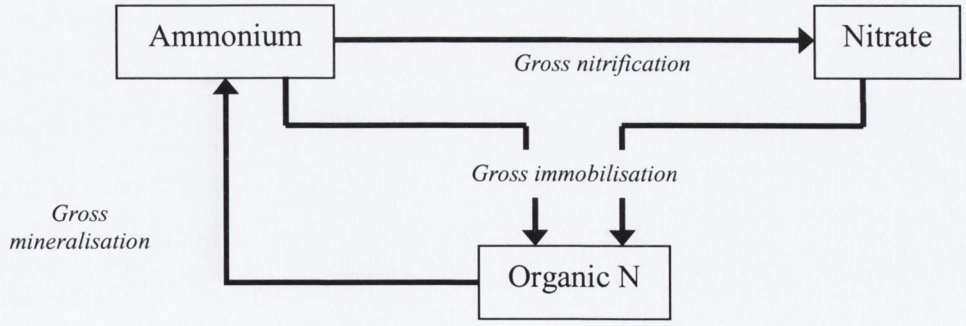
Mineralisation:	organic N $\rightarrow$ NH_4^+ ($\leftrightarrows$ $NH_{3(aq)} + H^+$)	(Equation 2.1)
Nitrification:	$NH_4^+/NH_3 \rightarrow NH_2OH \rightarrow N_2O \rightarrow NO_2^- \rightarrow NO_3^-$	(Equation 2.2)
Immobilisation:	NO_3^- and $NH_4^+ \rightarrow$ organic N	(Equation 2.3)

Each of the three processes is characterised by a gross rate that describes the individual process (figure 2.2), and a net rate that represents the mathematical difference between the competing processes. In a qualitative approach, which consists of understanding the dynamics of nitrogen in soils and processes it goes through, gross rates are good indicators to understand the magnitude of microbial processes, unlike net rates alone that can be misleading because they only refer to the net change in N. In reality, the magnitude of

gross rates is usually found to be much larger than net rates in agricultural systems (Murphy *et al.*, 2003), which is likely to have some effect on nitrate isotopic composition given that these processes involve isotopic fractionation (section 2.6).

Because mineralisation, nitrification and immobilisation of N occur simultaneously, N is continually transferred within soil from organic to inorganic forms and *vice versa* through what was referred to by Jansson and Persson (1982) as Mineralisation-Immobilisation Turnover (MIT). Until recently, the immobilisation process was thought to concern primarily ammonium, whereas nitrate involvement was deemed insignificant by a number of studies. But this was challenged over the last few years by recent experiments, which showed that nitrate can be immobilised even in the presence of high levels of ammonium (Bentgson and Bengtsson, 2005). Depending on the soil context, a variable part of mineral N that has been assimilated by microorganisms and referred to as "labile organic N" (Mengis *et al.*, 2001) undergoes some subsequent remineralisation and nitrification, which can take between several weeks and several years (Bristow *et al.*, 1987). Davidson *et al.* (1992) estimated the average turnover time of N in microbial biomass to be 1-2 months. This is consistent with other findings where recently immobilised N was found to be more readily mineralised than the N in the older soil organic matter (Smith and Power, 1985). What remain largely unknown to date are the factors determining the rate of remineralisation (Bentgson and Bengtsson, 2005).

Figure 2.2: Nitrogen turnover in soil (adapted from Luxhøi, 2002).



- Production of nitrate: mineralisation and nitrification

Mineralisation involves the action of a wide range of heterotrophic microorganisms, most of which prefer aerobic conditions, although it can also take place in anaerobic environments through putrefaction. Various protease and deaminase enzymes decompose dead organic matter into proteins, amino-acids and then ammonium and ammonia.

Nitrification is caused by a smaller group of microorganisms, mainly autotrophic bacteria (although heterotrophic nitrification also occurs, as detailed by Wrage *et al.*, 2001), for which aerobic conditions are essential. *Nitrosospira* and *Nitrosomonas* oxidise ammonium to nitrite, and *Nitrobacter* complete the oxidation step to nitrate generation. During this step, intermediate reaction products like N_2O and NO are generated (Whitehead, 1995 / p.114; Cheng *et al.*, 2004). A key feature of nitrification was revealed by some laboratory experiments under neutral pH, which indicated that nitrate produced by nitrification derived from the incorporation of two water-derived oxygen atoms and one air-derived oxygen atom (Andersson and Hopper, 1983; Kumar *et al.*, 1983; Hollocher, 1984). All this has important implications for the isotopic composition of groundwater nitrate, as discussed in sections 2.5.3 and 2.6.

Because mineralisation and nitrification are caused by different types of microorganisms, they are influenced differently by many parameters that affect their respective gross rates. The fact that mineralisation involves a much wider range of soil microorganisms implies a better adaptability to environmental changes in comparison with nitrification, which is more dependent on any parameter variation. Some of these features are developed below and reflect the results of laboratory experiments in most cases, which is why they should be interpreted cautiously as most parameters are often interdependent and vary substantially *in situ*.

As with most microbial processes, mineralisation and nitrification are controlled by soil temperature. Studies carried out in temperate regions showed that gross rates are curtailed by decreasing temperatures, whereas they rise with increasing temperatures (Harrison *et al.*, 1994; Cookson *et al.*, 2002). Nonetheless, nitrification appeared to become far less effective at low temperature (< 5°C) than mineralisation (Harrison *et al.*, 1994). At the same time, mineralisation and nitrification are dependent on soil water content and soil oxygenation, which are closely related to soil texture and structure, hence to clay content. Because moisture shortage causes microbial activity to decline and because water logging renders soils anoxic, mineralisation and nitrification are favoured in coarse well-oxygenated deposits that guarantee adequate soil moisture content (Gormly and Spalding, 1979; Jarvis *et al.*, 1996). In addition, precipitation history and the succession of short wet and dry events appear to boost nitrification (Moore and Russell, 1970; Haynes, 1986 – cited by Whitehead, 1995 / p. 112). Variations in soil pH influence mineralisation less sharply than nitrification. Nitrification is curtailed below pH 6.0 and becomes negligible below pH 4.5 (Paul and Clark, 1989), whereas extreme soil pH (above 8.0) inhibits the

oxidation of nitrite to nitrate (Whitehead, 1995 / p.115). In comparison, low pH (< 4.5) would only start to curtail mineralisation (Whitehead, 1995 / p.113), whereas it is generally possible to increase its gross rate by increasing the pH of acidic soil, for instance by liming (Haynes, 1986 - cited by Whitehead, 1995 / p. 112).

The amount of organic matter in soils controls the gross rates of mineralisation and nitrification. Apart from positive priming effects resulting in the short term increase in mineralisation and nitrification rates immediately following an addition of readily available N (Kuzyakov *et al.*, 2000), higher availability of C and N in soil usually sustain higher gross rates of mineralisation (Purnomo *et al.*, 2000) and nitrification (Cookson *et al.*, 2002). Farming practices play an important part in the control of gross rates of mineralisation and nitrification. In tillage areas, ploughing generally stimulates gross rates of mineralisation and nitrification by improving soil oxygenation and increasing the loading with organic matter (C and N) by burying organic substrates (Kreitler, 1979; Ostrom *et al.*, 1998). It also helps to break down aggregates and expose nitrogen otherwise out of reach of bacterial activity. The type of ploughing (i.e. minimum/reduced/conventional) is another important parameter since it controls the amount of organic matter buried (Kandeler and Böhm, 1996).

Because soil organic matter content, microorganism population and aeration decline with depth, most mineralisation and nitrification occurs in the surface few centimetres of soil. Most conversion of organic N into mineral N (equation 2.1 and equation 2.2 p.30) was shown to take place in the first 10 cm and to decrease with depth (Black *et al.*, 1998; Purnomo *et al.*, 2000).

- Removal of nitrate: immobilisation

Immobilisation involves the action of heterotrophic microorganisms and was thought to concern NH_4^+ preferentially to NO_3^- when both are present (Jansson, 1958; Recous *et al.*, 1990; Whitehead, 1995 / p.120; Stark and Hart, 1997). Although conditions under which it happens remain uncertain, according to Bengtson and Bengtsson (2005), it is acknowledged that NO_3^- immobilisation can take place when NH_4^+ is limited, as is often the case in arable soils (Azam *et al.*, 1986; Rice and Tiedje, 1989; Recous *et al.*, 1990), but also at high NH_4^+ concentrations (Bengtson and Bengtsson, 2005). During immobilisation, nitrate and ammonium can also be in concurrence with soluble, low molecular weight nitrogenous organic compounds like urea and amino acids (Barraclough, 1997).

The balance between gross mineralisation and nitrification on one side and gross immobilisation on the other side is decided by the quality of decomposing soil organic matter and its C to N ratio. The ratio of total C to total N is less important than the ratio of available C to available N, i.e. C and N that is readily biodegradable. Some plants or organic residues are more resistant than others to decomposition and tend to sequester C, out of reach of bacteria. For instance, highly lignified materials have high C:N ratios but decompose slowly and release little C in comparison to N, hence favouring net mineralisation (Whitehead, 1995 / p.111). However, C:N ratios below 20 to 1 favour gross mineralisation and nitrification over gross immobilisation and result in net mineralisation and net nitrification. Conversely, C:N ratios above 20 to 1 cause net immobilisation, i.e. that gross immobilisation overcomes gross production of ammonium and nitrate. Overall, the C:N ratio of the entire soil organic matter pool is often low enough to observe net N mineralisation in agricultural soils. Nonetheless, some substantial gross immobilisation rates can still be witnessed in these types of soils. Since soils are not homogenous and because soil organic matter is a heterogeneous aggregation of substrates displaying different ranges of C:N ratios, immobilisation is always likely to take place in pockets of high C:N materials, even though low overall C:N ratio may suggest otherwise. Furthermore, the C:N ratio was found to increase with depth in conjunction with decreasing net mineralisation, causing net negative mineralisation and positive immobilisation gradients through the soil profile (Black *et al.*, 1998; Paul *et al.*, 1998).

Some of the parameters discussed in relation to mineralisation and nitrification also affect the rate of gross immobilisation in various ways. Good soil oxygenation, reasonable soil moisture content, moderate pH and large quantities of organic matter are factors expected to improve gross immobilisation rates along with mineralisation and nitrification. Soil temperature is a more controversial parameter, where recent studies have reported contradictory results. In general, increasing soil temperature results in higher microbial activity and consequently a larger gross immobilisation along with other processes. But what remains unclear is how temperature variation affects gross immobilisation in comparison with gross mineralisation and nitrification. Andersen and Jensen (2001) observed that low temperatures have a more negative influence on gross immobilisation than gross mineralisation, which appears to be less temperature dependent: the net outcome of incubation experiments involving Italian ryegrass (C:N > 20) was net mineralisation at 3 °C and net immobilisation between 9 °C and 15 °C. In addition, Esala and Leppänen (1998) concluded that microbial immobilisation is only likely to occur at temperatures

higher than 5 °C. But other studies from Cookson *et al.* (2002) contradict these findings, suggesting that decreasing temperature caused gross immobilisation to increase together with a growth of microbial biomass.

The extent of gross immobilisation is also determined by the quantities of available C and N in soils. Large reservoirs of both available C and N are expected to increase gross rates of immobilisation along with mineralisation and nitrification, when compared with poorly supplied soils (Cookson *et al.*, 2002). The time of residence of N-bearing compounds and the speed with which nitrate leaches downwards may also play a role in determining the gross rate. Taking the example of nitrate, the slower it leaches, the longer it stays in soils and the higher the chance of being assimilated by some bacteria, as assumed by Mengis *et al.* (2001). From this assumption, well-drained soils with rapid vertical movements of water may limit the potential for N immobilisation.

Farming practices can modify the C:N ratio and sometimes reverse the balance between mineralisation and immobilisation, although the effects are limited in time and space. For instance, the addition and incorporation of straw is likely to curtail mineralisation because it has a low N content and a high C:N ratio, which results in net immobilisation (Ocio *et al.*, 1991). In general, additions of organic matter like plant residues bring high quantities of available C together with N, which may result in temporary net immobilisation, which is itself followed by net mineralisation (Lemaire *et al.*, 2004). This is consistent with studies showing that any addition of organic wastes generally favours net mineralisation and nitrification in the long term in both arable and pasture lands (MAFF, 1995).

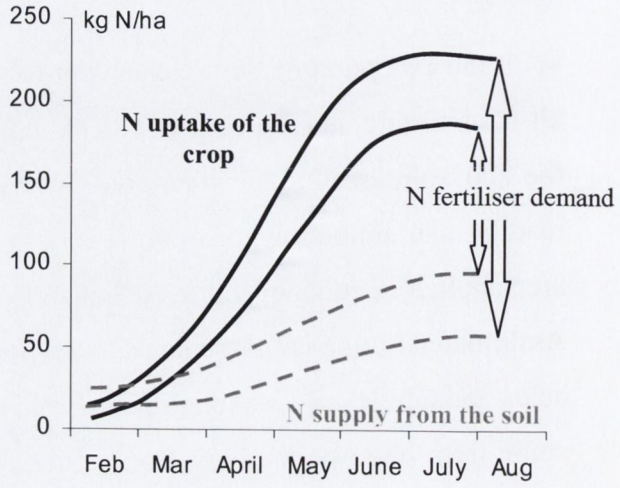
2.4.2 Plant uptake

With the exception of those depending on symbiotic fixation, higher plants absorb almost all N as nitrate and ammonium. Plants take up nitrates and ammonium (figure 2.1) from the soil solution through their root system. Although most plants take up nitrate more readily than ammonium, grass often shows greater uptake of ammonium when both ions are supplied in equal quantities (Clarkson *et al.*, 1986 – cited by Whitehead, 1995 / p. 18). Assimilated nitrate is first reduced to ammonium prior to the incorporation of N into amino acids and amides. Reduction proceeds via nitrate and nitrite reductase and the energy may come from photosynthesis or from oxidation of organic carbon (Whitehead, 1995 / p.19).

The rate of nitrate uptake is controlled by several factors such as temperature and pH (Whitehead, 1995 / p.18). Plant uptake varies during and between growing seasons as described in figure 2.3 (black lines). In temperate regions, plant biological requirements become significant as temperature increases during late winter and early spring. They reach a maximum during summer. Quantities of soil N mineralised also vary annually and during the year (between dashed grey lines). Therefore, the correct application rate of N fertiliser for the same crop in the same field (arrows) will be different from year to year. The rate of nitrate uptake is also controlled by the agricultural system and the type of plant grown. In general, grassland systems take up inorganic N like nitrate more efficiently than annual crops because the rooting system is well established, and plant cover remains throughout the year.

Not all types of plants are equally efficient at taking up nutrients like nitrate from soil-water, and some types of plants tend to leave substantial quantities of fertiliser N in the soil. For instance, Powlson *et al.* (1992) observed that 50 % to 80 % fertiliser N applied in late spring was found in winter wheat (above ground crop). Similar figures are given by MAFF (1995), percentage N recovery by crops ranging from 40 % to 90 %. Given that some crops, such as potatoes or sugar beet, have far less extensive rooting system than most cereals, this percentage should drop for root crops. Percentage recovery of fertiliser N in harvested herbage also ranges between 50 % and 80 %, and is often around 65-70 % (Whitehead, 1995 / p.209). Furthermore, the concentration of N in organic tissues is dependent on the availability of N bearing nutrients in soils. High rates of fertiliser N increase the concentration of N in plants, which can then result in more N being mineralised after plant residues are incorporated into soils (Whitehead, 1995 / p.264).

Figure 2.3: Plant N requirements during the growing season (EFMA, 2005).



2.4.3 Denitrification

Denitrification generally consists of a microbial multi-step reduction process of nitrate under anaerobic or anoxic conditions, which leads to the generation of gaseous intermediate products (Whitehead, 1995 / p.181; Wrage *et al.*, 2001) in the following sequence:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \qquad \text{(Equation 2.4)}$$

Denitrifiers include a wide range of heterotrophic microorganisms that are facultative anaerobes, e.g. *Pseudomonas*, *Bacillus denitrificans* and others (Firestone, 1982). These bacteria need energy for their respiration, which is supplied by redox reactions involving the oxidation of an electron donor and the reduction of a suitable electron acceptor. The usual electron donor is dissolved organic carbon DOC (Korom, 1992, Puckett and Cowdery, 2002) derived from soil organic matter. Nevertheless, denitrification can also occur during the chemo-autotrophic respiration of *Thiobacillus denitrificans*, which can react with pyrite FeS_2 if present in subsoil and oxidize the product of this respiration S and Fe^{2+} as a last resort (Hübner, 1986; Pauwels *et al.*, 2000). Thermodynamically, dissolved O_2 would be the favourable terminal electron acceptor, but concentrations are often low in water-saturated parts of the subsoil (aquifers or water-logged parts of the unsaturated zone). To cope with such anaerobic and anoxic conditions, denitrifiers can make use of other terminal electron acceptors for their respiration and favour the following reactions, sorted by decreasing energy yield (Chapelle *et al.*, 1995 – cited by Puckett and Cowdery, 2002): nitrate reduction > manganese reduction > iron reduction > sulphate reduction. Hence, in the presence of large quantities of carbon and nitrate, heterotrophic denitrifiers can operate and consume nitrate following the general equation:

$$5\ C_{DOC} + 4\ NO_3^- + 2\ H_2O \leftrightarrows 2\ N_2 + 4\ HCO_3^- + CO_2 \qquad \text{(Equation 2.5)}$$

Unlike some other bacterial processes, denitrification not only takes place within the unsaturated zone, but also within and throughout the aquifer (Böttcher *et al.*, 1990; Cey *et al.*, 1999; Pauwels *et al.*, 2000, Puckett and Cowdery, 2002). This is especially true for aquifers with a very shallow water table (Starr and Gillham, 1993).

As is the case for all microbial reactions, several factors influence denitrification, most of which are closely related to levels of dissolved oxygen, which appears to be the main limiting parameter. In fact, increasing levels of oxygen inhibit particularly the reduction of nitrous oxide (N_2O) into N_2, whereas high concentrations of O_2 promote the aerobic metabolism of denitrifiers so that reduction of nitrate no longer takes place (Knowles, 1982). Conversely, the absence of O_2 favours denitrification, as showed by Cey *et al.* (1999) or Puckett and Cowdery (2002), who observed a positive correlation between nitrate and dissolved oxygen concentrations, both declining with increasing depth below the water-table. Nonetheless, even an oxygenated environment can produce some substantial denitrification if there are some anoxic pockets (Koba *et al.*, 1997). Such anaerobic conditions would be often encountered in heavy and poorly drained soils (clayey soils), but also in confined aquifers or impermeable/porous rocks. In general, low redox potentials (Eh) and associated high reducing properties of water help denitrification, which was witnessed by Cey *et al.* (1999) who reported a decrease in both nitrate concentration and Eh with increasing depth below water-table. Soil moisture content is usually closely related to oxygen content. Water-logging or high moisture content (above 60-70 % of the water-holding capacity according to Cooke, 1967) favours anaerobic conditions that favour denitrification, and is again often associated with clayey soils. For related reasons, and inadequate soil moisture, denitrification declines during summer when soils are drier.

Like most bacteria, denitrifiers are sensitive to temperature variations and their activity declines as temperature decreases. Studies by Firestone (1982) suggest that denitrification can operate at 0 °C, but there is a pronounced decline in denitrifying activity below 10 °C. This indicates that the lowest winter temperatures significantly inhibit denitrification. Denitrification is inhibited by strongly acidic conditions (pH < 4) but soil pH seems to have little effect on denitrification in the range 6-8 (Firestone, 1982). It is nonetheless important to note that nitrous oxide (N_2O) production increases at the expense of N_2 as acidity increases (Firestone, 1982; Addiscott *et al.*, 1991).

As reviewed by Whitehead (1995 / p.187), some studies have shown that high nitrate and low O_2 concentrations are not sufficient for denitrification to occur. Available carbon is necessary for bacterial respiration (Starr and Gillham, 1993), and high DOC concentrations favour the growth not only of denitrifiers, but also other microorganisms that consume oxygen, which can be promoted by the application of slurry and other organic wastes, but also by clayey soils and the associated argilo-humic complex. Soil structure and texture are

important factors that can promote denitrification. Clayey soils promote not only anaerobic conditions, but also a slow travelling time for nitrate, which increases the chance for bacteria to operate. For similar reasons, the thicker the unsaturated zone, the longer the travel time to the water table across anaerobic and anoxic pockets.

2.4.4 Other processes

- Ammonia volatilisation

Ammonia volatilisation influences nitrate leaching because it reduces ammonium concentration in soils. Ammonia in solution in soil water is in equilibrium with ammonium, but it is also in equilibrium with atmospheric ammonia according to the following equations:

$$NH_{3(aq)} + H_2O \leftrightarrows NH_4^{+}{}_{(aq)} + OH^- \qquad \text{(Equation 2.6)}$$

$$NH_{3(aq)} \leftrightarrows NH_{3(atm)} \qquad \text{(Equation 2.7)}$$

Ammonia volatilisation is an important factor to be taken into account when investigating nitrate leaching in rural areas because many N sources described in section 2.3 contain, or else generate, large quantities of ammonium (animal wastes and urine especially) that will cause N losses by ammonia volatilisation. This will have some serious implications for the isotopic composition of nitrate as referred to in section 2.6.

Ammonia volatilisation principally concerns organic wastes that are deposited on the soil surface where parameters controlling volatilisation are the most effective. These parameters are firstly the weather conditions such as air temperature, rainfall and soil moisture, relative humidity of the air and wind speed (Whitehead, 1995 / p.157). The drier, the warmer and the more wind, the bigger the ammonia volatilisation. Ammonia volatilisation is also dependent on ammonia occurrence in soil. Ammonia being a weak base, its concentration increases with increasing pH, whereas ammonium concentration rises at lower pH, at the expense of ammonia. Although initial soil pH is usually not significantly alkaline and does not favour ammonia volatilisation, the hydrolysis of urea in urine patches left by livestock generates a quick and large increase in pH, which favours ammonia occurrence, hence ammonia volatilisation (Whitehead, 1995 / p.153). Some other

factors such as plant uptake and MIT mobilise ammonium and diminish the potential for ammonia volatilisation.

- Ammonium adsorption by clay and humus

The ability of soils to adsorb cations depends on their Cation Exchange Capacity (CEC), which is determined by the amount of clay and/or humus that is present. This process affects nitrate leaching because it can temporarily decrease the availability of cations like ammonium in soil. Ammonium, along with potassium, can be immobilised at the exposed surface of clay minerals that have a three-layer lattice structure, such as vermiculite, illite or montmorillonite (Whitehead, 1995 / p.122). This phenomenon happens because hexagonal spaces with similar diameters to NH_4^+ or K^+ are opened to positively charged species. On the other hand, humus, the end product of decomposed organic matter, has a range of CEC values even higher than clay minerals (Brady and Weil, 1999), the binding capacity dropping with pH value. Soil capacity to retain ammonium is extremely variable and ranges from a few kg N to a few hundred kg N per ha. High potassium concentration is a limiting factor for ammonium adsorption, whereas high NH_4^+ concentrations combined with drying conditions tend to increase the amounts fixed (Whitehead, 1995 / p.122).

- Nitrate dilution and dispersion

Water acts as a transport agent for solutes like nitrate, but it also acts as a diluting agent where diffusion takes place (Addiscott *et al.*, 1991; Mook and de Vries, 2000). During percolation, nitrate is subjected to both vertical and transversal dispersion, which causes nitrate concentrations in soil water and groundwater to decrease. It should be added that once nitrate has reached the aquifer, nitrate concentration in a contaminated aquifer may drop if a low nitrate-loaded source discharges into it, resulting in a dilution of all contaminants. The source could be some older and deeper groundwater that has been less subject to nitrate pollution (Green *et al.*, 1998). Similarly dilution of nitrate concentration in groundwater can occur due to prolonged or consecutive heavy precipitation events. This phenomenon would be seen during heavy precipitation events in karstic or unconfined aquifers underlying free-draining soils.

2.5 Nitrate leaching and potential implications for groundwater chemistry

2.5.1 The nitrate leaching process

- Overview

'Piston flow' or 'piston displacement' happens when a soil is already at field capacity and receives more water than is needed for evapotranspiration, so that no more water can be retained and the surplus moves downwards. The movement of percolating water through the unsaturated zone is due to gravity and can induce the transportation of any soluble species downwards out of the rooting zone of the plants, as far as the water-table. In temperate soils, the transportation of nitrate, known as nitrate leaching, is facilitated by the fact that most soils have negatively charged clay particles, which means that the highly mobile and negatively charged molecules of nitrate can migrate with little interaction with repelling soil surfaces or with organic colloids, which are also negatively charged. It should be noted that in acidic soils, clay particles are often positively charged and can retain nitrate and retard its leaching, a situation that prevails in tropical regions (Wong *et al.*, 1987).

Other N-bearing species like NO_2^-, NH_4^+ and organic N are susceptible to leaching, but quantities involved are often quite small in comparison with nitrate. Most ammonium is usually adsorbed onto negatively charged soil particles (section 2.4.4) before it can reach the water-table, although some might still go through if the exchange capacity of clay is exceeded. This situation might happen with point sources that release highly concentrated effluents. Nitrite (NO_2^-) is an unstable precursor of nitrate that occurs as an intermediary during nitrification and tends not to accumulate in soils unless they exhibit high ammonia concentration and pH (Whitehead, 1995 / p.115). Thus, NO_2^- concentrations in soil-water are generally low, and risk for groundwater contamination is very small. Although unusual, some organic N may manage to contaminate aquifers in a situation where large vertical cracks occur across the unsaturated zone, leading to quick transportation and little time for biochemical processes to take place.

- Factors influencing nitrate leaching

From a general point of view, two fundamental parameters determine the amount of nitrate leached from the plant root zone to groundwater: the volume of drainage water and the

amount of nitrate accumulated in the soil, surplus to plant requirements, at the onset of leaching (Di and Cameron, 2002). Over the years, studies have identified in detail a combination of interdependent factors in the context of agricultural diffuse sources of N, (Daly, 1981; Nolan, 2001; Shaffer & Delgado, 2002) or point sources of N, like septic tanks (Yates, 1985; Bicki & Brown, 1991; Nolan, 2001). The following factors influencing nitrate leaching are related to the intrinsic characteristics of the study area and to human activities:

- Soil physical and chemical properties: soil texture and structure determine the draining capacity, C:N ratio, and also pH and oxygenation, influence competitive processes detailed in sections 2.4.1and 2.4.2
- Climate factors: effective rainfall, soil moisture content and temperature influence drainage and microbial activity.
- Aquifer characteristics: the natural protection of groundwater depends on the type of aquifer (unconfined or confined) and the thickness and permeability of the unsaturated zone.
- Presence of N point sources: for example the density of septic tank systems, the design and the maintenance of such systems, the density of population, the presence of leaky farm storage systems for organic wastes influence the net inputs of N in soils.
- Farming system and practices: the potential for nitrate leaching typically follows the order cut grassland < grazed pasture or arable cropping < ploughing of pasture < market gardens (Di and Cameron, 2002), whereas the sequence in cropping systems is often cereals < sugar beet < beans < peas < oilseed rape << potatoes (MAFF, 1999).
- Fertiliser management: the application rate of N and the number of applications (Thorn, 1986), the use of farmyard organic wastes or inorganic N fertilisers (MAFF, 1995), the time of application in regard of meteorological conditions and the use of nitrification inhibitors influence directly the amounts of N left in soil.

Light soils are more vulnerable between autumn (end of the growing season) and spring (beginning of the next growing season) because all the nitrogen that has been left unused in soil can still be mineralised and nitrified (before soil temperature drops), but is not taken up anymore (situations where soils are left bare) so that it can freely be leached. In addition, intensive farming in tillage areas implies high N fertiliser application rates to sustain high yields. This can leave large fractions of N and nitrate unused in soils if the

crop's biological requirement is exceeded (see nitrate surplus curve in Chaney, 1990). Nitrate leaching increases quickly once N fertiliser application goes beyond this point (MAFF, 1999). The risk is worsened for shallow unconfined aquifers overlain by agricultural systems (Burkart and Stoner, 2002). Finally, autumn cultivation and fertilisation, although not common practice, has been shown to cause large accumulation of mineral N (100 to 139 kg/ha) in the soil before winter drainage (Cameron and Wild, 1984; Francis *et al.*, 1992, 1995).

2.5.2 Impact of some N point and diffuse sources on groundwater contamination by nitrate

In natural systems, the interdependence of parameters, the heterogeneity of soils and subsoils, changes of weather conditions from one year to another, the intricate nature of the N cycle (see figure 2.1) and the difficulties of measuring a range of nitrogen transformations and transfers *in situ* explain why the understanding of nitrate leaching is such a complex task. An extensive literature review threw up contrasting results, with nitrate leaching and nitrate concentrations in groundwater underneath diffuse and point sources found to be extremely variable in regard of the legal limit for nitrate, set at 50 mg/l NO_3^- in both the Drinking Water and the Nitrate Directives (section 2.1.4). This section briefly overviews different studies and shows that some N sources *a priori* thought to generate nitrate contamination may not necessarily contribute to the general increase in groundwater nitrate levels, which brings some justification for the use of a new tool such as isotopic analysis in order to identify the source of groundwater nitrate. This is particularly needed in areas like the Barrow Valley where both point and diffuse N sources coexist and can both contribute to groundwater contamination.

- Nitrate contamination from N point sources

Studies from septic tank systems showed that nitrate becomes the predominant form of N underneath the point of release if large proportions of released ammonium and organic N are nitrified, which is generally the case under oxic conditions (McQuillan, 2004). Most of the transformations take place in the unsaturated zone, although studies suggest they could also take place below water table (Robertson *et al.*, 1991). Subsequent leaching can then result in variable nitrate levels in groundwater depending on the local hydrogeological context. If denitrification occurs, almost complete nitrate attenuation can be observed

within a few metres of the point of release (Gerritse *et al.*, 1995). But where denitrification is absent or restricted, dispersion is the main attenuation process taking place, and nitrate can be carried far downgradient of the point of release, which can extend the plume of contamination with nitrate levels higher than the drinking water limit for more than 100 m (Robertson *et al.*, 1991).

Although little research has addressed specifically the impact of farmyard N point sources on groundwater quality as such, a similar pattern has been witnessed by a few studies. Krapac *et al.* (2002) addressed the issue in an area vulnerable to nitrate and showed that manure deep-pits do not always increase groundwater nitrate concentration above background levels. This was attributed to several factors such as a very deep water-table (about 80 m bgl), in conjunction with the possible occurrence of denitrification and dilution with deeper groundwater.

- Nitrate leaching effects from diffuse agricultural sources

Farming has always been seen as a main contributor to nitrate contamination, and extensive research has been carried out on nitrate leaching generated by agriculture over the last few decades. Studies have investigated nitrate leaching in the context of a wide range of soils (from heavy to light soils), aquifers (confined, unconfined, different unsaturated zone thickness), under all sorts of farming systems (grassland, cereals, potatoes, etc), with different agricultural practices (no tillage, conventional tillage, reduced tillage, winter crops, etc) and with different types of fertiliser use and application rates (animal wastes, manufactured fertilisers, no N application to high N application rates). Some of the recent work carried out on temperate agroecosystems was reviewed by Di and Cameron (2002), who reported the NO_3^- leaching loss in kg N /ha/year for different farming systems (pasture and tillage). It appears that nitrate losses are extremely variable from one system to another, and even within the same system, and can range from a few kg N/ha/year (no N applied in a grazed system overlying sandy loam) to more than 100 kg N/ha/year. Hooker (2005), in a similar review, reported some extreme losses up to 300 kg N/ha/year in ploughed pasture with mixed soils and mixed application rates. In fact, attention should be focussed on nitrate concentrations in soil-water, rather than on quantities of nitrate leached alone. According to Davies (2000), it is possible to lose over 50 kg N/ha/yr when the rainfall is greater than 400 mm before groundwater exceeds the drinking water limit of 50 mg/l NO_3^-. Whitehead (1995 / p.132) stressed that with

increasing rainfall, there is often an increase in the amount of nitrate that can be leached before the concentration in the leachate exceeds that limit. This is reflected in the high critical amounts of nitrate found to be leached in wetter regions of western England (as much as 200-250 kg N/ha/year in comparison to 30 kg N/ha/year in drier eastern regions).

2.5.3 What type of nitrate contaminates groundwater?

Addiscott *et al.* (1991) stated that 'it is quite irrelevant to talk about nitrates' (plural) instead of nitrate (singular) because whatever their origins, all molecules of nitrate are identically constituted with one atom of nitrogen bound to three atoms of oxygen. Chemically speaking, this is undoubtedly true, but not from the isotopic point of view. If one considers the way nitrate is generated, two types of NO_3^- can be found in soils and groundwater (section 2.2.2 and figure 2.1): artificially pre-formed nitrate coming from manufactured fertilisers and nitrate coming from the nitrification of ammonium in soils (regardless of the origin of nitrogen).

The motive behind this project lies in the fact that nitrate in artificial fertilisers has a very distinctive isotopic composition ($^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios) from nitrate derived from nitrified organic wastes. This may enable the discrimination between groundwater contamination from diffuse fertiliser application, and groundwater contamination from septic tanks or farmyard sources. If nitrate reaching groundwater has a similar isotopic composition to its near-surface N source, it would be possible to identify its origin. From section 2.4, it emerges that N inputs from diffuse or point sources are in fact quite likely to undergo some microbial or physical processes. The question is whether such processes significantly alter the original isotopic composition of nitrate beyond recognition - a point that is specifically discussed in section 2.6. This section relates to studies that suggest most preformed nitrate contained in N fertiliser applied to fields is in fact taken up by plants to a large extent (section 2.4.2), most of the remainder being incorporated into soil microorganisms before undergoing later remineralisation and nitrification (section 2.4.1). This point appears crucial for the $^{18}O/^{16}O$ ratio in nitrate for reasons explained in section 2.4.1.

The use of ^{15}N-labelled fertilisers (i.e. $^{15}NH_4{}^{15}NO_3$ or $K^{15}NO_3$) revealed that very little fertiliser preformed nitrate applied to fields is actually left in soils in its original nitrate

form. Powlson *et al.* (1992) showed that after labelled fertiliser was applied to winter wheat in spring within recommended rates (up to 234 kg N/ha/year), an average 68 % of labelled fertiliser N was actually recovered in above-ground crops, whereas an average 18 % was left in the soil at harvest. More importantly, almost all this N was in organic form (roots, microorganisms, etc), whereas about 2 % of the fertiliser was left unused in the soil as nitrate. This is consistent with authors like McDonald *et al.* (1989) who found that after fertilisation of winter wheat in spring, 79 to 98 % of inorganic N in the soil at harvest was nitrate derived from the mineralisation and nitrification of organic N rather than unused fertiliser nitrate. Similar findings were found by Cookson *et al.* (2000) after autumn fertilisation (50 kg N/ha applied to perennial ryegrass). Such findings hardly come as a surprise when considering the soil potential for nitrate assimilation by microbial immobilisation and plant uptake (sections 2.4.1 and 2.4.2).

Lysimeter experiments from Barraclough *et al.* (1984) revealed that with perennial ryegrass grown on sandy loam soil, the proportion of nitrate leached that is derived directly from the fertiliser (labelled ammonium nitrate) increases with increasing rates of fertiliser application, ranging from 9 % with 250 kg N/ha/year application rate to 39 % with 500 kg N/ha/year and 75 % with 900 kg N/ha/year. Such application rates were largely beyond what is common usage, but results suggests that if applied within recommended rate, which is crop-specific but often largely below 200 kg N/ha/year, artificial fertiliser may not generate massive losses of fertiliser nitrate to groundwater. Instead, it is more likely that the application of artificial fertiliser increases nitrate leaching losses by increasing the amount of mineralisable nitrogen, plant residues becoming more N enriched if there is plenty of available N to be taken up.

2.5.4 Groundwater chemistry associated with contamination by nitrate

Under uncontaminated conditions, groundwater hydrochemistry depends on the nature of the subsoil and rocks that groundwater passes through. Background values of nine chemical parameters are displayed in table 2.7 for five types of aquifer commonly found in Ireland (EPA, 2003), which includes Carboniferous limestone and sand/gravel (of Carboniferous limestone parent material at Mortarstown, Co. Carlow).

Table 2.7: Natural hydrochemistry of different types of Irish aquifers (adapted from EPA (2003)).

Parameter	Ordovician Volcanics [1)]	Devonian Sandstones [2)]	Westphalian Sandstone [3)]	Carboniferous Limestone [4)]	Sand and Gravel [5)]
Nitrate (mg/l NO_3^-)	0.5	3.0	1.4	0.9	2.8
Chloride (mg/l Cl^-)	35	20	17	26	22
Potassium (mg/l K^+)	3.1	1.9	1.3	3.0	0.6
Sodium (mg/l Na^+)	24	16	18.8	8.8	12
Ammonium (mg/l NH_4^+)	0.1	0.02	0.04	0.13	0.05
Sulphate (mg/l SO_4^{2-})	45	ND	2.0	ND	2.0
Calcium (mg/l Ca^{2+})	80	54	60	102	118
Alkalinity (mg/l $CaCO_3$)	60	185	225	307	320

ND Not Determined
1) Gorey, Wexford
2) Knocktopher, Kilkenny
3) Ballincurry, Tipperary
4) Ballaghdereen, Roscommon
5) Mortarstown, Carlow

It can be seen that where bedrock or subsoils are dominated by limestone, groundwater is hard and naturally contains high concentrations of calcium (above 100 mg/l) and bicarbonate (alkalinity around 300 mg/l $CaCO_3$). In contrast, other parameters like nitrate, sulphate, chloride, sodium and potassium have natural concentrations that range from very low to low. Although not displayed in the table, faecal coliforms should not be present in uncontaminated groundwater. It should be added that sodium concentrations may naturally become high in confined aquifers due to cation exchange (Daly, 2000). Any deviation from these background levels towards higher values should be considered as abnormal and may be related to anthropogenic inputs. The description of potential sources of nitrogen in rural areas (section 2.3) revealed that, besides nitrogen, artificial fertilisers and organic N sources can release other contaminants that may also be leached: potassium, chloride, sulphate, phosphate and calcium are the major non-nitrogenous compounds of animal/human organic wastes and many inorganic fertilisers, whereas sodium is a major component of organic wastes but it is rarely found in artificial fertilisers. Except for nitrate and chloride, some anions (in particular PO_4^{3-}) and all cations are subject to adsorption onto soil particles, which may considerably retard the leaching of these species through the unsaturated zone (Böhlke, 2002). They also have the capability of displacing a variety of other cations from exchange sites in soils. Combined with dispersion and dilution processes, this may result in percolating water contaminant concentrations diverging from expectations based on original soil inputs.

- Parameters indicative of organic contamination

In the case of organic point sources, the soil cation exchange capacity may be easily exceeded due to the continuous discharge of highly concentrated effluents within a small

area, which could lead to a 3-dimentional plume of groundwater contamination. Typically, the concentrations of non-nitrogenous compounds within the plume is intermediate between the effluent and the upgradient uncontaminated groundwater, which was illustrated by Robertson *et al.* (1991) who investigated the groundwater chemistry in plumes of contamination originating from two different septic tank systems in a shallow unconfined sand aquifer. Their study revealed that elevated nitrate levels aside (more than three times the drinking water limit), potassium, chloride and especially sodium concentrations were also found higher than background levels, but lower than the source. The mean chloride levels in the plume cores ranged between 24 and 38 mg/l (background level below 17 mg/l), whereas the mean potassium concentrations ranged between 11 and 14 mg/l (background level below 2 mg/l). More striking was the difference between the mean sodium concentrations, which ranged between 45 and 95 mg/l against background levels measured at below 4 mg/l.

In the Irish context, the Geological Survey of Ireland (GSI) developed a list of key indicators for groundwater quality that are indicative of organic contamination (adapted from Daly, 2000; EPA, 2003):

- $[NO_3^-] > 25$ mg/l NO_3^- ⇨ either organic source or artificial fertilisers; to check with other parameters.
- $[K^+] >$ 4-5 mg/l ⇨ the source of contamination is probably organic waste.
- $[K^+]/[Na^+] > 0.3$ (Daly, 1981; Thorn and Hanna, 1989), with concentrations in mg/l ⇨ farmyard waste rather than septic tank effluent is the source of contamination; if < 0.3, no conclusion is possible for reasons explained below.
- $[Cl^-] >$ 25-30 mg/l ⇨ the source may be organic waste source (does not apply within 20 km or less from the coast due to higher salt content in rain).
- Presence of faecal coliforms such as *E. coli* ⇨ indicative of contamination by nearby animal/human organic waste sources, usually either a septic tank or a farmyard (except in karst areas where bacteria can travel longer distance). But it may also occur in wells poorly protected against outside contamination coming from any kind of small animal (birds, mice, etc) or from direct entry of contaminated water from the surface.
- Absence of faecal coliforms ⇨ groundwater either not polluted by organic waste, or else bacteria have not survived due to attenuation or time of travel to the well greater than 100 days.

The use of the potassium to sodium ratio to distinguish septic tank contamination from farmyard contamination is based on the fact that animal wastes contain a higher proportion of potassium in relation to sodium, compared with human wastes. In table 2.6, which refers to different types of animal wastes, the potassium to sodium ratio is above 5 (ratio of concentrations in mg/l). On the other hand, potassium and sodium concentrations measured in some septic tank effluents by Robertson *et al.* (1991) suggests a much lower ratio between 0.12 and 0.23, which is a consequence of human diet and salt addition to food. Nonetheless, this potassium to sodium ratio should be used carefully because, whilst a $[K^+]/[Na^+]$ ratio above 0.3 may be indicative of contamination by farmyard effluents, a ratio below 0.3 does not necessarily mean that the contamination is from a septic tank. Indeed, potassium contained in animal wastes effluents travelling through soils and the aquifer matrix can be subjected to high rates of adsorption onto soil particles, which can mask the original potassium to sodium ratio.

Other parameters may also be indicative of point source contamination. In septic tank plumes, Roberston *at al.* (1991) observed elevated levels of alkalinity, dissolved organic carbon (DOC), together with depressed levels of pH and dissolved oxygen, which may also be detected in plumes of contamination coming from farmyards. Correlations between some physico-chemical parameters may also be observed. For instance, McQuillan (2004) reported a positive linear relationship between concentrations of chloride and nitrate in oxic groundwater of a residential area served by individual septic tanks, which was attributed to contamination by organic wastes. More sophisticated chemical analyses may also involve the measurement of compounds such as caffeine (see section 2.3.4).

- Parameters indicative of artificial fertiliser contamination

In comparison with organic point sources, the characterisation of agricultural diffuse sources of contamination using major ions is far more difficult and less well documented in the literature. This could be attributed to the fact that, except for nitrate, diffuse applications of artificial fertiliser often do not result in large quantities of non-nitrogenous compounds penetrating the topsoil. Under arable land, groundwater enrichment in potassium over background level is sporadic (Böhlke, 2002). Nonetheless, a study by Gallardo and Tase (2006) suggests that the concentration of potassium may be increased several times over after NPK fertiliser application, suggesting that soil adsorption capacity is sometimes exceeded after large inputs. In his review of groundwater contamination by

agriculture, Böhlke (2002) reported some positive correlations between nitrate concentration and other inorganic compounds contained in fertilisers applied to soils. Such a relationship with chloride was observed after application of potash (also reported by Panno *et al.* (2006)), whereas magnesium and calcium levels increased with nitrate after application of dolomite (liming), which was also reported by Hamilton and Helsel (1995) or Gallardo and Tase (2006).

- Parameters indicative of denitrification

Denitrification, which can occur in both the unsaturated and the saturated zone, was discussed earlier in section 2.4.3. Several techniques are generally used to trace this microbial process, although they do not work in every situation. The first one consists of comparing levels of reactants and products of denitrification (equation 2.5) with conservative elements. Commonly, the concentration of 'excess N_2' produced by denitrification in groundwater is estimated by comparing the measured concentrations of Ar and N_2 with those expected from atmospheric sources, assuming the Ar is a conservative tracer (Böhlke, 2002; Kendall and Arena, 2000; Puckett and Cowdery, 2002). Other supporting evidence for denitrification under anaerobic or anoxic conditions was provided by Puckett and Cowdery (2002). They witnessed a simultaneous decline in nitrate and oxygen concentrations and increase in HCO_3^- and N_2 levels (above atmospheric N_2 concentration). The latter two species are products of denitrification, as outlined in equation 2.5. Denitrification may also be detected in groundwater by observing a decrease in the ratios of nitrate to conservative constituents such as chloride. But this approach with Cl^- is limited by the fact that chloride inputs can be variable from site to site, which can depend on factors such as the use of KCl fertiliser.

2.6 Stable isotopes in nitrate and isotopic fractionations during the N cycle

2.6.1 Isotope fundamentals

- General definitions

This project relates to the use of both stable isotopes of nitrogen, which are ^{14}N (99.63 % of whole-Earth abundance) and ^{15}N (0.37 %), two stable isotopes of oxygen, which are ^{16}O

(99.76 %) and ^{18}O (0.2 %), and both stable isotopes of hydrogen, which are ^{1}H (99.985 %) and ^{2}H or D (0.0015 %) (Wiley-VCH, 1997).

$^{15}N/^{14}N$, $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios in chemical compounds such as NO_3^- or H_2O are reported in permil (‰), relative to a reference (atmospheric N_2 for nitrogen, and Vienna Standard Mean Ocean Water V-SMOW for oxygen and hydrogen) and using the standard definition of δ (delta) (Kendall and Aravena, 2000), defined as follows:

$$\delta^{15}N\ (‰) = \{[(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{AIR}]-1\}\times 1000 \qquad \text{(Equation 2.8)}$$

$$\delta^{18}O\ (‰) = \{[(^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{V\text{-}SMOW}]-1\}\times 1000 \qquad \text{(Equation 2.9)}$$

$$\delta^{2}H\ (‰) = \{[(^{2}H/^{1}H)_{sample}/(^{2}H/^{1}H)_{V\text{-}SMOW}]-1\}\times 1000 \qquad \text{(Equation 2.10)}$$

The following notations are used in this thesis: $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ for $\delta^{15}N$ and $\delta^{18}O$ in nitrate, $\delta^{15}N\text{-}NH_4^+$ for $\delta^{15}N$ in ammonium, $\delta^{15}N\text{-TN}$ for $\delta^{15}N$ in Total Nitrogen, $\delta^{15}N\text{-}N_2$ for $\delta^{15}N$ in diatomic nitrogen, $\delta^{18}O\text{-}O_2$ for $\delta^{18}O$ in diatomic oxygen, $\delta^{18}O\text{-}H_2O$ and $\delta^{2}H\text{-}H_2O$ for $\delta^{18}O$ and $\delta^{2}H$ in water.

- Kinetic fractionation factor

Nitrogenous compounds (e.g. nitrate), but also water, can be subjected to physical and biochemical reactions (sections 2.4 and 2.5). Such processes generally discriminate between heavy and light isotopes. This results in some isotopic fractionation where reaction products and substrates eventually have a slightly different isotopic composition. A kinetic fractionation factor $\alpha_{p\text{-}s}$, as opposed to equilibrium fractionation factor (for equilibrium reactions), applies to unidirectional reactions and is defined as follows (Kendall and Aravena, 2000):

$$\alpha_{p\text{-}s} = R_p/R_s \quad (\text{often} < 1) \qquad \text{(Equation 2.11)}$$

where R_p and R_s are isotopic ratios $^{15}N/^{14}N$ or $^{18}O/^{16}O$ in reaction products and substrates respectively (e.g. N_2 and nitrate are product and substrate respectively in the denitrification process). In most reactions of the N cycle involving NO_3^-, $\alpha_{p\text{-}s}$ is smaller than 1 because the lighter isotopes react faster than the heavier ones, causing enrichment of lighter elements and depletion of heavier elements in reaction products. However, the fractionation factor

$\alpha_{p\text{-}s}$ is highly variable, depending on the reactions involved, the concentrations, the environmental conditions, and the organism involved (type of bacteria and plants).

- Enrichment factor

The enrichment factor ($\epsilon_{p\text{-}s}$), which is preferentially used to the fractionation factor, is defined as follows (Kendall and Aravena, 2000):

$$\epsilon_{p\text{-}s} = 1000 \times (\alpha_{p\text{-}s} - 1) \qquad \text{(Equation 2.12)}$$

It is typically negative for kinetic physical, chemical and biological reactions of the N cycle because the kinetic fractionation factor ($\alpha_{p\text{-}s}$) is often smaller than 1. In a situation where the reactant concentration is large and the fractionation is small (i.e. $\alpha_{p\text{-}s}$ very close to 1), the enrichment factor can be determined as follows (Kendall and Aravena, 2000):

$$\epsilon_{p\text{-}s} \approx \delta_p - \delta_s = \Delta_{p\text{-}s} \qquad \text{(Equation 2.13)}$$

where $\Delta_{p\text{-}s}$ is called apparent fractionation, which is measured in the laboratory and deducted directly from the isotopic composition of reaction products and substrates (δ_p and δ_s are defined according to equation 2.8 or equation 2.9 for reaction products and substrates respectively). It represents a rough estimate of the enrichment factor. The enrichment factors mentioned in the following sections of this chapter are generally apparent fractionation, unless stated otherwise.

- Rayleigh equation and description of the fractionating process

Equation 2.14 is common approximation used to describe the evolution of δ_s (but also δ_p) in well mixed- and closed-systems during kinetic reactions with a constant $\epsilon_{p\text{-}s}$ factor (Kendall and Aravena, 2000):

$$\delta_s \approx \delta_0 + \epsilon_{p\text{-}s} \ln C / C_0 \quad \text{(at time t)} \qquad \text{(Equation 2.14)}$$

where δ_0 is the initial isotopic composition of the substrate, and C/C_0 the remaining fraction of substrate (C concentration at time t, C_0 the initial concentration). As $\epsilon_{p\text{-}s}$ is

typically negative during kinetic reactions in the N cycle and substrate concentration C decreases with time ($C < C_0$), δ (i.e. $\delta^{15}N$ or $\delta^{18}O$ in the context of this study) becomes exponentially bigger. Equation 2.14 is often used to illustrate the denitrification process and the evolution of $\delta^{15}N\text{-}NO_3^-$ in residual NO_3^-.

2.6.2 Isotopic composition of N sources and derived nitrate in soils

This section reviews $\delta^{15}N$-TN values for the N sources described in section 2.3, together with $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values for nitrate contained in or derived from these N sources. Values reported in this section do not concern groundwater nitrate, but represent the original isotopic signature of nitrate at the time of release or genesis in soil, before any isotopic fractionation operates. It should be noted that very little literature, if any, addresses specifically the $\delta^{18}O\text{-}NO_3^-$ signature of nitrate after nitrification in soils, although some work has been carried out on groundwater nitrate (section 2.6.4). $\delta^{18}O\text{-}NO_3^-$ values found in this section are given according to some assumptions commonly made in the literature and detailed in section 2.6.3 (see mineralisation and nitrification).

- Artificial N fertilisers

Most manufactured N fertilisers described in section 2.3.2 are produced by industrial fixation of atmospheric N_2 and O_2. Such industrial processes generally generate little isotopic fractionation, so that N fertilisers have isotopic compositions similar to their precursors, i.e. atmospheric N_2 ($\delta^{15}N\text{-}N_2$ = 0 ‰) and atmospheric O_2 ($\delta^{18}O\text{-}O_2$ = 23.5 ‰ according to Kroopnick and Craig, 1972). As described in section 2.3.2, there are different types of artificial fertilisers. Most display $\delta^{15}N$ for TN and pre-formed nitrate ranging between -4 and 4 ‰ (Wassenaar, 1995; Kendall and Aravena, 2000), although some report an even wider range that extends from -8 to 7 ‰ (Hübner, 1986; Macko and Ostrom, 1994). The fraction of artificial fertiliser N that is not already in nitrate form (i.e. NH_4^+, NH_3, urea, etc) undergoes mineralisation and/or nitrification once deposited in soils and displays $\delta^{15}N\text{-}NO_3^-$ values for soil-water nitrate that are often between -5 and 5 ‰ (figure 2.4), i.e. somewhat similar to the fertiliser N source.

$\delta^{18}O$ values for artificial pre-formed nitrate typically range between 18 and 22 ‰ (Amberger and Schmidt, 1987) because all three oxygen atoms come from atmospheric O_2

(figure 2.4). Comparatively, nitrate derived from the nitrification of artificial NH_4^+ displays much lower $\delta^{18}O$ values characteristic of nitrate biologically-formed in soil, ranging in theory between 0 and 5 ‰ (see nitrification in section 2.6.3). In the case of ammonium and nitrate fertilisers like NH_4NO_3 or CAN (calcium ammonium nitrate), an expected overall $\delta^{18}O\text{-}NO_3^-$ value can be calculated for the whole pool of fertiliser-derived nitrate (i.e. pre-formed nitrate plus the nitrified fraction). It is dependent on the ratio of NO_3^- to NH_4^+ originally contained in the fertiliser. For instance, since half of the nitrogen in NH_4NO_3 fertiliser is already in nitrate form, it can be assumed that after the remaining NH_4^+ half has undergone nitrification, the final overall $\delta^{18}O\text{-}NO_3^-$ value will be somewhere around 10 ‰, i.e. half way between the ranges 0-5 ‰ and 18-22 ‰. In the case of CAN application where three quarters of N is in pre-formed nitrate form, the overall $\delta^{18}O\text{-}NO_3^-$ value can be expected to be higher.

- Human and animal organic wastes

Most of the nitrogen present in animal and human wastes (urine and faeces) is found in NH_4^+ and organic N forms available for mineralisation and subsequent nitrification, whereas there is very little nitrate originally present (table 2.6, and sections 2.3.3 and 2.3.4). Urine excreted is generally ^{15}N-depleted relative to the diet and displays original $\delta^{15}N\text{-}TN$ values between -1.5 and -3 ‰ (Kreitler, 1975; Knobbe *et al.*, 2006), whereas faeces can be expected to show higher values (Létolle, 1980). The hydrolysis of urea causes a temporary increase in local pH that favours ammonia over ammonium, which results in increasing the loss of ^{15}N-depleted NH_3 (see volatilisation in section 2.6.3). TN in solid waste (faeces) shows usually higher $\delta^{15}N\text{-}TN$ than urine, with values ranging from 8 to over 20 ‰ (Wassenaar, 1995; Krapac *et al.*, 2002; Karr *et al.*, 2003), although Gormly and Spalding (1979) recorded lower $\delta^{15}N\text{-}TN$ for cow and pig excrements ranging between 1.7 and 4.8 ‰.

Farmyard organic wastes derive mainly from urine and faeces. In accordance with the above information, slurry containing large amounts of urine and ammonium is likely to be subjected to NH_3 volatilisation that contributes to generate ^{15}N-enriched nitrate with $\delta^{15}N\text{-}NO_3^-$ over 10 ‰ (figure 2.4). In comparison, manures contain mainly organic N coming from faeces and little ammonium. Since mineralisation is a much slower process than nitrification, there is little accumulation of NH_4^+, which should result in smaller rate of NH_3 volatilisation (Aravena *et al.*, 1993). As a result, the nitrification of farmyard wastes

once in soils can generate heavy nitrate with $\delta^{15}N\text{-}NO_3^-$ often reported between 10 and 22 ‰ (Macko and Ostrom, 1994; Kendall and Aravena, 2000).

A review by Fogg *et al.* (1998) emphasised how difficult it is to differentiate animal from human waste contamination because both types of N sources generate nitrate with $\delta^{15}N\text{-}NO_3^-$ that often overlap (figure 2.4). Nonetheless, Fogg *et al.* (1998) showed that although being within close ranges, nitrate from both sources could yet display $\delta^{15}N\text{-}NO_3^-$ values significantly different at the 90-95 % confidence levels. During his experiments, mean $\delta^{15}N\text{-}NO_3^-$ of 7.31 ±0.94 ‰ and 10.26 ±2.82 ‰, reported under two septic tank systems from two sampling areas, were found to be significantly lower than values displayed under animal feedlot sites from the same areas (9.97 ±0.30 ‰ and 14.46 ±1.14 ‰ respectively). The reason may be that septic tank effluents are less subject to NH_3 volatilisation because of their subsurface location.

$\delta^{18}O\text{-}NO_3^-$ values for nitrate derived from animal or human wastes may be expected to be within the characteristic range of biologically formed nitrate, i.e. between 0 and 5 ‰ (see nitrification in section 2.6.3 and figure 2.4), not differing from $\delta^{18}O\text{-}NO_3^-$ values for the nitrification of artificial ammonium. However, some differences between animal and human waste nitrate may well occur under special conditions. Kendall and Aravena (2000) suggested that nitrification taking place close to the surface might incorporate more ^{18}O than below ground level because of water volatilisation and subsequent ^{18}O-enrichment. As a consequence, nitrate derived from animal waste N may have higher $\delta^{18}O\text{-}NO_3^-$ than nitrate nitrified deeper in the subsoil where human waste effluents are released.

- Silage effluent

Karr *et al.* (2003) determined a $\delta^{15}N$-TN value of 3.9 ‰ in one silage 'juice' sample. To the present knowledge, there is little information in relation to the isotopic composition of this type of organic waste, although some assumptions can be made about the isotopic signature of subsequent nitrate. Since silage effluents contain a large fraction of ammonium along with organic N (section 2.3.5), NH_3 volatilisation is likely to enrich the remaining substrate with ^{15}N and increase $\delta^{15}N$ values of derived nitrate, although maybe not to the extent usually witnessed for urine-derived nitrate. As for $\delta^{18}O$, it should fall into the range of biologically formed nitrate, i.e. between 0 and 5 ‰ (see nitrification in section 2.6.3) since all nitrate arising from silage effluent is formed through nitrification.

- Soil organic matter

Most of the nitrogen found in soils is organically bound, as mentioned in section 2.3.6, and displays a wide range of δ^{15}N-TN values for reasons developed below. According to reviews from Létolle (1980) and Kendall (1998), δ^{15}N-TN in soil varies between -10 to 17 ‰, although most values fall between 2 and 5 ‰ (Kendall, 1998). Heaton (1986) restricted this range to 4 and 9 ‰, which is widely adopted in the literature. δ^{15}N-TN in soil is affected by several factors discussed by Kendall and Aravena (2000). It is typically witnessed in well-drained soils that δ^{15}N-TN increases with depth or decreasing organic N content. At the soil surface, δ^{15}N-TN is generally similar to or slightly greater than in plant litter, the values in plant tissues typically ranging between -5 and 2 ‰ in non-cultivated systems (Nadelhoffer and Fry, 1994). Soil δ^{15}N-TN then typically increases to around 5 to 9 ‰ at depths of 20-40 cm (reviews by Létolle, 1980; Nadelhoffer and Fry, 1994), and stays relatively constant at greater depths. This can be attributed to the fact that deeper soil layers contain less but older organic N that has been ^{15}N-enriched by mineralisation for longer than more recent organic N newly deposited at the soil surface. As explained in section 2.6.3, mineralisation generates a product of reaction (i.e. ammonium) slightly ^{15}N-depleted relative to the substrate (soil organic N). Therefore, subsequent N losses through plant uptake, denitrification and nitrate leaching mean that TN in soils becomes more ^{15}N-enriched with time, hence with depth.

Soil cultivation also appears to have a certain impact by causing low δ^{15}N-TN (0.65 ±2.6 ‰) in comparison with uncultivated soils (2.73 ±3.4 ‰) according to a soil survey by Broadbent *et al.* (1980). This goes along the lines of Choi *et al.* (2002) who reported that maize treated with composted pig manure (δ^{15}N-TN in compost = 13.9 ‰) was significantly more enriched in ^{15}N than when treated with artificial urea (δ^{15}N-TN in urea = -2.3 ‰). It suggests that the δ^{15}N of nitrogen applied as fertiliser impacts on δ^{15}N-TN in organic matter that grows and then decomposes in soils. Other parameters like vegetation, climate and agricultural history, along with processes in the N cycle (section 2.6.3) also impact on δ^{15}N-TN in soil.

Nitrate derived from the mineralisation and then nitrification of soil organic matter, which is often referred to as "natural nitrate", has been commonly found to have δ^{15}N-NO_3^- values somewhat intermediate between fertiliser and animal/human waste-derived nitrate. Most frequently quoted values range between 4 and 9 ‰ for soil-water nitrate (Kreitler,

1975; Gormly and Spalding, 1979; Heaton, 1986; Ostrom *et al.*, 1998). However, this characteristic is moderated by the fact that $\delta^{15}N\text{-}NO_3^-$ of this type of nitrate frequently overlaps with values for fertiliser-derived nitrate (figure 2.4). For instance, a review by Fogg *et al.* (1998) showed that nitrates sampled in the unsaturated zone beneath fertilised and unfertilised soils had average $\delta^{15}N\text{-}NO_3^-$ ranging from 0 to 5 ‰ for the former and -3 to 5 ‰ for the latter. As for $\delta^{18}O\text{-}NO_3^-$, the original value for soil organic matter-derived nitrate can be expected in the characteristic range of nitrification, i.e. between 0 and 5 ‰, although few studies, if any, have addressed this specific topic.

- Atmospheric deposits

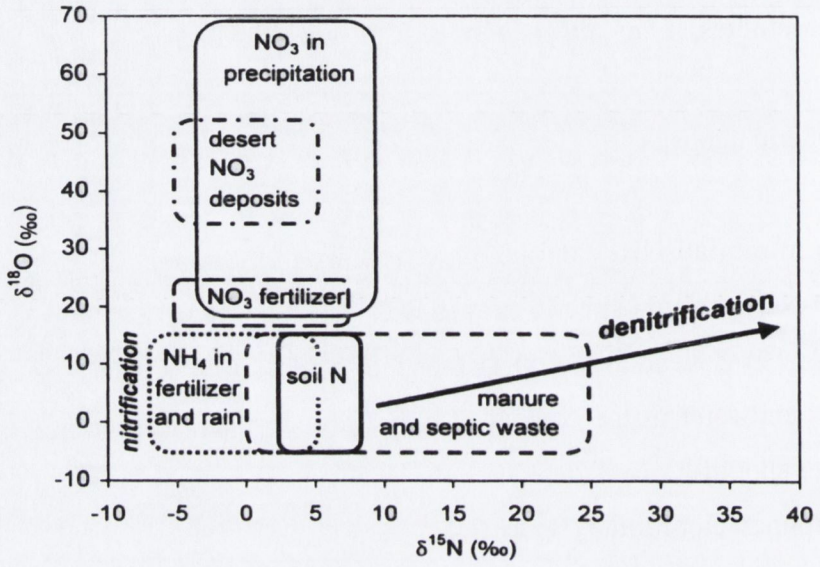
$\delta^{15}N$ values in rainfall NH_4^+ and NO_3^- are usually in the range of -15 to 15 ‰ (Kendall, 1998). $\delta^{18}O\text{-}NO_3^-$ in atmospheric nitrate was generally recorded between 25 and 75 ‰ (Durka *et al.*, 1994; Kendall, 1998). Atmospheric deposition is probably a minor source of nitrate to groundwater in the context of our study as stated in section 2.3.7, although all nitrate inputs should be considered for the explanation of high $\delta^{18}O\text{-}NO_3^-$ values in soil-water and groundwater nitrate (figure 2.4).

2.6.3 Processes causing isotopic fractionation to nitrate during leaching

The downward movement of nitrate with percolating water through the unsaturated zone, known as nitrate leaching (section 2.5.1), is a physically conservative process from the isotopic point of view, which does not cause isotopic fractionation to nitrate alone. Other processes taking place during leaching are likely to be responsible for altering the original isotopic signature of nitrate, and are discussed in this section. As illustrated earlier in section 2.2.2 and figure 2.1, nitrate that reaches groundwater has often undergone a series of complex physical and biochemical transformations that take place within the unsaturated zone, bearing in mind that potential changes can also occur within the saturated zone. While general features of each process and chemical implications for water are discussed in section 2.4, this section reviews the isotopic fractionation caused by these reactions and the implications for the nitrate that will contaminate groundwater. In figure 2.4, Kendall (1998) links some of the N sources described in section 2.6.2 with $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values that can be expected for nitrate after the action of nitrification and denitrification, which are two processes further explained in this section. It should be noted

that immobilisation, which is not pictured in this figure, is always omitted on similar diagrams from the literature. It is important to keep in mind that values from this diagram can change from one author to another, the delineation of areas being sometimes very subjective and dependant on what values the author deemed most relevant.

Figure 2.4: Typical range of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values of soil-water nitrate derived from various sources (Kendall, 1998).



As with most natural processes, nitrification and denitrification consist of several steps. Each step has the potential for isotopic fractionation, and the overall fractionation caused by the whole reaction is highly dependent on parameters that include number and type of intermediate steps, size of the reactant reservoir, soil pH, organisms involved, etc. A first 'rule of thumb' is that most of the fractionation is caused by the so-called 'rate-determining step' which is the slowest step (e.g. micro-organisms have time to be more selective and save energy by preferentially breaking light-isotope bounds). This step commonly involves a large reservoir of reactant where little is actually transformed. In contrast, a step that is not 'rate-determining' generally involves a small pool of reactant that is rapidly converted into reaction product. The isotopic compositions of reactant and product can be successfully modelled with the Rayleigh equation (Equation 2.14) during a multi-step reaction if the net fractionation is controlled by a single rate-determining step. A second 'rule of thumb' is that microbial, and some physical, processes from the N cycle usually preferentially involve light isotopes because bounds are easier to break, and thus leave the unreacted soil substrate enriched with the heavier isotopes (^{15}N, ^{18}O or ^{2}H).

- Mineralisation

Mineralisation, which is defined in this thesis as the conversion of organically bound N into NH_4^+ (section 2.4.1 and equation 2.1), is reported to cause only a small fractionation (^{15}N enrichment or depletion by ±1 ‰) between newly formed NH_4^+ and soil organic matter (Kendall, 1998). The $\delta^{15}N\text{-}NH_4^+$ value is generally within a few permils of $\delta^{15}N\text{-}TN$ of the N source. Hence, the isotopic composition of the products of mineralisation that lead to the generation of nitrate appears to be very similar to their respective N source.

- Nitrification

Nitrification generally consists of the autotrophic transformation of ammonium into nitrate (section 2.4.1 and equation 2.2). It can cause newly formed nitrate to be variably depleted in ^{15}N with respect to the ammonium source. The extent of the isotopic fractionation actually depends on the amount of total nitrogen and ammonium available. In N-limited systems, the N fractionation is small and the $\delta^{15}N\text{-}NO_3^-$ of subsequent soil nitrates is usually within a few permils of the composition of the original total organic N in soil. However under conditions of non-N limited systems, e.g. after application of manure or ammonium on fields, nitrification is likely to cause some large fractionation as observed in figure 2.5. As a result, the first nitrates produced can be depleted in ^{15}N by -5 to -35 ‰ (Delwiche and Steyn, 1970; Mariotti *et al.*, 1980). But as the N reservoir is used up, the nitrification rate decreases and so does the isotopic fractionation, the oxidation of ammonium no longer being a rate-determining step. $\delta^{15}N\text{-}NO_3^-$ of nitrate increases toward the original $\delta^{15}N\text{-}NH_4^+$ values as seen in figure 2.5.

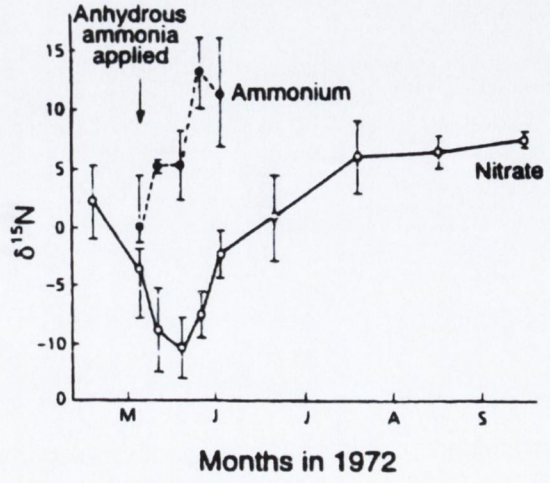


Figure 2.5: Evolution over time of $\delta^{15}N\text{-}NH_4^+$ and $\delta^{15}N\text{-}NO_3^-$ following the application of anhydrous NH3 fertiliser to an agricultural field (Feigin *et al.*, 1974).

While the typical ranges of $\delta^{18}O\text{-}NO_3^-$ in atmospheric and fertiliser nitrates are well known, few experimental data exist for the oxygen isotope composition of nitrate generated by nitrification in soils (Mayer *et al.*, 2001). Laboratory experiments with *Nitrosomonas* and *Nitrobacter agilis* conducted under neutral pH conditions suggested that out of the three oxygen atoms incorporated during the oxidation of ammonium, two come from H_2O and one from dissolved O_2 (Andersson and Hopper, 1983; Kumar *et al.*, 1983; Hollocher, 1984). If the assumption is made that oxygen is incorporated without any fractionation, which is debatable, then the $\delta^{18}O\text{-}NO_3^-$ of newly formed nitrate could theoretically be calculated as follows (Kendall and Aravena, 2000):

$$\delta^{18}O\text{-}NO_3^- = 2/3\ \delta^{18}O\text{-}H_2O + 1/3\ \delta^{18}O\text{-}O_2 \qquad \text{(Equation 2.15)}$$

In the literature, $\delta^{18}O\text{-}H_2O$ is reported to range from -25 to 5 ‰ (Gat, 1996; Kendall, 1998) depending on season and geographical location (section 2.6.5), whereas $\delta^{18}O$ in O_2 is around 23.5 ‰ (Kroopnick and Craig, 1972). If assumptions made in Equation 2.15 are correct, it means that $\delta^{18}O\text{-}NO_3^-$ is expected to range between -10 and 10 ‰, which is the value reported by Kendall (1998) in figure 2.4. Durka *et al.* (1994) reported a narrower range (0 to 5 ‰) because the $\delta^{18}O\text{-}H_2O$ values under consideration were between -10.5 and -3 ‰.

The fact that some studies reported $\delta^{18}O\text{-}NO_3^-$ values for groundwater nitrate that were significantly higher may challenge the model described above for the incorporation of oxygen during nitrification (Aravena *et al.*, 1993; Wassenaar, 1995; Kendall, 1998). In addition, it was also suggested that in NH_4^+ limited systems with low nitrification rates, significantly less than two thirds of the oxygen in newly formed nitrate was derived from water oxygen. This might indicate the occurrence of heterotrophic nitrification in acid forest floor horizons, during which incorporation of water oxygen into nitrate may be considerably lower than during autotrophic nitrification (Mayer *et al.*, 2001).

- Microbial immobilisation and MIT processes

Nitrate, along with ammonium, can be assimilated by some soil heterotrophic microorganisms under certain conditions (figure 2.2 and equation 2.3). As discussed in section 2.4.1, this process results in the incorporation of ammonium and nitrate N into

organic tissues and genetic material. Hübner (1986) compiled Δ values (apparent fractionation between the reaction product, i.e. the incorporated N, and ammonium and nitrate in soil-water), which ranged between -1.6 and 1 ‰, with an average of -0.52 ‰. This means that although bacteria appear to preferentially incorporate ^{14}N, the enrichment factor caused by microbial immobilisation is small enough to leave $\delta^{15}N\text{-}NO_3^-$ and $\delta^{15}N\text{-}NH_4^+$ of residual nitrate and ammonium relatively unchanged in soils. To the present knowledge, there are no studies addressing the O fractionation during the incorporation of nitrate into microbial biomass, although Kendall and Aravena (2000) made the assumption that bacteria might incorporate preferentially ^{16}O-bearing nitrate to ^{18}O-bearing one, which would leave residual nitrate in soil-water slightly ^{18}O-enriched.

One obvious outcome is that, if immobilised, a molecule of nitrate actually loses all its original oxygen atoms. This is a critical point when considering $\delta^{18}O$ analysis on nitrate as a complementary tool to $\delta^{15}N$ analysis, particularly with respect to the identification of fertiliser nitrate. Indeed, once re-mineralised and re-nitrified has proceeded through the MIT processes, newly formed nitrate should display a $\delta^{18}O\text{-}NO_3^-$ value characteristic of natural soil nitrate between 0 to 5 ‰ (see nitrification above), which contrasts with the original $\delta^{18}O\text{-}NO_3^-$ value that was above 18 ‰. In comparison and given information in this section, $\delta^{15}N\text{-}NO_3^-$ is not expected to change significantly during the MIT processes. In that context, Mengis *et al.* (2001) identified MIT as a major limitation for the use of $\delta^{18}O$ analysis on groundwater nitrate. It is currently the only study that clearly addresses the relative inefficiency of $\delta^{18}O$ analysis as a tool to identify nitrate sources in relation to the occurrence of MIT. This point is further developed in section 2.6.4.

- Plant uptake

Ammonium and nitrate are the preferential N-bearing nutrients taken up by plants from soil water (section 2.4.2). Although ^{14}N is slightly preferred to ^{15}N (Kendall and Aravena, 2000), the enrichment factor is often reported to be small. Mariotti *et al.* (1980) reported apparent N fractionations by vascular plants in the range of -2.2 to 0.5 ‰, with an average of -0.27 ±0.63 ‰. This means that the isotopic composition of the N source (NO_3^- or NH_4^+ from fertiliser or soil organic matter) is probably only slightly altered by plant uptake. Kendall and Aravena (2000) made the assumption that, similarly to what is witnessed with nitrogen, plants may also favour the assimilation of light nitrate in relation to oxygen

isotopes (i.e. nitrate with ^{16}O rather than ^{18}O), which would result in a slight enrichment of residual nitrates in ^{18}O.

- Nitrate attenuation: denitrification and mixing process

Denitrification is a multi-step process that consumes nitrate under anoxic conditions (section 2.4.3) and profoundly alters the isotopic composition of nitrate. In a single source closed system scenario, such a process can be described with the Rayleigh equation (Equation 2.14) where $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in residual nitrate increase exponentially as nitrate concentration decreases. Under favourable field circumstances, it may then be possible to characterise the occurrence of denitrification by plotting $\delta^{15}N\text{-}NO_3^-$ (y coordinate) versus ln $[NO_3^-]$ (x coordinate), which would give a straight line with a negative slope equal to $\epsilon_{N2\text{-}NO3}$. Unfortunately, such a decrease in nitrate concentration is not necessarily observed and correlated with nitrate isotopic composition because inputs of nitrate to terrestrial systems are generally variable and multiple, which is a condition that does not suit the model described by the Rayleigh equation. On the other hand, some studies have reported increases in $\delta^{15}N\text{-}NO_3^-$ to be between 1.3 and 2.0 times that of $\delta^{18}O\text{-}NO_3^-$ in groundwater systems (Böttcher *et al.*, 1990; Aravena and Robertson, 1998; Fukada *et al.*, 2004), or more specifically in riparian zones (Cey *et al.*, 1999; Mengis *et al.*, 1999; Fukada *et al.*, 2003). Therefore, denitrification may produce a characteristic linear relationship when plotting $\delta^{18}O\text{-}NO_3^-$ (y coordinate) versus $\delta^{15}N\text{-}NO_3^-$ (x coordinate) with slopes typically reported between 0.5 and 0.77, which is within a close range of the theoretical 0.51 value calculated by Chen and McQuarrie (2005). Apparent nitrogen fractionations associated with denitrification ($\Delta_{N2\text{-}NO3}$) have been measured at between -40 and -5 ‰ (Kendall and Aravena, 2000). The actual $\Delta_{N2\text{-}NO3}$ value depends on how far the process goes, so that if denitrification is close to complete, the apparent fractionation will be very high. This can for instance result in $\delta^{15}N$ in nitrate fertiliser (0 ±4 ‰) displaying values in the range of nitrate derived from animal or human wastes.

A decrease in groundwater nitrate concentration may be mistakenly attributed to denitrification when it actually involves another process described as the mixing process (Mariotti *et al.*, 1988; Kendall and Aravena, 2000). If groundwater contaminated by nitrate is mixed with nitrate-free water, the nitrate concentration of the mixture decreases but without any change in the isotopic composition of nitrate. Alternatively, mixing with low-

nitrate water results in a change of the isotopic composition of nitrate in the mixture, described by the following equation (Kendall and Aravena, 2000):

$$\delta_m = (Q_a\delta_a + Q_b\delta_b) / Q_m \qquad \text{(Equation 2.16)}$$

where δ_a and δ_b refer to $\delta^{15}N\text{-}NO_3^-$ of the high and low-nitrate sources, where δ_m represents $\delta^{15}N\text{-}NO_3^-$ of the mixture, and where Q is the amount of nitrate (i.e. $Q = V \times [NO_3^-]$ with V the volume of water and $[NO_3^-]$ the nitrate concentration). The mixing process can then be differentiated from denitrification by plotting $\delta^{15}N\text{-}NO_3^-$ against $1/[NO_3^-]$ to determine if it produces a straight line.

- Ammonia volatilisation

As discussed in section 2.3, most N sources in soils contain or produce some ammonium and are hence affected by NH_3 volatilisation (section 2.4.4). Animal wastes and ammonium/ammonia fertilisers happen to be strongly affected by this process. Ammonia volatilisation involves the preferential loss of lighter molecules ($^{14}NH_3$) and results in the ^{15}N-enrichment of residual ammonium that will undergo nitrification. This is illustrated in equations 2.17 and 2.18 (respectively related to equations 2.6 and 2.7), which display a cumulative equilibrium fractionation factor of 1.034 (Kreitler, 1975):

$$^{15}NH_{3(aq)} + {}^{14}NH_4^+{}_{(aq)} \leftrightarrows {}^{14}NH_{3(aq)} + {}^{15}NH_4^+{}_{(aq)} \qquad \text{(Equation 2.17)}$$

$$^{14}NH_{3(aq)} + {}^{15}NH_{3(atm)} \leftrightarrows {}^{15}NH_{3(aq)} + {}^{14}NH_{3(atm)} \qquad \text{(Equation 2.18)}$$

It should be noted that although ammonia volatilisation is controlled by equilibrium reactions, this process also involves some kinetic isotopic fractionation because the reaction product ammonia gas (i.e. $NH_{3(atm)}$) diffuses rapidly into atmospheric air and is therefore isolated from reactants.

This large shift towards high $\delta^{15}N\text{-}NH_4^+$ values in residual ammonium causes subsequent nitrified nitrate N to show much higher $\delta^{15}N\text{-}NO_3^-$ values than the original N source. Animal wastes can be strongly affected by ammonia volatilisation, depending on the type of storage, because they usually contain large quantities of ammonium and urea, the hydrolysis of which creates favourable conditions for severe volatilisation. $\delta^{15}N$-TN in a

manure pile may then become higher than 20 ‰ according to Kendall and Aravena (2000). This process also affects artificial fertilisers. Aravena *et al.* (1993) referred to N enrichment factors up to 6 ‰ for groundwater nitrate derived from ammonium fertiliser. At the same time, Aravena *et al.* (1993) did not rule out ammonia volatilisation in septic tank plumes, but its contribution to the increase of $\delta^{15}N$ in nitrified nitrate is thought to be limited. However, some substantial volatilisation may take place in the tank itself.

- Other processes

In temperate regions, adsorption on clay affects ammonium only and hence may indirectly affect nitrate (section 2.4.4). Some studies with kaolinitic clays (Delwiche and Steyn, 1970; Kreitler, 1975) suggest that ^{15}N is preferentially retained, though very little isotopic fractionation is caused.

It should be noted that although little information is available on this topic, early laboratory investigations suggested that water and nitrate in leachate and groundwater are unlikely to exchange oxygen atoms (Bunton *et al.*, 1952). Likewise, Kendall and Aravena (2000) suggested that dissolved O_2 and N_2 are probably too stable to exchange atoms with nitrate.

2.6.4 Review of combined $\delta^{15}N$ and $\delta^{18}O$ analyses on groundwater nitrate: success or failure?

Although $\delta^{15}N$ analyses on nitrate really started to blossom in the 1970's (Kreitler, 1975), and $\delta^{18}O$ analyses in the 1990's, few studies to date have combined both to elucidate the origin of groundwater nitrate. When conducted for this purpose, the outcome was somewhat disappointing because $\delta^{18}O$ analyses were generally of little help to improve the identification of nitrate sources and elucidate cases left unresolved by $\delta^{15}N$ analysis alone. However, valuable information related to processes affecting nitrate in subsoils and aquifers was obtained.

- Dual isotopic analyses as a tool to identify the origin of groundwater nitrate

Many studies that aimed to identify the origin of groundwater nitrate in agricultural areas gave conclusive results when using $\delta^{15}N\text{-}NO_3^-$ alone, regardless of some limitations. Although $\delta^{15}N$ analyses on groundwater nitrate have showed inefficiency at differentiating artificial fertilisers and soil organic matter as contamination sources (Kendall and Aravena,

2000), they have often been successful at distinguishing contamination by artificial fertiliser or soil organic matter from that caused by animal and human organic wastes. Studies showed that groundwater nitrate sampled underneath fields subjected to applications of artificial fertiliser nitrogen (N as NH_4^+, NO_3^-, urea, etc) often exhibited $\delta^{15}N\text{-}NO_3^-$ values significantly lower, by a few permils, than areas subjected to animal waste applications or septic tank contamination (Aravena *et al.*, 1993; Macko and Ostrom, 1994; Wassenaar, 1995; Kendall and Aravena, 2000; Panno *et al.*, 2001; Kellman, 2005). However, there were real problems using this method where denitrification occurred, due to the substantial increase in $\delta^{15}N\text{-}NO_3^-$ (section 2.6.3). Where the main N source of contamination was artificial fertiliser, $\delta^{15}N\text{-}NO_3^-$ values after denitrification proceeded could lead to some misinterpretation because measured $\delta^{15}N\text{-}NO_3^-$ could overlap with values expected for nitrate derived from animal wastes or septic tank effluents.

The use of $\delta^{18}O$ was originally supposed to overcome the problem generated by denitrification and other overlaps because artificial fertiliser nitrate, and also atmospheric nitrate, display $\delta^{18}O\text{-}NO_3^-$ values very distinct from nitrate produced by soil nitrification (section 2.6.2 and figure 2.4). Instead of measuring only one parameter (i.e. $\delta^{15}N$), the use of a second parameter ($\delta^{18}O$) seemed promising (Macko and Ostrom, 1994; Ostrom *et al.*, 1998). But to date, $\delta^{18}O$ analyses on groundwater nitrate have failed to improve the identification of artificial fertiliser contamination: $\delta^{18}O\text{-}NO_3^-$ higher than 18 ‰ in conjunction with $\delta^{15}N\text{-}NO_3^-$ close to 0 ‰ have not been observed in agricultural areas according to available literature. Such an outcome was typically illustrated by Aravena *et al.* (1993) whose study showed that although $\delta^{15}N\text{-}NO_3^-$ values in groundwater nitrate were in agreement with the N sources (4.6 ±0.8 ‰ for contamination partly by NH_4NO_3 fertiliser versus 9.9 ±1.5 ‰ in plume of septic tank effluent), $\delta^{18}O\text{-}NO_3^-$ values showed no difference between the non-plume groundwater and the plume of contamination (3.4 ±2.3 ‰ versus 3.5 ±1.4 ‰). In fact, the only successful studies that managed to identify nitrate with high $\delta^{18}O\text{-}NO_3^-$ values (between 10 and 35 ‰ in absence of denitrification) were conducted by Durka *et al.* (1994) and Kendall *et al.* (1995), but in the context of forested watersheds where the purpose was to evaluate the relative contribution of atmospheric nitrate versus nitrate derived from soil organic matter. In this situation of declining forests, Durka *et al.* (1994) suggested that atmospheric nitrate leached unchanged due to a significant reduction of nitrate consumption by soil microorganisms and trees.

Reasons given in the literature to explain the limitations of $\delta^{18}O$ analysis on groundwater nitrate are multiple:

1) Most artificial fertilisers (section 2.3.2) in use are a mixture of nitrate and ammonium (e.g. NH_4NO_3 or CAN) instead of nitrate alone. Consequently, the expected $\delta^{18}O\text{-}NO_3^-$ value for the whole pool of fertiliser-derived nitrate is lower than that for pre-formed nitrate alone (i.e. > 18 ‰). For instance, the calculated $\delta^{18}O\text{-}NO_3^-$ value for NH_4NO_3 is 10 ‰ (section 2.6.2), and gets closer to values expected for nitrate derived from soil organic matter or organic wastes.
2) Roadcap *et al.* (2002) suggested that ammonium and nitrate fertilisers (e.g. NH_4NO_3 or CAN) leach primarily nitrate that derives from the nitrification of artificial NH_4^+, whereas the pre-formed nitrate fraction is more readily taken up by plants. Consequently, $\delta^{18}O\text{-}NO_3^-$ in groundwater nitrate would not display high values but values of nitrified ammonium instead.
3) Mengis *et al.* (2001) took into account the fact that nitrate may be immobilised by soil bacteria through the MIT processes (sections 2.4.1 and 2.6.3), which would result in masking the original $\delta^{18}O\text{-}NO_3^-$ values. It means that artificial nitrate would no longer display $\delta^{18}O\text{-}NO_3^-$ values above 18 ‰, but rather in the typical range of nitrification (0-5 ‰).

In reality, it is probably a combination of these three reasons that resulted in the failure of $\delta^{18}O$ analysis on groundwater nitrate to identify artificial nitrate. In fact, the limitations of dual isotopic analysis as a tool to identify the origin of groundwater nitrate were foreseen in section 2.5.3, where it was already clear that little fertiliser nitrate is usually left in soil in its original form for leaching.

$\delta^{18}O$ analysis on groundwater nitrate may nonetheless prove successful in the identification of artificial nitrate under favourable conditions. For instance, lysimeter experiments by Mengis *et al.* (2001) showed that winter leachate displayed $\delta^{18}O\text{-}NO_3^-$ values as high as 16.2 ‰ after calcium nitrate was applied. This is consistent with results from Durka *et al.* (1994) who suggested that low microbial activity and low microbial assimilation (because of low pH) resulted in atmospheric nitrate (high $\delta^{18}O\text{-}NO_3^-$ value) being able to leach through the unsaturated zone unchanged. Mengis *et al.* (2001) also suggested that coarser subsoil or higher precipitation might allow nitrate leaching to proceed faster (lower residence time), which would limit the effect of MIT because bacteria would be given less time to operate. In addition, Aravena *et al.* (1993) concluded from their experiments that $\delta^{18}O$ analysis in groundwater could be a sensitive tracer in an aquifer affected by direct leaching of artificial fertiliser nitrate. Alternatively, it may be reasonably assumed that

application rates of fertiliser nitrate higher than the biological requirement may also result in groundwater contamination by a higher proportion of nitrate directly derived from fertiliser itself, which would be consistent with experiments carried out by Barraclough *et al.* (1984).

- Dual isotopic analyses as a tool to identify denitrification

For all their limitations, $\delta^{15}N$ and $\delta^{18}O$ analyses on groundwater nitrate showed they can be used successfully to characterize the occurrence of denitrification (Böttcher *et al.*, 1990; Aravena and Robertson, 1998; Cey *et al.*, 1999; Mengis *et al.*, 1999; Panno *et al.*, 2001; Fukada *et al.*, 2003). As described in section 2.6.3 and figure 2.4, denitrification produces a characteristic signature when plotting $\delta^{18}O\text{-}NO_3^-$ (y coordinate) versus $\delta^{15}N\text{-}NO_3^-$ (x coordinate), which typically shows a slope gradient between 0.5 and 0.77. The reason for that may be that denitrification and MIT generally do not occur at the same time, but under different conditions. Denitrification takes place in anoxic environments, potentially across the whole section of unsaturated zone (section 2.4.3), whereas the re-mineralisation and re-nitrification of immobilised nitrate during MIT processes take place in oxic environments generally near soil surface (section 2.4.1).

2.6.5 Other isotopic tools

- The utilisation of $\delta^{18}O\text{-}H_2O$ and $\delta^{2}H\text{-}H_2O$ values in groundwater and precipitation

Depending on the season, meteoric water in temperate regions exhibits very different $\delta^{2}H\text{-}H_2O$ (or $\delta D\text{-}H_2O$) and $\delta^{18}O\text{-}H_2O$ values, which may be used to investigate when groundwater recharge occurs. Precipitation typically displays $\delta^{2}H\text{-}H_2O$ and $\delta^{18}O\text{-}H_2O$ values lower in winter than in summer, which is mainly controlled by the amount of water rained-out. As water vapour derived from the evaporation of low-latitude oceans moves northwards with air masses, winter precipitation, which is more intense than summer one because of colder condensation temperature, discharges larger amounts of ^{2}H- and ^{18}O-enriched rainfall than during summer. Consequently, remaining water vapour that reaches temperate countries like Ireland shows lower $\delta^{2}H\text{-}H_2O$ and $\delta^{18}O\text{-}H_2O$ values in winter, which generates lower $\delta^{2}H\text{-}H_2O$ and $\delta^{18}O\text{-}H_2O$ values in winter precipitation (in comparison with summer rainfall).

In addition to the seasonal effect (in temperate regions), it should be noted that δ^2H-H_2O and $\delta^{18}O$-H_2O values in precipitation are also subjected to several other effects causing regional and temporal variations (Mook and de Vries, 2000): i) latitudinal effect (lower δ values at increasing latitude), ii) continental effect (more negative δ values the more inland), iii) altitude effect (decreasing δ values at higher altitude), and iv) amount effect (lower δ values during heavy storms).

δ^2H-H_2O and $\delta^{18}O$-H_2O in Irish meteoric water have been recorded on a monthly basis by the International Atomic Energy Agency (IAEA) on Valentia Island between 15 January 2000 and 15 December 2002 (IAEA, 2004). A local meteoric water line (local MWL) can be drawn by plotting the isotopic composition of local precipitation, which may then be used to investigate the recharge process on the basis that shallow groundwater reflects the local average precipitation δ values (see Figure 2.6). Nonetheless, as rain falls on the ground and percolates through the unsaturated zone, the original δ^2H-H_2O and $\delta^{18}O$-H_2O values may be altered to some extent by processes such as evaporation, selective recharge and exchange with atmospheric vapour. Once it has reached the saturated zone, infiltrating rain water undergoes little physical transformation and isotopic fractionation other than mixing.

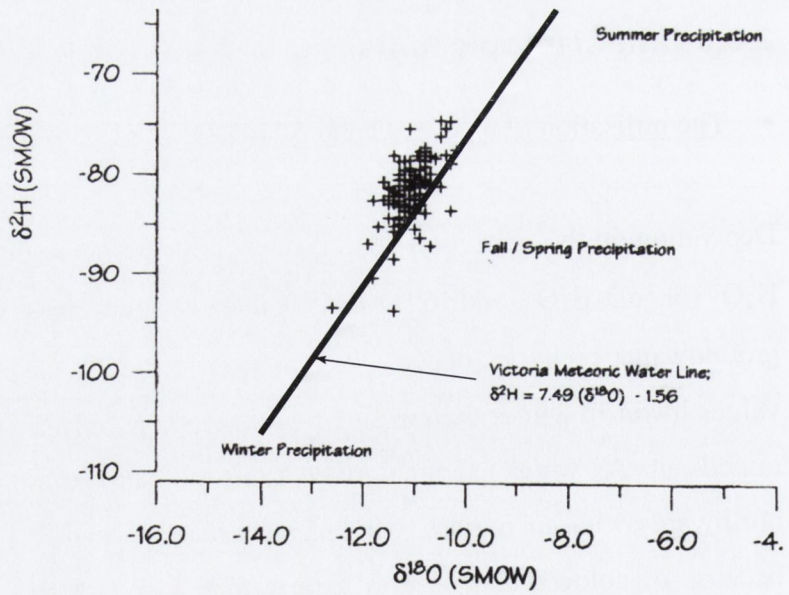


Figure 2.6: $\delta^{18}O$ and δ^2H composition of groundwater (crosses) in the Abbotford aquifer, plotted with the local meteoric water line (Wassenaar, 1995).

Another important application of $\delta^{18}O$-H_2O values is related to the use of Equation 2.15 to estimate $\delta^{18}O$-NO_3^- during nitrification, in accordance with some hypotheses made in section 2.6.3. In addition, Aravena *et al.* (1993) referred to the use of $\delta^{18}O$-H_2O in order to

identify nitrate contamination by a septic tank. It was observed that water in the plume of contamination displayed a distinctive $\delta^{18}O\text{-}H_2O$ value from the surrounding non-plume water, which was attributed to the fact that water in the plume had a different origin (water used for domestic usage is generally abstracted from a deeper well or comes from a different location).

- Isotopic analyses on contaminants other than nitrate

Widory *et al.* (2004) presented a multi-tracer isotopic approach by associating $^{11}B/^{10}B$ ($\delta^{11}B$) and $^{87}Sr/^{86}Sr$ ratio with measurement of $\delta^{15}N\text{-}NO_3^-$. Firstly, boron (B) is not affected by denitrification but can fractionate in contact with the aquifer matrix, whereas strontium does not fractionate through any biological process. For these reasons, B and Sr can be used to assess any mixing process. In addition, groundwater displays some contrasting $^{11}B/^{10}B$ and $^{87}Sr/^{86}Sr$ ratios depending on the type of contaminants. In addition, several studies reviewed by Kendall and Aravena (2000) aimed to evaluate the extent of denitrification in aquifers by measuring $\delta^{15}N\text{-}N_2$ of dissolved N_2 to determine whether groundwater contains excess N_2 (i.e N_2 arising from denitrification, which adds to atmospheric N_2 incorporated during recharge).

2.6.6 Summary of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in nitrate

Values in table 2.8 represent the isotopic fingerprint of nitrate derived from several N sources that are described in section 2.6.2. δ values for groundwater nitrates can then be predicted in the event, or absence, of physical and biochemical processes described in section 2.4, which may, or may not, result in isotopic fractionation, as seen in section 2.6.3.

Table 2.8: Predicted $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values for groundwater nitrates in relation to their N source (values subjected to variations depending on the author, as shown in section 2.6.2).

Origin	$\delta^{15}N\text{-}NO_3^-$ (AIR)	$\delta^{18}O\text{-}NO_3^-$ (V-SMOW)
1. Artificial NO_3^- fertiliser	-4 to 4 ‰	18 to22 ‰
2. Artificial NH_4^+ or urea fertilisers	-4 to 4 ‰	0 to 5 ‰
3. Animal/human wastes N	10 to 22 ‰	0 to 5 ‰
4. Soil organic N	4 to 9 ‰	0 to 5 ‰
5. Atmospheric nitrate deposit	-15 to 15 ‰	25 to 75 ‰
6. After denitrification	Up to 40 ‰	Up to 20 ‰
7. After MIT	unchanged	0 to 5 ‰

- Parameters indicative of organic contamination

Lines 3 and 4 in table 2.8 give $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ predicted values for contamination by animal/human wastes and soil organic matter respectively, in the absence of any fractionating process such as denitrification and MIT (line 6 and 7).

- Parameters indicative of artificial fertiliser contamination

Lines 1 and 2 in table 2.8 sum up $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values for contamination by nitrate derived from artificial fertilisers. The predicted $\delta^{18}O\text{-}NO_3^-$ value in absence of any fractionating process (like denitrification and MIT in line 6 and 7) depends on the proportion of pre-formed nitrate contained in the fertiliser used. It is to be noted that high $\delta^{18}O\text{-}NO_3^-$ values may also result from the deposition of atmospheric nitrate.

- Parameters related to denitrification

Denitrification produces a characteristic signature when plotting $\delta^{18}O\text{-}NO_3^-$ (y coordinate) versus $\delta^{15}N\text{-}NO_3^-$ (x coordinate), which typically shows a slope between 0.5 and 0.77. If denitrification occurs, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values increase simultaneously. This trend is illustrated in figure 2.4 for nitrates that originally displayed low $\delta^{18}O\text{-}NO_3^-$ values.

CHAPTER 3: STUDY AREAS AND SAMPLING SITES DESCRIPTION

3.1 Introduction

In order to aid the testing of isotopic analyses as a tool to identify nitrate sources in groundwater, the research involved the sampling not only of the saturated zone, but also of the unsaturated zone. This was carried out at several locations (see section 4.1.1 for the choice of the study areas): in the River Barrow catchment in south Co. Kildare and north Co. Carlow, which was the main region studied, and at Curtin's farm in Moorepark Research Centre (north Co. Cork) because of contrasting land use. Within the Barrow Valley, groundwater was collected from three small areas, namely Castlemitchell, Ballyroe and Oak Park, while soil-water was collected from Knockbeg and Oak Park Research Centre. This chapter describes general features of the Barrow Valley sampling area in relation to geography, geology, hydrogeology, climate and land use (section 3.2), before detailing soil-water and groundwater sampling sites in sections 3.3 and 3.4 respectively. In each of these sections, reference is also made to Moorepark Research Centre sampling sites, which have been extensively discussed by Bartley (2003) and Gibbons *et al.* (2006) within the context of EPA ERTDI Projects 2000-LS-2.3.1.3-M2 and LS 2.3.2 respectively. Emphasis is put on agricultural land use and associated diffuse sources of nitrogen, but also on the identification of potential point sources of nitrogen in the vicinity of sampling wells, which is a critical aspect of this research.

3.2 General description of the Barrow Valley and Moorepark RC

3.2.1 Location and topography

- Barrow Valley

Soil-water and groundwater sampling was carried out in the Barrow Valley area that extends between the Castlecomer Plateau in the west, the foothills of the Leinster Mountains in the east, the surroundings of Athy (Co. Kildare) in the north, and Carlow town in the south. At the centre of the valley flows the River Barrow, whose bed slopes gently north to south from elevation less than 60 m AOD at Athy to barely 50 m AOD at

Carlow, 17 km to the south. The valley narrows progressively towards Carlow and the topography is also relatively gentle from east to west. From the foot of the Castlecomer plateau and Leinster Mountains to Athy, the elevation decreases slowly from 100 m AOD to 60 m over 6 km distance on each side of the valley in a nearly-symmetrical way. A similar decrease in elevation is observed on the left bank of the river around Carlow, although slope is steeper on the right bank as the valley narrows. Further details are available in the Ordnance Survey Discovery Series maps No.55 and 61 (scale 1:50,000).

Groundwater sampling was not evenly spread across the Barrow catchment area described above. Instead sampling sites, which were chosen on criteria explained in section 4.1.1, were grouped within three smaller areas as shown in figure 3.1. Castlemitchell is the area located west of Athy in south Co. Kildare, more precisely in the Electoral Divisions (EDs) of Churchtown and Athy Rural. The second area of interest was Ballyroe, also in south Co. Kildare but southeast of Athy, almost entirely in the EDs of Grangemellon and Kilkea. Finally, the third area to be investigated was Oak Park, which is mainly located in north Co. Carlow (ED of Carlow Rural, north of Carlow town), but also overlaps on its northeast side with south Co. Kildare (ED of Ballaghmoon). In the case of the latter area, detailed monitoring work was undertaken in Oak Park Research Centre (Oak Park RC), which is the national centre for arable crop research owned by Teagasc and located at the centre of the Oak Park area. The sampled wells are fully described in section 3.4.

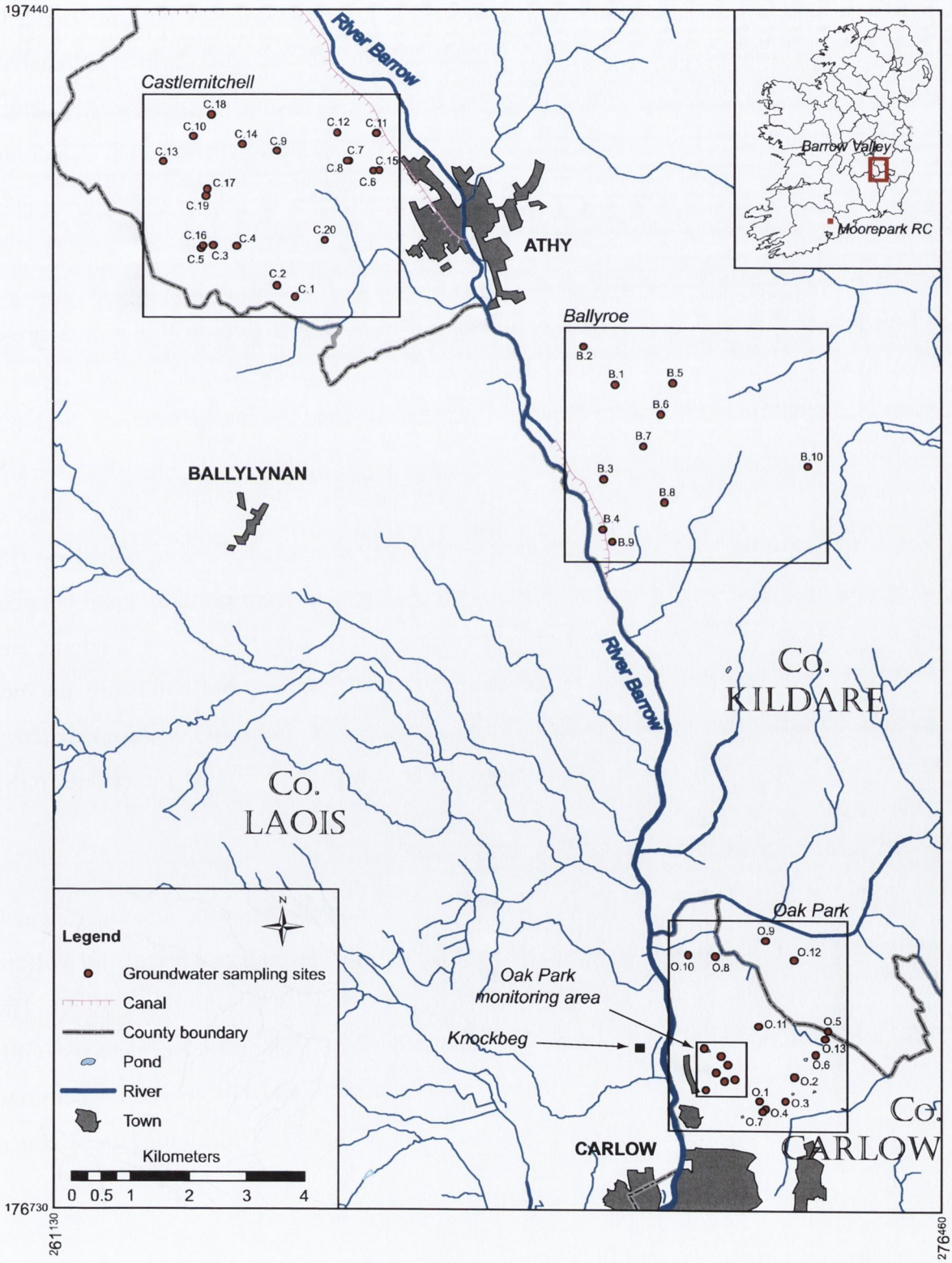
In the Barrow Valley, soil-water sampling was carried out at the Knockbeg site, which is located northwest of Carlow town in County Laois, almost facing Oak Park RC on the right bank of the River Barrow (figure 3.1). Soil-water was also collected from Oak Park RC soils that had been transported to Johnstown Castle (Wexford) as monolith lysimeters. Full description of both sites is given in section 3.3.

- Moorepark RC

The other area sampled for both soil-water and groundwater was Curtin's farm, a 52 ha Teagasc experimental dairy farm owned and managed by Moorepark Research Centre in north Co. Cork (see inset map of Ireland in figure 3.1). Located on a plateau about 2 km north of Fermoy at an altitude of 50 m AOD, it is bounded on the east by the N8 road to Dublin and 1.5 km on the northeast by the River Funshion, towards which elevation slopes

sharply until it reaches about 20 m AOD. The sampled wells are fully described in section 3.4.

Figure 3.1: Location of Moorepark RC and the Barrow Valley study areas (see inset map of Ireland), and detail of the soil-water and groundwater sampling sites in the Barrow Valley (adapted from digital OSI maps, with OSI grid coordinates around the edge).



3.2.2 Bedrock

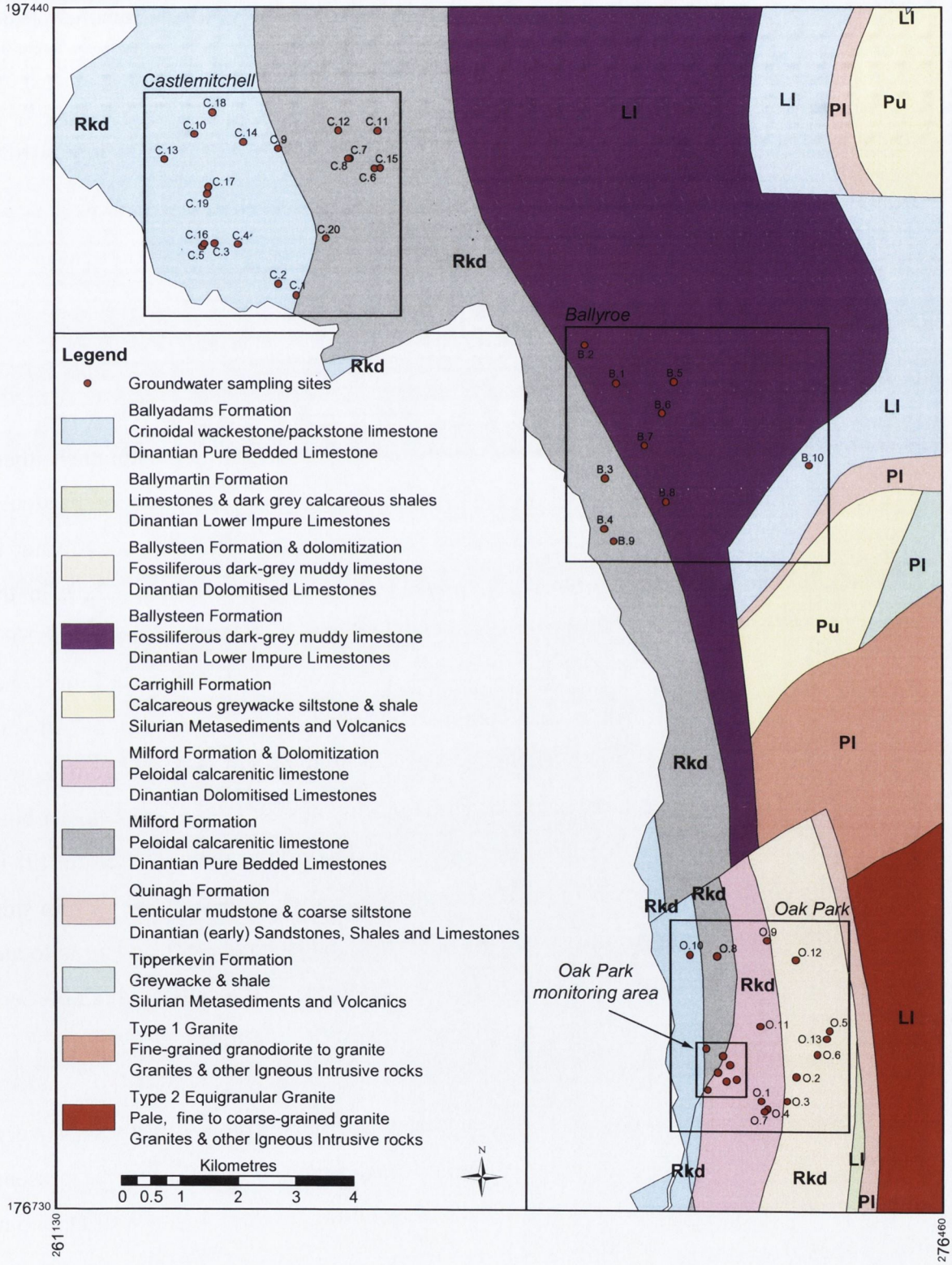
- Barrow Valley

In his description of the Barrow Valley bedrock, which underlies the Quaternary deposits, Daly (1981) referred to the geological structure as follows: 'the Carboniferous strata [at the centre of the valley] dip gently to the west (5-15 °), off the Leinster Granite and under the Castlecomer Plateau'. The Leinster Granite is of Caledonian age and is present extensively to the east of Co. Carlow. Further north, in east Co. Kildare, Silurian rocks (sandstone, greywacke and shale) were reported to form a syncline. Both Silurian and Caledonian rocks, which are considered as aquitards, are located outside groundwater sampling areas and hence are not further described in this thesis.

West of both Silurian and Caledonian, dipping Carboniferous strata of limestones are of Dinantian age. Lying underneath the Quaternary deposits, they account for two types of bedrock aquifer that are further described in section 3.2.5. From east to west, there is a succession of several formations that are displayed in figure 3.2 as identified by GSI mapping (GSI, 2006). The lowest strata, named by Daly (1981) as the Dolomite, consist of Courceyan limestone from the Ballysteen Formation, which has been described by GSI (2006) as fossilised dark-grey muddy limestone. It stretches from north to south between the Silurian and Caledonian rocks and the eastern side of the river's left bank, edging east Athy and including most of Ballyroe and the east side of Oak Park. In Co. Kildare, the rock unit has been categorised as Dinantian Lower Impure Limestones (GSI, 2006), whereas further south in Co. Carlow, it was classified as Dinantian Dolomitised Limestones (GSI, 2006).

Most sampling sites are located further west in Visean shelf limestone and shale, which was named by Daly (1981) as the Upper Limestone. The lowest strata are of the Milford Formation and have been described as peloidal calcarenitic limestone (GSI, 2006). The rock units were categorised as Dinantian Pure Bedded or Dolomitised Limetones (GSI, 2006). Further west, the Ballyadams Formation has been described as crinoidal wackstone and packstone limestone, and the rock unit categorised as Dinantian Pure Bedded Limetones (GSI, 2006).

Figure 3.2: Bedrock in the Barrow Valley sampling areas showing groundwater sampling wells (adapted from GSI (2006), with OSI grid coordinates around the edge) and aquifer classification (Rkd: regionally important karstified bedrock aquifer; LI: locally important bedrock aquifer which is moderately productive only in local zones; PI: poor bedrock aquifer which is generally unproductive except for local zones; Pu: poor bedrock aquifer which is generally unproductive).



- Moorepark RC

The Curtin's farm area is underlain in the middle of the Fermoy syncline by 500 to 700 m of Waulsortian Limestone, whose upper surface is on average 2.5 m bgl (Shearley, 1988). The rock unit is described as pale grey massive unbedded lime-mud stone (Bartley, 2003). Although no karst features have been described by GSI for the area, the drilling of boreholes at Curtin's farm revealed the presence of cavities, many of them gravel filled (Bartley, 2003).

3.2.3 Quaternary deposits

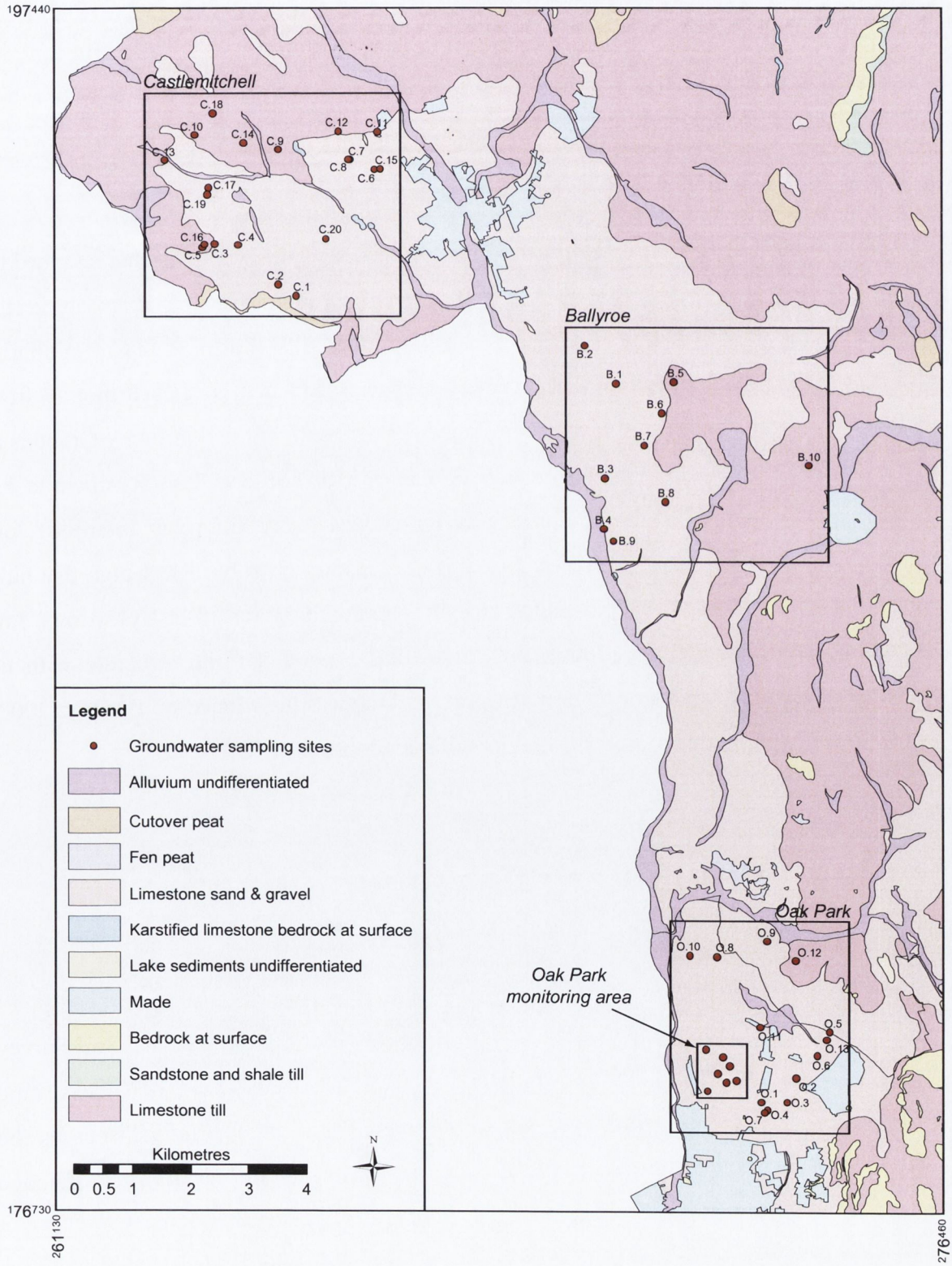
- Barrow Valley

Quaternary deposits are often referred to as subsoil by GSI to distinguish these unconsolidated materials between the topsoil and the bedrock. They are of particular importance in the Barrow Valley because they are largely saturated with groundwater to form very productive aquifers (this point is further developed in section 3.2.5). In the sampling areas of Castlemitchell, Ballyroe and Oak Park, the subsoil identified by the EPA (2006) consists mainly of sand and gravel derived from Lower Carboniferous Limestone, as shown in figure 3.3, which occurs continuously from the surroundings of Athy to Carlow town, and stretches south along the Barrow Valley. Till derived from Lower Carboniferous Limestone replaces sand and gravel to the north of Athy and also on both sides of the valley to the west and to the east down to Carlow town. Therefore, till is present in the north and west part of the Castlemitchell area while it edges the eastern side of the Ballyroe area and the northeast side of Oak Park. Undifferentiated alluvium is found in the immediate proximity of the river bed at the very centre of the valley, which borders the east and south of Castlemitchell area, and also the west of Ballyroe.

Early investigations by Daly (1981) showed that Quaternary deposit thickness is very variable but can be up to 25 m. Information collected from land owners in the present study, and displayed in table 3.5, confirms this with solid rock at 21 m bgl at well O.12 but only 3 m bgl at well C.2. In addition, eighteen of the fifty-one wells sampled during this project, whose known depths range from 5 to 18 m bgl, did not reach the bedrock and were entirely drilled within the unconsolidated deposits. The individual sand and gravel unit, which is usually very coarse, can be up to 10 m thick at Oak Park and thins considerably

when moving south of Carlow town (Daly, 1981). But in general, the Quaternary deposits consist of interbedded sands and gravels, sands and clays, with frequent clays or tills above and below the individual sand and gravel units.

Figure 3.3: Quaternary deposits in the Barrow Valley sampling areas, showing groundwater sampling wells (adapted from EPA (2006), with OSI grid coordinates around the edge).



Considerable lateral and vertical variation was also reported and observed when monitoring boreholes were drilled in 2002 at Oak Park RC by Minerex Environmental Ltd. Borehole logs in Appendix 1 showed the succession of the following layers in various order:

- slightly to very sandy and/or gravelly clay (soft to firm)
- fine to coarse sandy/clayey gravel
- fine to medium grained clayey/ gravelly sand
- occasional presence of sandy silt with clay and limestone cobbles

- Moorepark RC

The situation at Curtin's farm is typical of the north Cork region, which is characterised by a thin layer of glacial deposits, seldom more than three to four metres thick above the bedrock, as reported by Bartley (2003). In their description of soil profiles at Curtin's farm, Gibbons *et al.* (2006) referred more precisely to glacial drift that is derived mainly from Old Red Sandstone and Carboniferous limestone. The subsoil was classified by Gibbons *et al.* (2006) as a free-draining gravelly sandy silt (sandy loam) of low plasticity down to 1.5 m depth, underlain by a free-draining gravelly clayey sandy silt (clay loam) of low plasticity down to about 3.0 m depth. Beneath the topsoil, the subsoil has high dry bulk density, low porosity and a field-saturated hydraulic conductivity of 160-1130 mm/day. According to Gibbons *et al.* (2006), the subsoil has a good uniform structure with no evidence of fissures, cracks or other macropores, which was questioned by Bartley (2003) whose tracer experiments provided evidences of macropores.

3.2.4 Soils

- Barrow Valley

Soils from County Carlow and County Kildare were classified for the National Soil Survey of Ireland in the 1960's and 1970's (Conry and Ryan, 1967; Conry *et al.*, 1970) according to Great Soil Groups and subcategorised soils series. This section briefly discusses the main soil series found in the Barrow study area and provides an indication of drainage capacities.

West and southeast of Athy (i.e. Castlemitchell and Ballyroe areas), soils are mainly of the Fontstown series, which occupies almost 17 % of County Kildare, mainly in the south, but is absent from County Carlow. The parent material consists of calcareous, non-tenacious, compact stony till, composed almost entirely of limestone, with small pockets of loose gravelly material that are commonly observed in profile sections. These soils, classified as Grey Brown Podzolic, are moderately deep to shallow, well drained, and of sandy loam to loam texture.

The second most important series encountered is the Athy complex series, which occupies 6.5 % of County Kildare, mainly in its southern part below Athy, and almost a tenth of County Carlow, almost exclusively in the Barrow Valley. The western part of the Ballyroe area on the left bank of the River Barrow is covered with this soil complex, along with most of the Oak Park area, which is located further south, just north of Carlow town. The parent material consists of calcareous, fluvioglacial coarse gravels and sands, composed mainly of limestone with a small proportion of sandstone, schist, shale and even conglomerate. Four major soils have been recognised within the Athy complex:

- The moderately deep component, classified as Grey Brown Podzolic, is the most common soil of the series and is described as well-drained, friable to gravelly sandy loam.
- The shallow component, classified as Brown Earth, is described as excessively drained, of stony or gravely coarse sandy loam texture (see Oak Park soil lysimeters experiments in section 3.3.3).
- Imperfectly drained component, classified as Brown Earth with gleying, is of sandy loam texture and is generally found on flattish low-lying areas.
- Poorly drained component, classified as Gleys, is of sandy loam texture and is found on the lowest portions of the topography where the water-table is permanently high.

Third according to surface coverage within the sampling areas, the Mortarstown series occurs in a few large isolated pockets in the Fontstown series on the north side of the Castlemitchell area (i.e. west of Athy), and in the Athy complex series on the north side of Oak Park RC (i.e. north of Carlow). It barely covers 3 % of County Kildare and 0.4 % of County Carlow. The parent material consists of relatively fine-textured, compact but non-tenacious, calcareous, glacial till composed mainly of limestone. These soils, classified as Grey Brown Podzolic, are deep, well drained and of loam to clay loam texture.

Soils of the Knockbeg series are present where the Knockbeg experimental plots were set up across the River Barrow from Oak Park RC. It covers less than 5 % of County Laois. The parent material is mixed glacial till of predominantly limestone composition with an admixture of sandstone and shale. These soils, classified as Grey Brown Podzolic, are moderately deep to deep, well drained and of loam to clay loam texture (i.e. medium to heavy texture). Further details of soil profiles at Knockbeg are available from Hooker (2005).

- Moorepark RC

There are no detailed soil-maps for the north Cork area. But according to the General Soil Map of Ireland (Gardiner and Radford, 1980), the soil at Curtin's farm is described as an acid Brown Earth dominated association with 70 % acid Brown Earth derived from mixed sandstone and limestone till, and 30 % Grey Brown Podzolic. In their description of soil profiles at Curtin's farm, Gibbons *et al.* (2006) referred to soil 0.3m to 0.4 m deep, consisting mainly of brown to dark brown loam, which is a typical texture for a Brown Earth. These soils are associated with good drainage, which was confirmed by field measurements that revealed a 250 mm/day surface infiltration capacity.

3.2.5 Hydrogeology and groundwater vulnerability

- Barrow Valley

There are three aquifers in the Barrow Valley sampling areas. Research in this thesis primarily focuses on the aquifer that consists of Quaternary deposits (sand/gravel, see section 3.2.3), in which many shallow sampled wells have been drilled. The surface area of the sand and gravel aquifer, which has been classified as regionally important, was originally reported by Daly (1981) to be of 60 km^2, but this figure should be considered an underestimate since Daly restricted the aquifer boundaries to 10 km north and 16 km south of Carlow town on a strip of land no wider than 3.5 km. But figure 3.3 (EPA, 2006) shows that the unconsolidated deposits stretch at least up to the north of Athy. Underneath the unconsolidated layer, the second most important aquifer sampled during this project consists of the karstified limestone of Dinantian age, which is classified as regionally important (Rkd) in figure 3.2 and consists of Daly's Upper Limestone (i.e. Milford and

Ballyadams Formations classified as Rkd in figure 3.2) and the Carlow part of Daly's Dolomite (i.e. the part of Ballysteen Formation classified as Rkd in figure 3.2). This aquifer has probably been reached by some deep wells of Castlemitchell and Oak Park, and extends to the west of the River Barrow left bank from north to south of the study area. Finally, the third aquifer is the Dinantian Lower Impure Limestone, which is classified as locally important (LI) in figure 3.2. It consists of the Kildare part of Daly's Dolomite (i.e. the part of Ballysteen Formation classified as LI in figure 3.2), in which some deep wells in the east Ballyroe area may have been drilled.

In his geological picture of the Barrow Valley, Daly (1981) also referred to the presence of three aquifers, but did not differentiate between the different formations of the Courceyan limestone (Kildare and Carlow parts of the Dolomite). Hydrogeological characteristics of the whole area were described as follows:

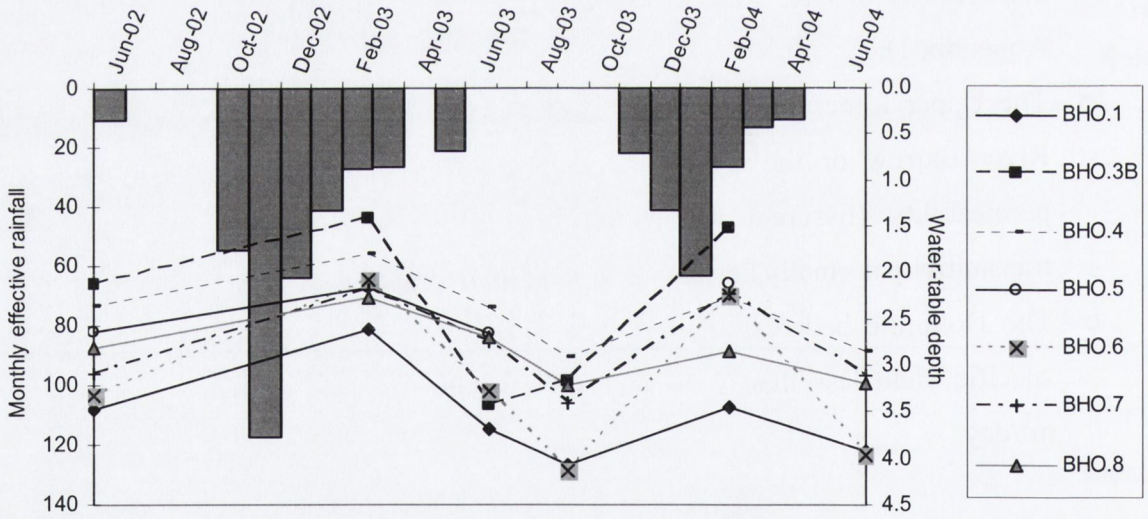
- The shallow sand and gravel aquifer, with intergranular permeability, specific yield of 5-10 % and transmitivity usually ranging from 200 to 2000 m^2/day (hydraulic conductivity at Oak Park RC reported between 1.31×10^{-7} and 6.18×10^{-6} m/s in Appendix 1).
- The Upper Limestone karstified aquifer in the parts that are in contact with the River Barrow or the sand and gravel aquifer, with well-developed secondary permeability (fissures) within the first 20 m, specific yield of 2-4 % and transmitivity normally between 200 and 500 m^2/day.
- The Dolomite bedrock aquifer, with deep primary and secondary permeability, specific yield less than 2 % and transmitivity that ranges between 20 and 200 m^2/day.

Generally speaking, the sand and gravel aquifer is largely unconfined, although confined conditions may be created by local topographic features, depending on the nature of the deposit (Daly, 1981), and underneath the alluvial flats of the flood plain in the vicinity of the river bed.

In the region as a whole, groundwater in the Quaternary deposits flows to the south and also towards the River Barrow (Daly, 1981). In the proximity of Athy and Carlow, large abstraction rates of groundwater are expected to generate large cones of depression that cause water to flow towards the towns. But in general, groundwater movement is expected to be slow due to the relatively even and gentle topography. The flow regime in the

bedrock aquifers under natural non-pumping conditions may be severely restricted because there is less (or no) natural discharge down dip (Daly, 1981). However, some movement may occur at the interface with the Quaternary deposits and the River Barrow. According to Daly (1981), the water-table depth in the Barrow Valley is within 7 m below ground level (bgl). In the Oak Park monitoring area, it was measured on six occasions between the drilling of boreholes on early June 2002 and the final sampling event in late June 2004. Results for the seven shallow boreholes are plotted in figure 3.4, which also displays for the same period monthly effective rainfall (definition in section 3.2.6, equation 3.1) that was calculated by Kirsty Hooker from TCD Met Oak Park data. Borehole BHO.5 went dry on two occasions during summer 2003 and 2004 (water-table was below the bottom of the borehole at 4.5 m), and BHO.3B could not be sampled on the last field trip for technical reasons, which explains why three measurements are missing.

Figure 3.4: Water-table depth measured at the Oak Park monitoring area between July 2002 and July 2004 and associated monthly effective rainfall. *(monthly effective rainfall is reported in mm/month, water-table depth in m bgl)*



The water-table was measured at between 4.1 m bgl (at its deepest) and 1.4 m bgl (at its shallowest) during sampling, the highest seasonal fluctuation being of 2.1 m at borehole BHO.6. According to the geological and hydrogeological conditions governing vulnerability mapping (previously discussed in section 2.1.5) and considering that most of the groundwater body is unconfined underneath a permeable unsaturated zone, the sand and gravel aquifer of the Barrow Valley is classified as extremely vulnerable to contamination (including nitrate leaching) depending on whether the unsaturated zone is less than 3 m thick. If the unsaturated zone is thicker than 3 m thick, the aquifer can be classified as highly vulnerable.

Water-table levels appeared to be very responsive to effective rainfall, which is not surprising considering the permeability of the area's soils. The highest piezometric levels were recorded during winter months after effective rainfall recharged the aquifer. Again, this reflects the permeability of the area's soils.

- Moorepark RC

The limestone bedrock aquifer underneath Curtin's farm was described by Bartley (2003) as karstified with collapsed structures and cavities filled with sand. Reported hydraulic conductivity was measured between 10^{-8} and 10^{-6} m/s. The water-table was found to be about 20 m bgl in winter and 29 m bgl in summer, and overall dipped northeast towards the River Funshion, which confirmed that groundwater was draining into the river. The aquifer has been classed as regionally important. The predominant sand content of the subsoil referred to earlier aids rapid infiltration to bedrock. In some areas, the bedrock may be an impermeable monolithic unit that water can only penetrate when it encounters fissuring to move downward (Bartley, 2003). Nonetheless, the very permeable nature of the thin Quaternary deposits qualifies the aquifer as extremely vulnerable, depending on whether the Quaternary deposit thickness is below 3 m.

3.2.6 Climate and groundwater recharge

- Barrow Valley

Generally speaking, southeast Ireland, like the rest of the country, enjoys a temperate maritime climate. Winters are generally cool and rainy, while summers are warm with lower rainfalls. For the period 1961-1990, the mean daily temperature recorded at the Kilkenny station, 30 km southwest to Carlow town, ranged between 4.6 °C for January and 15.2 °C for July. At the same station, the monthly rainfalls ranged between 50.5 mm in June and increased to its maximum in December with 88.6 mm, the annual average being of 822.8 mm. Within the Barrow study area is the TCD Met Oak Park weather station, from which meteorological data were used to estimate drainage since 2001. In the water balance at the soil surface, the amount of water available for percolation is called effective rainfall and it can be determined from the following simplified equation:

Effective rainfall = rainfall - evapotranspiration - surface runoff (Equation 3.1)

If surface runoff is negligible, which is usual on flat and relatively free-draining areas such the majority of the Barrow Valley and Moorepark RC, effective rainfall accounts for the difference between rainfall and evapotranspiration. Evapotranspiration can be estimated with a modified Penman-Monteith equation (FAO, 1998) that takes into account rainfall, wind speed, air temperature, irradiance and soil drainage type. Such calculations were carried out by Kirsty Hooker who applied a simulator model developed by Schulte *et al.* (2005) to Oak Park data. Groundwater recharge (or effective drainage) is the defined as the effective rainfall moving vertically minus any water moving laterally. Effective rainfall is then the maximum potential recharge, which generally corresponds to the recharge in a flat and free-draining area like the Barrow Valley (see topography in section 3.2.1, subsoil in section 3.2.3 and soil in section 3.2.4).

Figure 3.5: Monthly precipitation, monthly effective rainfall and daily air temperature at TCD Met weather station in Oak Park Research Centre between February 2002 and June 2004. *(precipitation and effective rainfall are reported in mm/month, temperature in °C/day)*

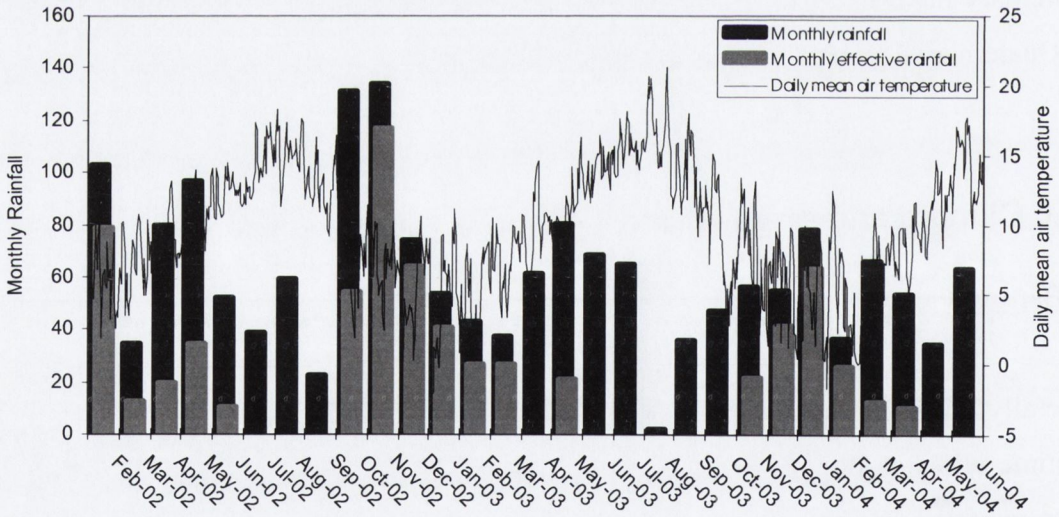
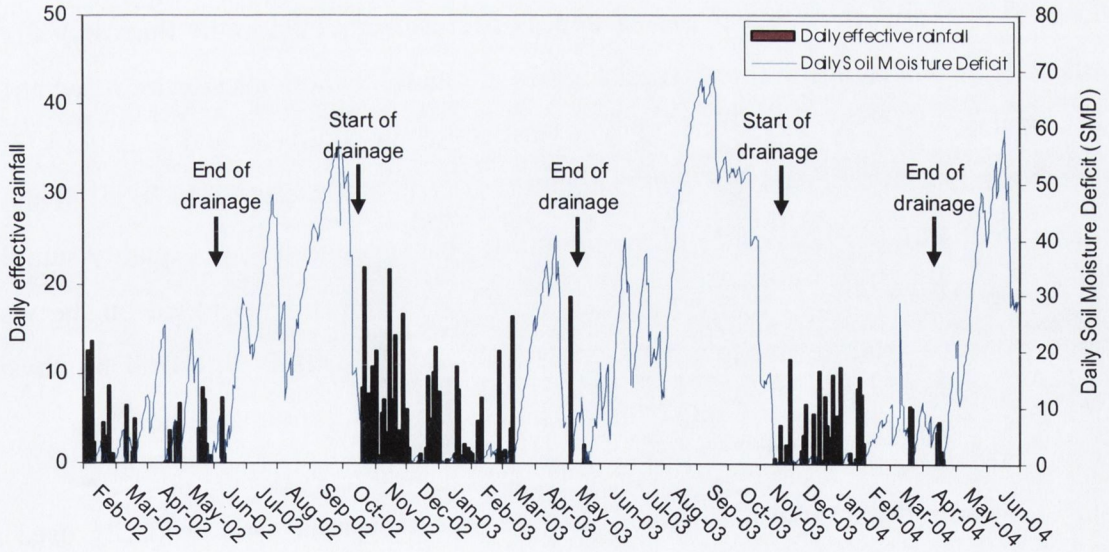


Figure 3.5 displays monthly precipitation along with calculated monthly effective rainfall and daily air temperature at Oak Park RC between February 2002 and July 2004. It can be seen that the amount of rainfall that infiltrates is deeply influenced by seasons. In 2002 and 2003, recharge was estimated as nil during summer months of July, August and September, despite some precipitation. Recharge occurred during late autumn and winter months according to the model, with a peak of 117 mm effective rainfall for November 2002. Variations also appear between years, 2003 being far drier than 2002 and 2004. Calculated effective rainfall for the year 2003 was only of 179 mm (606 mm precipitation), whereas it

was of 464 mm for the year 2002 (917 mm precipitation) and 324 mm for the year 2004 (753 mm precipitation) - in line with the findings of Daly (1981). Temperature also followed a seasonal pattern with minimum and maximum temperatures around January and August respectively (lowest and highest means daily measured at -2.2 and 21.3 °C respectively).

Figure 3.6 displays in some detail calculated daily effective rainfall and daily soil moisture deficit (SMD). The model described a similar pattern every year with drainage starting during autumn and stopping towards the end of spring. During summer months, SMD is positive, which results in soil-water being retained in soil pores and not percolating downward. In 2002, the model estimates that drainage stopped on 10th June before it started again on 20th October, conditions during this year being wetter than during the following years. In 2003, the model estimates that drainage stopped on 17th May and started again on 19th November. In 2004, the model estimates that drainage stopped on 20th April 2004.

Figure 3.6: Calculated daily drainage and soil moisture deficit (SMD) at Oak Park RC between February 2002 and June 2004, using a model developed by Schulte *et al.* (2006). *(drainage is reported in mm/day, and SMD in mm)*



Because percolating water can transport chemical species like nitrate through the unsaturated zone, the occurrence of drainage is closely associated with the occurrence of nitrate leaching and groundwater contamination if there is any nitrate available in soils. Soil moisture deficit was calculated continuously positive from late spring to early autumn,

hence the likely absence of nitrate leaching at this time of the year. Conversely, soil moisture deficit was nil from late autumn to late spring, implying drainage and possible nitrate leaching, depending on nitrate availability.

- Moorepark RC

At Moorepark weather station, rainfall was recorded along with the other parameters used for the calculation of effective rainfall by the same methods as at Oak Park RC. For the period 2000-2003, Bartley (2003) reported annual rainfall between 995 and 1163 mm. When comparing times at which drainage is predicted to start, a similar pattern with Oak Park was observed by Bartley (2003), with recharge occurring during winter times from October to May or June of the following year. Effective rainfall per year was estimated to range between 464 and 679 mm during this three-year period.

3.2.7 Land use and housing

- Barrow Valley

Except for two golf courses and a few patches of forest, rural land in the Barrow Valley is entirely dedicated to farming activities. Figures 3.7 and 3.8 show a snapshot of what land use was in 1989-1990 and 1995-1996 in Castlemitchell, Ballyroe and Oak Park areas (CORINE Land Cover maps CLC 1990 and CLC 2000 respectively: EPA, 2006). It should be noted that CLCL 1990 relates to the period of previous groundwater quality sampling (Coxon and Thorn, 1991). CORINE maps, whose development was based on the visual interpretation of satellite imagery and aerial photography, identify up to 44 biophysical land cover classes, with a minimum mapping unit of 1-5 ha depending on the class.

In the Barrow Valley sampling areas, it can be seen that soils were primarily used for tillage, and also, to a lesser extent, for grassland. Despite some changes over time between 1989-1990 and 1995-1996, Castlemitchell had the highest tillage to grassland ratio, followed in decreasing order by Ballyroe and Oak Park, most tillage of the latter area being in fact located in the Oak Park monitoring area (which is located in the west part of Oak Park RC). Calculations within each sampling area gave the following results (as percentage

of total area delineated by dashed lines, which were drawn around the outer sites with a buffer zone of 300 m):

- Castlemitchell area: 94 % tillage and 6 % grassland in CLC 1990, 57 % tillage and 41 % grassland in CLC 2000.
- Ballyroe area: 63 % tillage and 32 % grassland in CLC 1990, 62 % tillage and 33 % grassland in CLC 2000.
- Oak Park area: 54 % tillage and 33 % grassland in CLC 1990, 59 % tillage and 27 % grassland in CLC 2000.

The drastic decrease in tillage and associated increase in grassland observed in the Castlemitchell area between 1989-1990 (figure 3.7) and 1995-1996 (figure 3.8) appears in fact to reflect a mistake arising from satellite imagery interpretation. According to the local Teagasc Crop Advisor Officer (Hugh McCreevy, Teagasc Crop Advisor Officer, personal communication), most of the Castlemitchell area was used for tillage in 1995-1996, and crop-rotation systems rarely included grass. There is then a possibility that young crops were misclassification as grass. Meanwhile, recent field observations carried out during sampling events confirmed that only a few small unconnected pockets of grass remain in the Castlemitchell area, which was already observed in 1989-1990 (figure 3.7). Most sampled wells were found to be in tillage between 2002 and 2004. This is highlighted in table 3.6 (section 3.4.2), which give details on the percentage of tillage within 300 m around each site.

Figure 3.7: Land use in Castlemitchell, Ballyroe and Oak Park areas in 1989-1990 (adapted from CLC 1990 map (EPA, 2006), with OSI grid coordinates around the edge). (*percentage of tillage and grassland was calculated within areas delineated by dashed lines*)

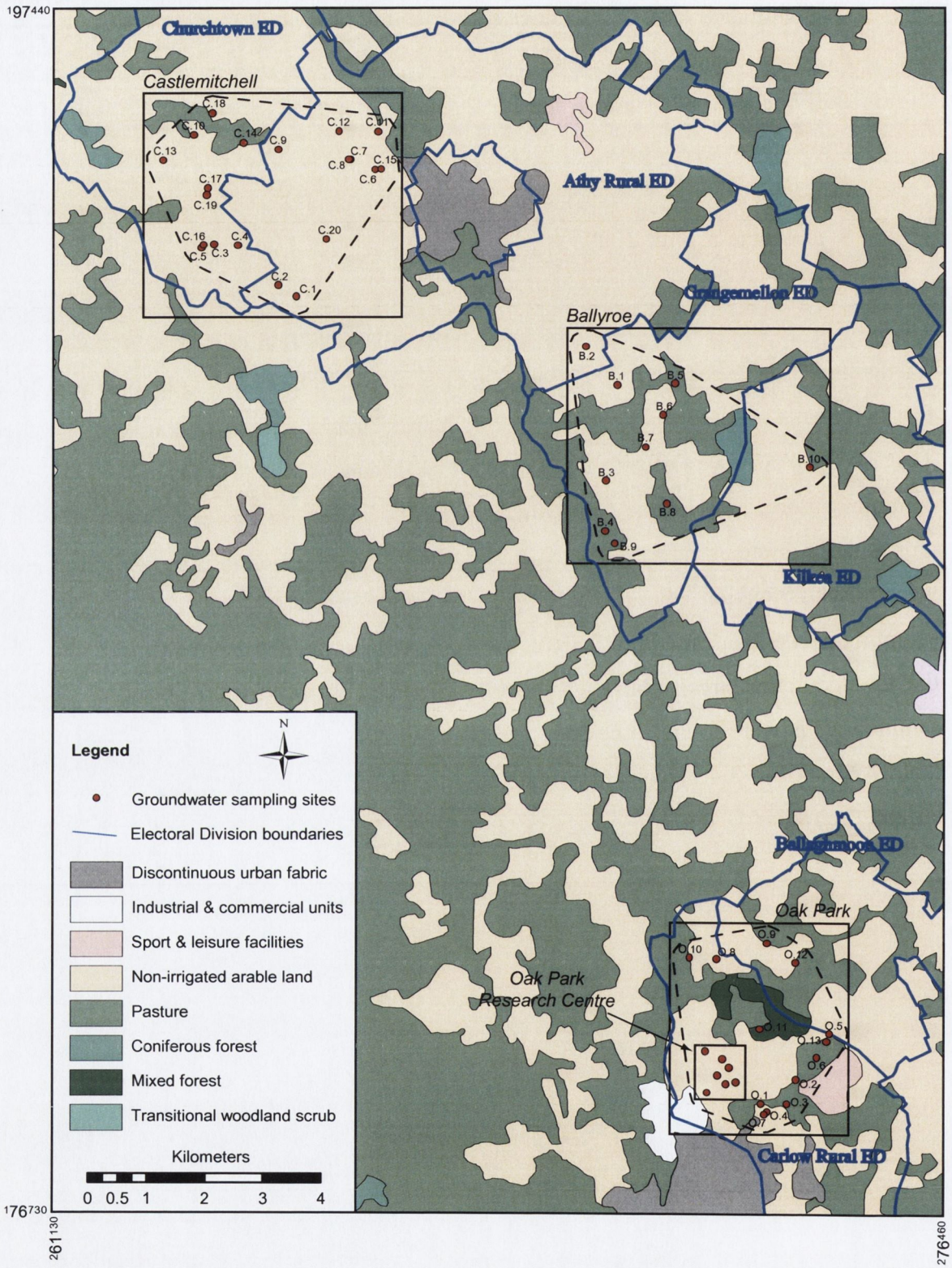


Figure 3.8: Land use in Castlemitchell, Ballyroe and Oak Park areas in 1995-1996 (adapted from CLC 2000 map (EPA, 2006), with OSI grid coordinates around the edge). (*percentage of tillage and grassland was calculated within areas delineated by dashed lines*)

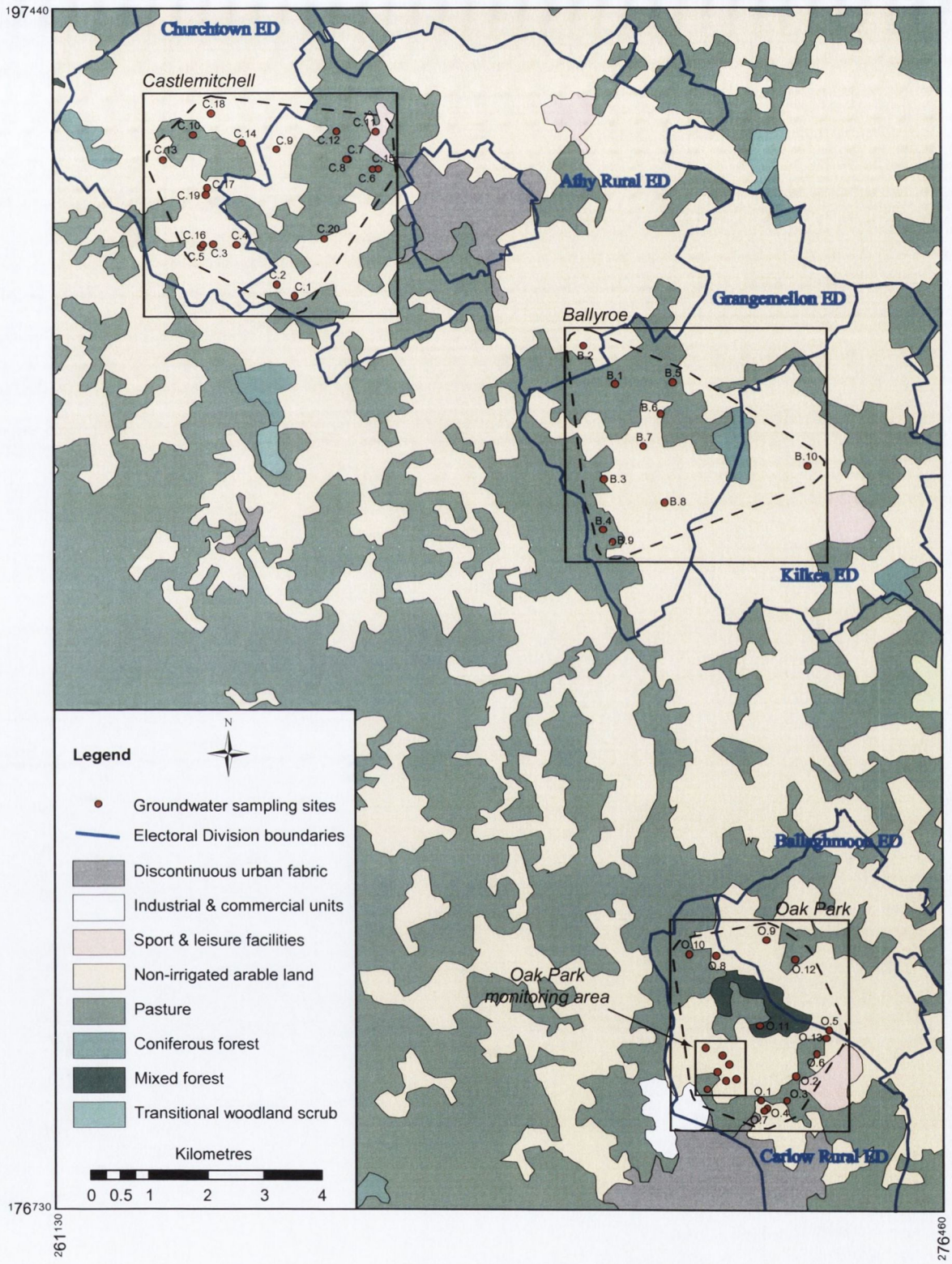


Table 3.1 details the agricultural activities recorded by Central Statistics Office (CSO) in year 2000 (CSO, 2002) in the six EDs covering the three study areas (see ED boundaries in figures 3.7 & 3.8). Predictably, most farms were specialised in tillage, and more precisely

in the production of barley and wheat. The percentage of the total area farmed dedicated to cereals (barley, wheat and oats) ranged between 49 % and 55 % in the first five EDs of table 3.1, which cover Castlemitchell, Ballyroe and the north-east of Oak Park. But this percentage fell down to 33 % in Carlow Rural ED, which covers most of the Oak Park area. Sugar beet was also an important crop, which accounted for 10 % of the total area farmed in the Churchtown ED (Castlemitchell area), but was marginally present in the Oak Park area. Most farmers in this area usually operate 3-year crop-rotation systems. For instance, sugar beet may be followed by winter wheat, and then winter or spring barley (Hugh McCreevy, Teagasc Crop Advisor Officer, personal communication). Conversely, the total grassland area used for pasture, hay or silage was 53 % of the total area in Carlow rural ED, whereas it ranged between 31 % and 37 % in the other five EDs. This confirms the pattern indicated in figures 3.7 and 3.8. Many farms also housed livestock, and more precisely cattle and sheep. In EDs covering the Castlemitchell and Oak Park areas, the average number of cattle per farm was low, ranging between thirty and forty, whereas figures were almost twice as high in both EDs of the Ballyroe area.

Table 3.1: Characteristics of farming activities in 2000 in Electoral Divisions that cover Castlemitchell, Ballyroe and Oak Park groundwater sampling areas (adapted from CSO (2002)).

Farming characteristics	Castlemitchell area		Ballyroe area		Oak Park area	
	Churchtown	Athy Rural	Grangemellon	Kilkea	Ballaghmoon	Carlow Rural
Number of specialised farms by type of farm						
Specialist tillage	20	30	10	10	10	10
Specialist beef production	0	10	0	10	0	10
Mixed grazing livestock	0	10	0	0	0	0
Mixed crops and livestock	10	10	10	0	0	10
Total	35	55	20	17	14	36
Area farmed (ha) by type of crop						
Total area farmed	1,892	2,732	1,997	1,148	694	1,436
Total wheat	311	445	570	316	149	70
Total oats	2	ND	ND	ND	ND	ND
Total barley	659	1,050	456	238	208	395
Total cereals	972	1,510	1,105	566	367	477
Other non-cereal crops	65	ND	ND	43	24	ND
Total crops, fruit & horticulture	ND	1,854	ND	ND	462	668
Total hay	165	267	179	72	33	72
Total pasture	360	411	282	227	103	418
Total silage	85	169	188	130	96	277
Rough grazing in use	ND	32	ND	ND	0	1
Potatoes	0	ND	ND	0	0	ND
Sugar Beet	180	135	ND	ND	44	83
Number of livestock by type of livestock						
Total cattle	1,109	1,559	1,447	827	544	1,419
Total sheep	ND	896	ND	ND	ND	1,959

ND Not Determined

Outside the town areas of Athy and Carlow, the Barrow Valley is characterised by a low density of population and dwellings scattered in agricultural lands, similar to other rural

regions of Ireland. Table 3.2 displays figures for the six EDs that cover Castlemitchell, Ballyroe and Oak Park groundwater sampling areas. Results, which were calculated from the Census 1996 and 2002 data (CSO, 2003), reveal that the density of population ranged between 20 and 32 persons/km^2 in five out of the six EDs of interest. In the Carlow Rural ED though, the density was much higher, reflecting the large urban population living north of Carlow town, at the edge of the Oak Park area.

Table 3.2: Number of persons and density of population in 1996 and 2002 in Electoral Divisions covering Castlemitchell, Ballyroe and Oak Park groundwater sampling areas (adapted from CSO (2003)).

	Castlemitchell area		Ballyroe area		Oak Park area	
	Churchtown	Athy Rural	Grangemellon	Kilkea	Ballaghmoon	Carlow Rural
Surface area (km^2)	18.7	28.6	18.4	18.2	10.9	18.0
Persons (Census 1996)	453	821	525	426	204	3,146
Persons (Census 2002)	472	904	547	369	222	4,685
Density 1996 (pers/km^2)	24	29	29	23	19	175
Density 2002 (pers/km^2)	25	32	30	20	20	260

Typically, rural dwellings are not connected to a public sewerage system for the treatment of domestic waste effluents. Table 3.3 shows the percentage of houses with individual septic tank systems in rural Mid-East and South-East, i.e. regions which Co. Kildare and Co. Carlow are respectively part of. Figures calculated from the Census 2002 data (CSO, 2004) reveal that 75 % of rural houses have their own on-site wastewater treatment unit, which contrasts with the 2 % calculated for town houses of the same regions. Rural houses grouped within estates may also be connected to some communal septic tank systems. Further details of the study area in relation to the number of unsewered houses within 100 m and 300 m around each of the fifty-one sampled wells are then given in table 3.6 (section 3.4.2).

Table 3.3: Number of private dwellings by type of sewerage facilities in the Aggregate Rural and Town Areas [1] of Mid-East and South-East regions (adapted from CSO (2004)).

Type of sewerage facility	Aggregate rural areas [1]		Aggregate town areas [1]	
	Mid-East [2]	South-East [3]	Mid-East [2]	South-East [3]
Total dwellings	53,192	75,803	74,357	61,835
Public scheme	11,064	15,417	70,139	57,423
Individual septic tank	39,797	57,330	2,308	2,561
Other	925	1,180	239	233
No sewerage facility	441	840	33	53
Not stated	965	1,036	1,638	1,565
% dwellings with individual septic tanks	75%	76%	3%	4%

1) Aggregate Town Areas are clusters of 1,500 or more inhabitants, while Aggregate Rural Areas are all areas outside these clusters
2) Mid-East is defined as Counties of Kildare, Meath and Wicklow
3) South-East is defined as Counties of Carlow, Kilkenny, Tipperary South, Waterford, and Wexford

- Moorepark RC

The farm consists of 52 hectares entirely in long-term permanent grassland, where one hundred and seventeen dairy cows (stocking rate of 2.25 LU/ha) graze during the summer and are housed during the winter (Gibbons *et al.*, 2006). Cattle housing and organic-waste storage facilities are centrally located. There is also a septic tank serving six people on the farm (see section 3.4.3 for further details).

3.3 Description of the soil-water sampling sites

3.3.1 Moorepark RC experimental plots

Most soil-water sampling took place at Curtin's farm in Moorepark RC, where ceramic suction cups were used to sample the unsaturated zone of nine grassland experimental plots set up in May 2001 for EPA ERTDI Project No. LS 2.3.2 (Gibbons *et al.*, 2006). The following treatments were studied:

- Artificial fertiliser application at high rate (387 kg N/ha/year), medium rate (286 kg N/ha/year) and low rate (174 kg N/ha/year).
- Dairy wastewater application at high rate (50 mm/year) and medium rate (25 mm/year)
- Slurry application at high rate (4.5 mm/year), medium rate (3 mm/year) and low rate (1.5 mm/year)
- Control plot (no N application).

Application times for each treatment are displayed in table 3.4 for the year 2002 and were kept the same every year by Teagasc staff. Because total nitrogen content in dairy wastewater was measured at 257 and 430 mg/l TN in May 2003 and November 2001 respectively (Gibbons *et al.*, 2006), and considering the volumes applied, it is thus estimated that during experiments, high and medium application rates of dairy wastewater were around 343 kg N/ha/year and 171 kg N/ha/year respectively. Similarly, based on a total nitrogen content in slurry of 3548 mg/l N measured in March 2002, the high rate of slurry application was calculated at 160 kg N/ha/year, the medium rate around 105 kg N/ha/year and the low rate around 53 kg N/ha/year. In addition, grass was removed once a year around April. It should be noted that TN values in slurry and dairy wastewater agreed with values given for cattle slurry and soiled water in table 2.6 (section 2.3.3).

Table 3.4: Application of artificial fertiliser, dairy wastewater and slurry on Moorepark plots for year 2002 (adapted from Gibbons *et al.* (2006)).

Application date	Fertilisation type	High rate	Medium rate	Low rate
FERTILISER PLOTS				
21-Jan-02	Urea	67.2 kg N/ha	49.7 kg N/ha	30.2 kg N/ha
17-Apr-02	CAN	45.7 kg N/ha	33.8 kg N/ha	20.6 kg N/ha
08-May-02	CAN	45.7 kg N/ha	33.8 kg N/ha	20.6 kg N/ha
01-Jun-02	CAN	45.7 kg N/ha	33.8 kg N/ha	20.6 kg N/ha
29-Jun-02	CAN	45.7 kg N/ha	33.8 kg N/ha	20.6 kg N/ha
30-Jul-02	CAN	45.7 kg N/ha	33.8 kg N/ha	20.6 kg N/ha
21-Aug-02	CAN	45.7 kg N/ha	33.8 kg N/ha	20.6 kg N/ha
16-Sep-02	CAN	45.7 kg N/ha	33.8 kg N/ha	20.6 kg N/ha
TOTAL FOR 2002		387 kg N/ha	286 kg N/ha	174 kg N/ha
DAIRY WASTEWATER PLOTS				
05-May-02	Dirty water	50 mm ($500\ m^3/ha$)	25 mm ($250\ m^3/ha$)	
24-Nov-02	Dirty water	50 mm ($500\ m^3/ha$)	25 mm ($250\ m^3/ha$)	
SLURRY PLOTS				
27-Mar-02	slurry	4.5 mm ($45\ m^3/ha$)	3.0 mm ($30\ m^3/ha$)	1.5 mm ($15\ m^3/ha$)

NB: grass harvested from all plots once a year in April

Figure 3.9 below shows a sketch of the treatment plots, how they were situated in relation to one another, and the number of suction cups installed within them. Plots were 8 × 8 m and separated from each other by a 3 m wide buffer strip. Each plot was instrumented with shallow and deep suction cups which were sometimes replicated. Shallow soil-water, i.e. down to 1.5 m, was collected with standard ceramic cups (1900 series, Soil Moisture Equipment Corporation, USA), whereas greater depths, i.e. down to 3.0 m, were investigated with pressure-vacuum cups (1920 series, Soil Moisture Equipment Corporation). It should be noted that before the experiments were set up, the field was located in the grazing only area described in section 3.4.3, and received some organic N at rates described in table 3.10.

Figure 3.9: Distribution of treatment plots at Moorepark RC and replication of ceramic suction cups.

High Dirty Water (HD)	
Depth	*Replicates*
0.9 m	1
1.0 m	1
1.2 m	1
1.5 m	2
2.0 m	3
2.5 m	3
3.0 m	1

High Fertiliser (HF)	
Depth	*Replicates*
0.9 m	1
1.0 m	3
1.2 m	
1.5 m	1
2.0 m	3
2.5 m	3
3.0 m	1

High Slurry (HS)	
Depth	*Replicates*
0.9 m	1
1.0 m	
1.2 m	1
1.5 m	2
2.0 m	1
2.5 m	1
3.0 m	1

Medium Dirty Water (MD)	
Depth	*Replicates*
0.9 m	1
1.0 m	3
1.2 m	1
1.5 m	2
2.0 m	3
2.5 m	3
3.0 m	1

Low Fertiliser (LF)	
Depth	*Replicates*
0.9 m	1
1.0 m	1
1.2 m	1
1.5 m	2
2.0 m	
2.5 m	1
3.0 m	1

Low Slurry (LS)	
Depth	*Replicates*
0.9 m	2
1.0 m	1
1.2 m	1
1.5 m	2
2.0 m	1
2.5 m	1
3.0 m	1

Medium Fertiliser (MF)	
Depth	*Replicates*
0.9 m	1
1.0 m	2
1.2 m	1
1.5 m	2
2.0 m	3
2.5 m	3
3.0 m	1

Medium Slurry (MS)	
Depth	*Replicates*
0.9 m	1
1.0 m	
1.2 m	1
1.5 m	1
2.0 m	1
2.5 m	1
3.0 m	1

Control plot ©	
Depth	*Replicates*
0.9 m	1
1.0 m	
1.2 m	1
1.5 m	1
2.0 m	1
2.5 m	1
3.0 m	1

3.3.2 Knockbeg experimental plots

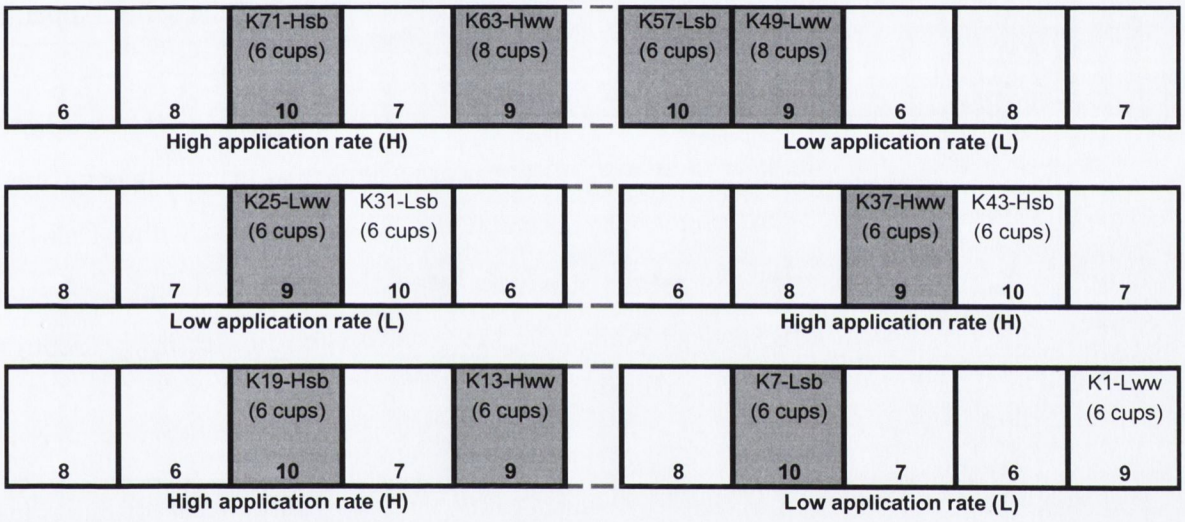
Soil-water samples were also collected from the Knockbeg site, which is situated in the Barrow Valley approximately 1 km west of Oak Park Research Centre, in county Laois. The unsaturated zone was studied with suction cups similar to those of Moorepark that had been set up in 2001 and 2002 for the needs of other projects – including Hooker's (2005) - and maintained by Teagasc staff. Only nine out of twelve tillage plots were successfully sampled, comprised of the following crops and application rates:

- Winter wheat at high artificial fertiliser rate (225 kg N/ha/year as CAN split between March and April), low fertiliser rate (187.5 kg N/ha/year as CAN split between March and April)

- Spring barley at high fertiliser rate (137.5 kg N/ha/year split between March and April as 77.5 kg N/ha/year of Super Net and 60 kg N/ha/year of 18-6-12 NPK compounds), low fertiliser rate (105 kg N/ha/year split between March and April as 45 kg N/ha/year of Super Net and 60 kg N/ha/year of 20-0-15 NPK compounds).

Figure 3.10 shows the spatial distribution of sampled plots with number of cups involved. Each plot was 12 × 30 m and was instrumented with six to eight ceramic suction cups (1900 series, Soil Moisture Equipment Corporation) at a single depth of 1.5 m. The field slopes gently towards the River Barrow (Hooker, 2005).

Figure 3.10: Sketch (not to scale) of Knockbeg soil-water sampling site (adapted from Hooker (2005)).



3.3.3 Oak Park soil lysimeter experiments

Soil-water samples were collected from a third site located in Johnstown Castle (Co. Wexford). It consisted of six outdoor cylindrical, undisturbed Oak Park soil monolith lysimeters, 60 cm diameter by 1 m depth, under perennial ryegrass (Ryan and Fanning, 1996). These soils were referred to by Ryan and Fanning (1996) as Brown Earth from the shallow component of Athy complex (see section 3.2.4). These lysimeters were installed in the early 1990's and are maintained by Teagasc staff. The following treatment and control,

which were triplicated (i.e. six lysimeters in total), were sampled for nitrate leaching investigation:

- High fertiliser rate (350 kg N/ha/year as NH_4NO_3).
- Control lysimeters (i.e. no N application).

3.4 Description of groundwater sampling sites

3.4.1 Well characteristics

- Barrow Valley

Between February 2002 and June 2004, fifty-one wells (OSI grid coordinates in Appendix 7) were sampled on at least one occasion (and generally on more than five occasions) in the Barrow Valley. As shown earlier in figure 3.1, the spatial distribution was as follows: twenty sites were in the Castlemitchell area, thirteen in the Ballyroe area and twenty-one in the Oak Park area, among which eight were research piezometers located within Oak Park RC (see section 3.4.3). Table 3.5 below discloses general information and a physical description for each of these wells in relation to the type of site, the depth, the depth to bedrock and the subsoil material found during drilling.

Most sites were either private farm water supplies (24/51) or domestic wells for individual dwellings (14/51). At five locations, groundwater was collected from groundwater group schemes, which are wells (private or public) that provide more than one houses with drinking water. Finally, eight monitoring boreholes drilled at the edge of tillage fields in Oak Park RC were also part of the sampling programme.

According to data collected in the 1980's (Coxon, unpublished data), private wells differed from each other by their depth, which ranged from very shallow (e.g. C.1 at 6 m bgl) to deep (e.g. C.14 at 90 m bgl). On the other hand, all monitoring boreholes were very shallow (between 5 and 9 mg bgl). Except for eleven wells whose depth could not be determined, fourteen sites were 10 m deep at most, nine were between 10 and 20 m deep, six between 20 and 30 m deep, and the remaining eleven were deeper than 30 m. Depth is an important parameter because it informs on the type of water that is abstracted. In general, shallow water comes from recent recharge, whereas very deep water is older and less likely to be contaminated by anthropogenic N inputs, if the well has been correctly constructed. Depth can also indicate the type of aquifer groundwater originates from: in

accordance with information from section 3.2.3 on Quaternary deposit thickness, shallow wells can only target the sand/gravel aquifer whereas deeper wells sample the underlying bedrock aquifers. In reality, it is likely that groundwater flowing into wells deeper than 25 m originates from both sand/gravel and bedrock aquifers.

Table 3.5: Description of sampling wells in relation to sampling area (CAS for Castlemitchell, BAL for Ballyroe, OAK for Oak Park and OAK RC for Oak Park Research Centre), type of well, depth, depth to bedrock (if applicable), subsoil found during drilling and type of casing (Coxon, unpublished data). *(depths are reported in m bgl)*

Site	Area	Well type	Well depth	Depth to solid rock	Material above rock	Casing
B.1	BAL	farm well	40	ND	sandy	metal
B.2	BAL	farm well	24	9	medium/light	plastic
B.3	BAL	farm well	18	> 18	gravel/sand	metal
B.4	BAL	domestic well	12	> 12	ND	ND
B.5	BAL	farm well	16	ND	sandy	metal
B.6	BAL	groundwater group scheme	33	ND	ND	ND
B.7	BAL	farm well	ND	ND	sandy	ND
B.8	BAL	farm well	7	> 7	sandy	concrete
B.9	BAL	farm well	9	> 9	sandy	ND
B.10	BAL	groundwater group scheme	ND	ND	ND	ND
C.1	CAS	domestic well	6	> 6	sandy	concrete
C.2	CAS	farm well	9	3	gravel/sand	concrete
C.3	CAS	farm well	25	ND	clayey	ND
C.4	CAS	domestic well	ND	ND	ND	ND
C.5	CAS	farm well	9	> 9	sandy	ND
C.6	CAS	domestic well	ND	ND	clayey	ND
C.7	CAS	domestic well	ND	ND	ND	ND
C.8	CAS	domestic well	13	> 13	sandy	concrete
C.9	CAS	farm well	18	8	clayey	stones
C.10	CAS	farm well	51	18	clayey	metal
C.11	CAS	farm well	18	> 18	clayey	metal
C.12	CAS	domestic well	ND	ND	ND	ND
C.13	CAS	farm well	ND	ND	ND	ND
C.14	CAS	farm well	90	ND	clayey	ND
C.15	CAS	domestic well	15	> 15	clayey	ND
C.16	CAS	domestic well	40	ND	sandy	ND
C.17	CAS	farm well	85	ND	sandy	metal
C.18	CAS	groundwater group scheme	19	ND	ND	ND
C.19	CAS	groundwater group scheme	ND	ND	ND	ND
C.20	CAS	groundwater group scheme	ND	ND	ND	ND
O.1	OAK	farm well	37	ND	ND	ND
O.2	OAK	domestic well	15	> 15	sandy	metal
O.3	OAK	farm well	9	ND	ND	metal
O.4	OAK	domestic well	41	ND	sandy	metal
O.5	OAK	domestic well	26	6	sandy	metal
O.6	OAK	domestic well	22	6	ND	ND
O.7	OAK	domestic well	24	ND	ND	ND
O.8	OAK	farm well	34	ND	gravel/sand	metal
O.9	OAK	farm well	23	ND	sandy	metal
O.10	OAK	farm well	37	18	sandy/shalem	ND
O.11	OAK	farm well	ND	ND	ND	ND
O.12	OAK	farm well	52	21	h clayey-boulders-gravel	metal
O.13	OAK	farm well	ND	ND	ND	ND
BHO.1	OAK RC	monitoring borehole	6	> 6	see Appendix	plastic
BHO.3B	OAK RC	monitoring borehole	6	> 6	see Appendix	plastic
BHO.4	OAK RC	monitoring borehole	5	> 5	see Appendix	plastic
BHO.4A	OAK RC	monitoring borehole	9	> 9	see Appendix	plastic
BHO.5	OAK RC	monitoring borehole	5	> 5	see Appendix	plastic
BHO.6	OAK RC	monitoring borehole	5	> 5	see Appendix	plastic
BHO.7	OAK RC	monitoring borehole	5	> 5	see Appendix	plastic
BHO.8	OAK RC	monitoring borehole	7	> 7	see Appendix	plastic

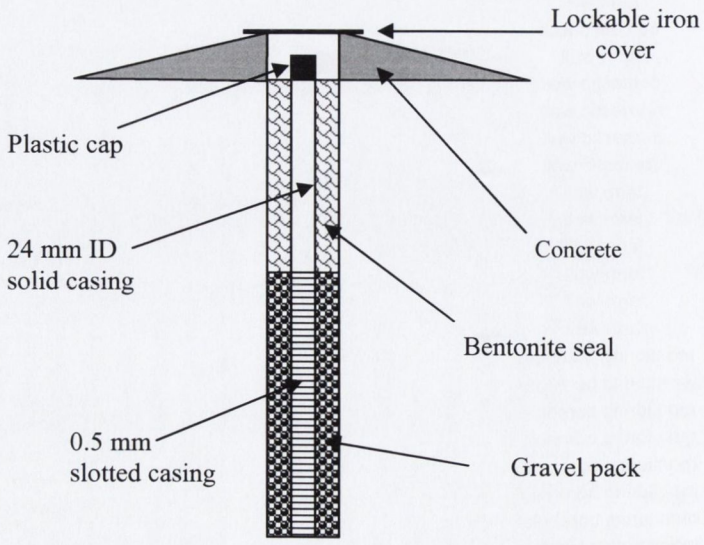
ND Not Determined

Complementary information collected in the 1980's was also available from land owners (Coxon, unpublished data), twelve of them confirming that the bedrock had been reached during the drilling. Information on the type of material found above the bedrock at thirty-five locations showed some diversity, indicating either sandy or clayey material. This information tended to confirm what is displayed in figure 3.3, i.e. that wells located north and west of Castlemitchell were in a zone of till deposits.

All but one well were satisfactorily capped by various means (concrete or metal cover, shed, sometimes plastic bags), and therefore were not directly open to air. The only noticeable exception was well B.9 in Ballyroe, which was half-covered by a large concrete block in a messy yard. The nature of the casing was not known for many of the private wells, although metal seemed to be widespread. It should be noted that most wells would be ungrouted, which presents a potential problem with possible contaminant entry down the outside of the casing.

At Oak Park RC, monitoring boreholes were drilled by Minerex Environmental Limited with a percussion window sampler, and installed according to the design showed in figure 3.11. Each piezometer consisted of a single PVC casing (24 mm internal diameter) with a 3 m-long PVC screen (1 m for BHO.4A) of 0.5 mm-wide slots and a fixed bottom cap. The top of the pipe was protected with a plastic cap and a bentonite seal prevented infiltration from the surface (Minerex Environmental Ltd, 2002).

Figure 3.11: Schematic of borehole design at Oak Park RC (Hooker, 2005).



- Moorepark RC

Ten deep monitoring boreholes had been drilled in Curtin's farm (see section 3.4.3 for further details) in 2001/2002 in the underlying karstified limestone aquifer for the needs of the EPA ERTDI Project 2000-LS-2.3.1.3-M2 (Bartley, 2003). Each borehole was made of a single casing (50 mm internal diameter) 34.5 to 38 m long, with a 3-4 m long PVC screen placed around 30 m bgl. For the present project, these boreholes were sampled between February 2002 and September 2003.

3.4.2 Diffuse and point N sources in the Barrow Valley

- Diffuse N sources in the Barrow Valley

As discussed earlier in section 3.2.7, the land in the groundwater sampling areas of the Barrow Valley was mainly used for tillage, although there were patches of grassland (especially in the Ballyroe and Oak Park areas). Based on recent field observation, table 3.6 details the approximate percentage of tillage within a 300 m-radius area around each sampling well. These areas were assessed for year 2005 with Ordnance Survey of Ireland six inch maps (scale 1:10.560; OSI (1910)) where tilled and grassland fields were reported. The 300 m-radius area is a convenient arbitrary limit occasionally used in Groundwater Protection Schemes (GSI/DELG/EPA, 1999) to delineate the Inner Protection Area (SI) for Source protection Zones (SPAs). In addition, it gives a reasonable picture of the land use in the vicinity of each well, which is likely to influence the water quality. This limit has no scientific basis, but it has the benefit of consistency between sites, in the absence of data on zones of contribution (ZOCs), for which a detailed water-table and groundwater flow maps would be required in addition to data on depression cones (which are presumably smaller than 300 m for private wells).

Four site categories were defined as follows:

- $75\ \% < T \leq 100\ \%$ tillage: 34 sites (primarily Castlemitchell, then Ballyroe, and all Oak Park monitoring boreholes)
- $50\ \% < T \leq 75\ \%$ tillage: 7 sites (four from Ballyroe)
- $25\ \% < T \leq 50\ \%$ tillage: 4 sites (all Oak Park)
- $0\ \% < T \leq 25\ \%$ tillage: 6 sites (five from Oak Park)

Table 3.6: Classification of the Barrow sampling sites according to the percentage of tillage within a 300 m-radius area around each well in 2005.

Site	% tillage within 300 m	Site	% tillage within 300 m
BHO.1	75% < T ≤ 100%	C.11#	50% < T ≤ 75%
BHO.3B	75% < T ≤ 100%	B.1	50% < T ≤ 75%
BHO.4	75% < T ≤ 100%	B.4	50% < T ≤ 75%
BHO.4A	75% < T ≤ 100%	B.6	50% < T ≤ 75%
BHO.5	75% < T ≤ 100%	B.9	50% < T ≤ 75%
BHO.6	75% < T ≤ 100%	O.9	50% < T ≤ 75%
BHO.7	75% < T ≤ 100%	O.12	50% < T ≤ 75%
BHO.8	75% < T ≤ 100%	O.3	25% < T ≤ 50%
C.1	75% < T ≤ 100%	O.5	25% < T ≤ 50%
C.2	75% < T ≤ 100%	O.10	25% < T ≤ 50%
C.3	75% < T ≤ 100%	O.11	25% < T ≤ 50%
C.4	75% < T ≤ 100%	B.5	0% < T ≤ 25%
C.5	75% < T ≤ 100%	O.1	0% < T ≤ 25%
C.6	75% < T ≤ 100%	O.4	0% < T ≤ 25%
C.7	75% < T ≤ 100%	O.6	0% < T ≤ 25%
C.8	75% < T ≤ 100%	O.7	0% < T ≤ 25%
C.9	75% < T ≤ 100%	O.13	0% < T ≤ 25%
C.10	75% < T ≤ 100%		
C.12	75% < T ≤ 100%		
C.13	75% < T ≤ 100%		
C.14	75% < T ≤ 100%		
C.15	75% < T ≤ 100%		
C.16	75% < T ≤ 100%		
C.17	75% < T ≤ 100%		
C.18	75% < T ≤ 100%		
C.19	75% < T ≤ 100%		
C.20	75% < T ≤ 100%		
B.2	75% < T ≤ 100%		
B.3	75% < T ≤ 100%		
B.7	75% < T ≤ 100%		
B.8	75% < T ≤ 100%		
B.10	75% < T ≤ 100%		
O.2	75% < T ≤ 100%		
O.8	75% < T ≤ 100%		

25-50 % of site C.11 is a grassland from a golf course

It should be noted that all sites of the Barrow Valley had some tillage within 300 m, which explains why the percentage tillage was always higher than zero. Because most sites are surrounded by tillage, and because the livestock density is low, the application of organic wastes cannot be considered as an important source of fertilisation. Rather, most nitrogen was applied in the form of artificial fertiliser, although no information was available regarding the types of fertiliser applied at sampling-site level. Recapping section 3.2.7, the main crops grown in the groundwater sampling areas were wheat, barley and sugar beet. Table 3.7 gives details on the land use management in the Mid-East and South-East regions for the main five crops based on the National Survey of Fertiliser Use in 2000 and 2001-2003 (Coulter *et al.*, 2002, 2005), along with some of Teagasc recommended application rates (soil and crop-dependent).

Table 3.7: Types of fertiliser used and estimated application rates (in kg N/ha/year) for the most common crops of the Barrow Valley sampling area, based on surveys by Coulter *et al.* (2002, 2005).

Crop and region	Main fertilisers used	Mean application rate (n [1])		Recommendation [2]
		2000	2001-2003	
Winter Wheat				
Mid-East	CAN >> urea > 10-10-20 > 18-6-12	209 ±7.2 (21)	198 ±8.3 (19)	185[2a]-140[2b]
South-East		185 ±12.1 (9)	231 ±11.9 (10)	
Spring Wheat				
Mid-East	CAN >> 18-6-12 > 10-10-20 > urea	171 ±2.4 (4)	159 ±14.9 (13)	140[2a]-110 [2b]
South-East		150 ±16.5 (7)	157 ±6.3 (24)	
Winter Barley				
Mid-East	CAN >> urea > 18-6-12 > 10-10-20	185 ±6.4 (10)	161 ±19 (12)	175[2a]-135 [2b]
South-East		172 ±16.4 (4)	167 ±17 (5)	
Spring Barley				
Mid-East	CAN >> 18-6-12 > 10-10-20	109 ±5.9 (20)	126 ±5.9 (29)	125[2a]-110 [2b]
South-East		119 ±4.5 (45)	126 ±4.3 (56)	
Sugar beet				
Mid-East	CAN > 13-4-14 > 10-7.5-17.5 > 8-5-18	160 ±8.2 (7)	107 ±13.8 (8)	180[2c]-110 [2d]
South-East		159 ±8 (32)	160 ±7.5 (35)	
Grazing				
Mid-East	CAN > High N compounds > urea > 18-6-12	121 ±11.1 (107)	92 ±7.5 (119)	0-100-390[2e]
South-East		138 ±7.7 (154)	120 ±5.8 (189)	
Hay				
Mid-East	High N compounds > > 18-6-12 > CAN > urea	65+4.4 (48)	60 ±6 (52)	65-80 (no manure)
South-East		48 ±4.7 (74)	56 ±4 (73)	35-50 (if manure)
Silage				
Mid-East	High N compounds > CAN > urea > 18-6-12	141 ±5.3 (93)	125 ±5.7 (110)	125 (1 cut + slurry)
South-East		136 ±5.5 (138)	126 ±3.4 (174)	

1) n represent the number of farms surveyed

2) Recommendations of the Code of Agricultural Good Practice (DE and DAFF, 1996) for medium textured soils according to a) Index 1 soils (last crop as cereals, and no manures), b) Index 2 soils (last crop as root crops and no manures), c & d) Index 1 & 2 soils (sandy loam) with 220 mm precipitation between April and June, e) 1.5 (or less)-2.1-3.0 LU/ha,

If compared with values recommended for Index 1 soil (last crop as cereal), the mean fertiliser application rates for winter and spring wheat in 2001-2003 seemed excessive, whereas other crops were within close range of or below the recommendations. But if compared with values recommended for Index 2 soil (last crop as root crop), most applied rates were in large exceedance of the recommendations. In the local context where rotational crop systems are common practice (section 3.2.7), it suggests that application rates of artificial fertiliser may be, overall, higher than recommendations. This is supported by local Teagasc Crop Advisor Officers who reported that many farmers in the area apply, on average, twenty percent more than the highest recommendations, and application rates higher than 250 kg/ha/year for winter wheat are not unusual (Hugh McCreevy, Teagasc Crop Advisor Officer, personal communication). However, the trend observed by Coulter *et al.* (2005) over the past few years suggests that the overall application rates of artificial fertiliser are declining towards recommendations.

National surveys of Coulter *et al.* (2002, 2005) also reveals that the most commonly used fertiliser was CAN (calcium ammonium nitrate), followed by urea and some NPK compounds such as 10-10-20 and 18-6-12 (table 3.7). Local Teagasc Crop Advisors added sugar beet compound No.1 and No.2 (also referred to as 13-4-14 and 8-5-18 respectively) to this list of most popular artificial fertilisers used in south of Co. Kildare. Descriptions of these fertilisers were detailed in table 2.5 (section 2.3.2). Finally, the use of potash (KCl) is widespread in south Kildare and north Carlow (Hugh McCreevy, Teagasc Crop Advisor Officer, personal communication).

- Point N sources in the Barrow Valley

Of the fifty-one wells located in agricultural areas subjected to artificial fertiliser applications (i.e. inorganic N diffuse sources), the main differences between sites related to the presence or absence of organic point sources such as farmyards and unsewered houses. To assess the situation at each sampling site, farmyards and houses were pinpointed on OSI six inch maps (scale 1:10,560, OSI (1910)) after field observation and cross-checking with OSI Discovery Series maps No. 55 and 61 (scale 1:50,000). Then, 100 m and 300 m radius lines were drawn around each well (see subsection "Diffuse N sources in the Barrow Valley") and both types of N point sources were counted within these areas, for which results are displayed in table 3.8. Except for two sites where communal septic tanks serve a substantial number of houses (B.6 and C.10), the vast majority (if not all) of dwellings in the groundwater sampling areas have their own septic tank systems (Water Services of Kildare and Carlow County Councils, personal communication). Therefore, the density of septic tanks within the 100 m and 300 m zones equals the density of houses.

Table 3.8: Classification of the Barrow groundwater sampling sites according to the number of organic N point sources (farmyards and unsewered houses – this includes farms) within 100 m and 300 m-radius areas around each well. Four classes were identified: 1) no farmyard and no house (uncoloured classes), 2) no farmyard and one or more unsewered houses (grey-25 % classes), 3) one farmyard and its unsewered farm (grey-40 % classes), 4) one or more farmyards and more than one unsewered houses (grey-50 % classes)

Site	Farmyards within 100m	Unsewered houses within 100m
BHO.1	0	0
BHO.3B	0	0
BHO.4	0	0
BHO.4A	0	0
BHO.5	0	0
BHO.6	0	0
BHO.7	0	0
BHO.8	0	0
B.10	0	0
O.11	0	1
C.1	0	2
C.4	0	2
C.12	0	2
C.15	0	2
C.18 [1)]	0	2
C.6	0	3
C.7	0	3
C.8	0	3
C.19	0	3
B.4	0	3
O.5	0	3
O.7	0	4
O.4	0	5
C.20	0	6
O.6	0	6
B.6	0	11
C.2	1	1
C.9	1	1
C.10	1	1
C.11	1	1
C.13	1	1
C.14	1	1
B.1	1	1
B.2	1	1
B.3	1	1
B.5	1	1
B.7	1	1
B.8	1	1
B.9	1	1
O.3	1	1
O.8	1	1
O.9	1	1
O.10	1	1
O.12	1	1
C.5	1	2
C.3	1	3
C.16	1	3
O.13	1	3
C.17	1	4
O.2	1	4
O.1	2	4

Site	Farmyards within 300m	Unsewered houses within 300m
BHO.1	0	0
BHO.3B	0	0
BHO.4	0	0
BHO.4A	0	0
BHO.5	0	0
BHO.6	0	0
BHO.7	0	7 [2)]
BHO.8	0	7 [2)]
C.12	0	2
C.4	0	3
C.7	0	3
C.8	0	3
C.6	0	4
C.15	0	4
C.1	0	9
C.20	0	10
B.10	0	10
O.6	0	15
B.6 [3)]	0	48
C.11	1	1
C.14	1	1
B.2	1	1
B.3	1	1
B.7	1	1
B.8	1	1
O.8	1	1
O.9	1	1
O.10	1	1
O.12	1	1
C.9	1	2
O.11	1	2
C.13	1	3
B.9	1	4
C.2	1	6
C.17	1	6
C.19	1	6
O.2	1	6
O.3	1	6
C.18 [1)]	1	8
B.4	1	8
O.5	1	9
O.13	1	13
C.10 [4)]	1	15
B.1	2	3
B.5	2	4
C.3	2	6
C.16	2	6
O.7	2	16
O.4	2	18
O.1	2	19
C.5	3	6

1) Presence of a graveyard within 100 m
2) Houses located along the River Barrow downgradient of BHO.8
3) Two communal septic tanks serving 22 and 28 houses more than 100 m away from site B.6
4) One communal septic tank serving 8 houses more than 100 m away from site C.10

Four main classes of sites could then be identified and defined according to the most likely source of nitrogen within 100 m or 300 m:

1. No farmyard and no house (uncoloured classes in table 3.8): these sites are defined as "**artificial diffuse N source**" sites (9 sites at 100 m, 8 sites at 300 m), if one disregards animal wastes like manure or slurry as a important organic diffuse N source.
2. No farmyard and one or more unsewered houses (grey-25 % classes in table 3.8): these are defined as "**septic tank point source**" sites (17 sites at 100m, 11 sites at 300m)
3. One farmyard and its unsewered farm (grey-40 % classes in table 3.8): these sites are defined as "**farmyard point source**" sites, although there is a possibility that that farm's septic tank contributes to the overall contamination (18 site at 100 m, 10 sites at 300 m)
4. One or more farmyards and more than one unsewered houses (grey-50 % classes in table 3.8): these are "**undetermined point source**" sites (7 sites at 100 m, 22 sites at 300 m)

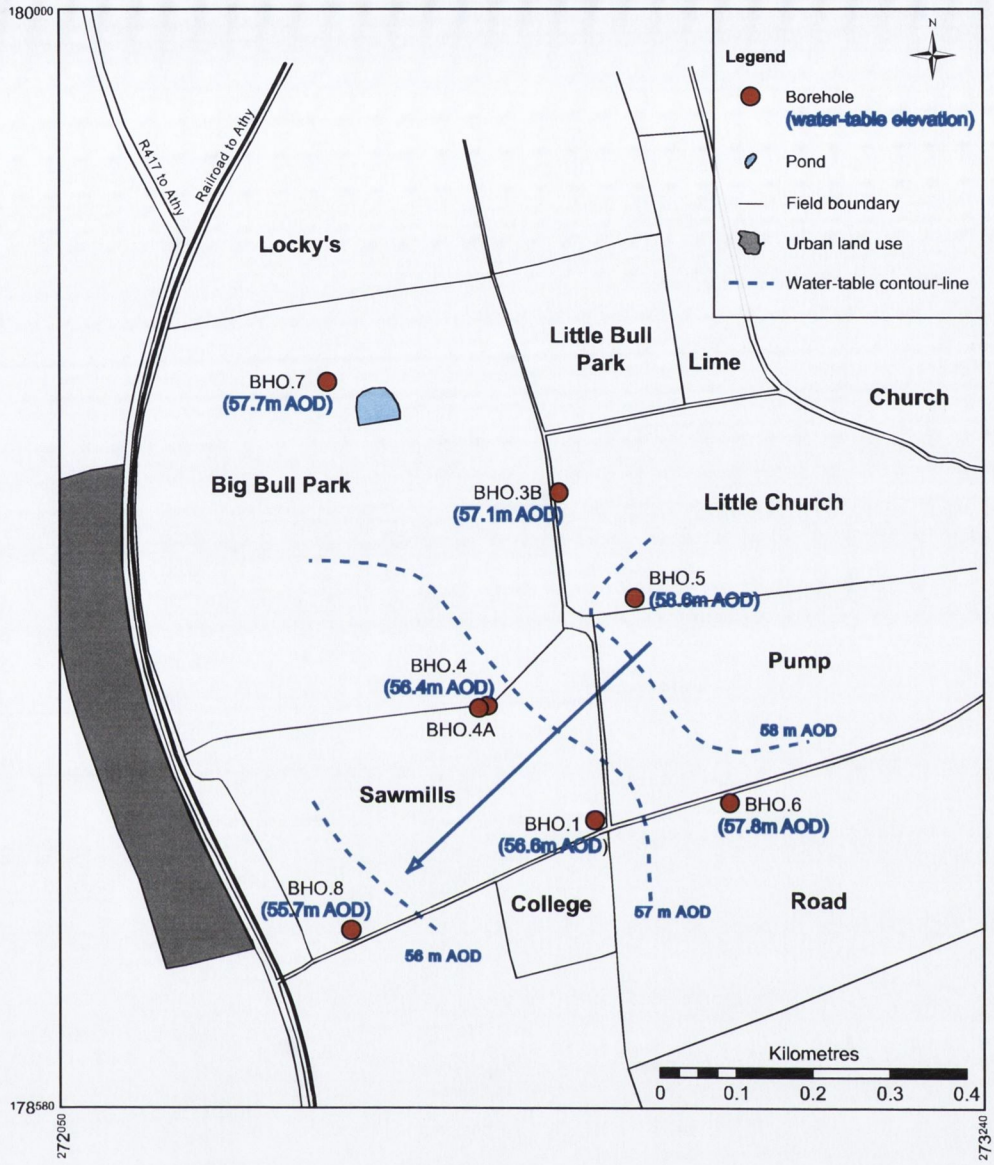
3.4.3 Case studies: Oak Park monitoring area and Moorepark Research Centres

- Oak Park monitoring area

Figure 3.12 gives a detailed description of the Oak Park Research Centre fields where monitoring boreholes were installed in 2002 (general location within the Barrow Valley in figure 3.1). The water-table elevation measured on 25th February 2003 shows that the local groundwater flow is directed towards the south-west, i.e. towards the River Barrow located 550 m west of BHO.8.

As already observed in table 3.8, no potential point source was present within the 100 m-radius area around each borehole. Some unsewered houses were nonetheless located within the 300 m-radius area of BHO.8 and BHO.7, but considering the groundwater direction flow and the proximity of the River Barrow, these downgradient dwellings were not categorised as potential point sources.

Figure 3.12: Borehole location in the Oak Park monitoring area (OSI grid coordinates around the edge), and water-table contour-lines constructed from groundwater and surface water level (m AOD) on 25/02/2003 (water-table elevation at each borehole between brackets).



Except for BHO.8 and BHO.7, there was no organic point N source within a 100 m or 300 m radius around the other six piezometers. Table 3.9 details the land use management relevant to artificial diffuse N sources for fields adjacent to the monitoring boreholes (John Hogan, Teagasc Oak Park Research Centre, personal communication). Due to occasional grassland trials in the Little Church and Sawmills fields, all sites had between 75 % and 100 % tillage within a 300 m radius, which was shown in table 3.6. It should be noted that grass had been sown in the Sawmills between 1994 and 1996, which explains why the CLC 2000 map in figure 3.8 (based on data from 1995-1996) shows grass around BHO.4, BHO.4A, BHO.1 and BHO.8.

Table 3.9: Annual cropping programme in the Oak Park monitoring area, fertiliser application rates (1cwt/ac = 125 kg/ha) and fertiliser N loading rates for each field of the Oak Park monitoring area between 2002 and 2004. *(rates are reported in kg N/ha/year)*

Field name	Crops	Fertiliser type	Application rate	kg N/ha/year
2002				
Big Bull Park	Spring barley	18-6-12	3.0 cwt/ac	67.5
		Super Net	2.0 cwt/ac	67.5
	Winter wheat	Super Net	6.6 cwt/ac	225
		0-10-20	3.0 cwt/ac	-
Sawmills	Spring barley	18-6-12	3.0 cwt/ac	67.5
		Super Net	2.0 cwt/ac	67.5
	Oil seed rape	Super Net	3.0 cwt/ac	67.5
		0-10-20	2.0 cwt/ac	67.5
	Potatoes	7-6-17	12 cwt/ac	105
College	Spring barley	Super Net	4.5 cwt/ac	152
		0-10-20	1.6 cwt/ac	-
Road	Winter barley	Super Net	5.0 cwt/ac	171
		0-10-20	3.0 cwt/ac	-
	Winter oat	Super Net	4.4 cwt/ac	100
		0-10-20	3.0 cwt/ac	-
Pump	Spring barley	Super Net	4.1 cwt/ac	140
		0-10-20	1.6 cwt/ac	-
Little Church	Spring barley	18-6-12	3.0 cwt/ac	67.5
		Super Net	2.0 cwt/ac	67.5
	Grass trial	24-25-10	11.5 cwt/ac	345
Little Bull Park	Spring barley	18-6-12	3.0 cwt/ac	67.5
		Super Net	2.0 cwt/ac	67.5
Locky' s	Spring barley	18-6-12	3.0 cwt/ac	67.5
		Super Net	2.0 cwt/ac	67.5
	Winter wheat	Super Net	6.6 cwt/ac	225
		0-10-20	3.0 cwt/ac	-
2003				
Big Bull Park	Spring barley	18-6-12	3.0 cwt/ac	67.5
		Super Net	2.0 cwt/ac	67.5
	Winter wheat	Super Net	3.4 cwt/ac	171
		0-10-20	3.0 cwt/ac	-
	Winter wheat	Super Net	6.6 cwt/ac	225
		0-10-20	3.0 cwt/ac	-
Sawmills	Spring barley	Super Net	4.1 cwt/ac	140
		0-10-20	1.6 cwt/ac	-
	Grass trial	Super Net	4.5 cwt/ac	152
		0-10-20	1.6 cwt/ac	-
College	Winter barley	Super Net	5.0 cwt/ac	167
		KCl	2.9 cwt/ac	-
Road	Winter barley	Super Net	5.0 cwt/ac	171
		0-10-20	3.0 cwt/ac	-
	Spring barley	18-6-12	3.0 cwt/ac	67.5
		Super Net	2.0 cwt/ac	67.5
Pump	Spring barley	Super Net	4.1 cwt/ac	140
		0-10-20	1.6 cwt/ac	-
Little Church	Spring barley	18-6-12	3.0 cwt/ac	67.5
		Super Net	2.0 cwt/ac	67.5
	Grass trial	24-25-10	11.5 cwt/ac	345
Little Bull Park	Winter barley	Super Net	5.7 cwt/ac	188
		KCl	1.4 cwt/ac	-
Locky' s	Winter oat	Super Net	4.4 cwt/ac	100
		0-10-20	3.0 cwt/ac	-
	Winter wheat	Super Net	6.6 cwt/ac	225
		0-10-20	3.0 cwt/ac	-
	Potatoes	7-6-17	12 cwt/ac	105

Table 3.9 (continued): Annual cropping programme in the Oak Park monitoring area, fertiliser application rates (in cwt/ac) and fertiliser N loading rates for each field of the Oak Park monitoring area between 2002 and 2004. *(rates are reported in kg N/ha/year)*

Field name	Crops	Fertiliser type	Application rate	kg N/ha/year
2004				
Big Bull Park	Spring barley	18-6-12	2.0 cwt/ac	45
		Super Net	2.5 cwt/ac	84.4
	Winter wheat	Super Net	5.6 cwt/ac	188
	Winter wheat	Super Net	6.6 cwt/ac	225
		0-10-20	3.0 cwt/ac	-
	Sugar beet	Beet Compound No2	10 cwt/ac	125
		Super Net	1.3 cwt/ac	45
Sawmills	Winter oat	Super Net	3.0 cwt/ac	100
		KCl	1.4 cwt/ac	-
College	Spring barley	Super Net	4.1 cwt/ac	140
		KCl	2.9 cwt/ac	-
	Winter barley	Super Net	5.0 cwt/ac	167
		KCl	2.9 cwt/ac	-
Road	Winter barley	Super Net	5.0 cwt/ac	171
		0-10-20	3.0 cwt/ac	-
	Spring barley	18-6-12	3.0 cwt/ac	67.5
		Super Net	2.0 cwt/ac	67.5
Pump	Spring barley	Super Net	4.1 cwt/ac	140
		0-10-20	1.6 cwt/ac	-
Little Church	Spring barley	20-0-15	3.0 cwt/ac	75
		Super Net	1.3 cwt/ac	45
	Grass trial	24-25-10	11.5 cwt/ac	345
Little Bull Park	Winter barley	Super Net	5.7 cwt/ac	188
		KCl	1.4 cwt/ac	-
Locky' s	Winter wheat	Super Net	6.6 cwt/ac	225
		0-10-20	3.0 cwt/ac	-
	Spring barley	18-6-12	3.0 cwt/ac	67.5
		Super Net	2.0 cwt/ac	67.5

The main crops sown between 2002 and 2004 in the monitoring area was spring barley, and winter wheat to a lesser extent. The main fertiliser used was Super Net (27.5 % N, see table 2.5) and NKP compound 18-6-18. Non-nitrogenous fertilisers like 0-10-20 compound and potash (KCl) were also used. It is also important to note that apart from manure spread on the Sawmills fields in 2000, and some occasional grazing in the Locky's field in the 90s, no animal organic wastes had been applied to the monitoring area over the last fifteen years (Eddie Keogh, Teagasc Oak Park RC, personal communication).

- Moorepark RC

Figure 3.13 shows how the groundwater sampling sites were distributed in Curtin's farm at Moorepark RC. Four zones were defined according to the land use management, which is detailed in table 3.10. One site (BHC.1) was located at the extreme south-west side in the 2nd cut silage area (plus grazing), two sites (BHC.9 and BHC.10) were located north in the

two cut silage area, two sites (BHC.4 and BHC.7) were located within the dirty water zone, and the four other sites (BHC.2, BHC.3, BHC.5 and BHC.8) were in the grazing zone.

Figure 3.13: Borehole locations and land use at Curtin's farm (OSI grid coordinates: 100 950, 181 350). (adapted from Bartley (2003).

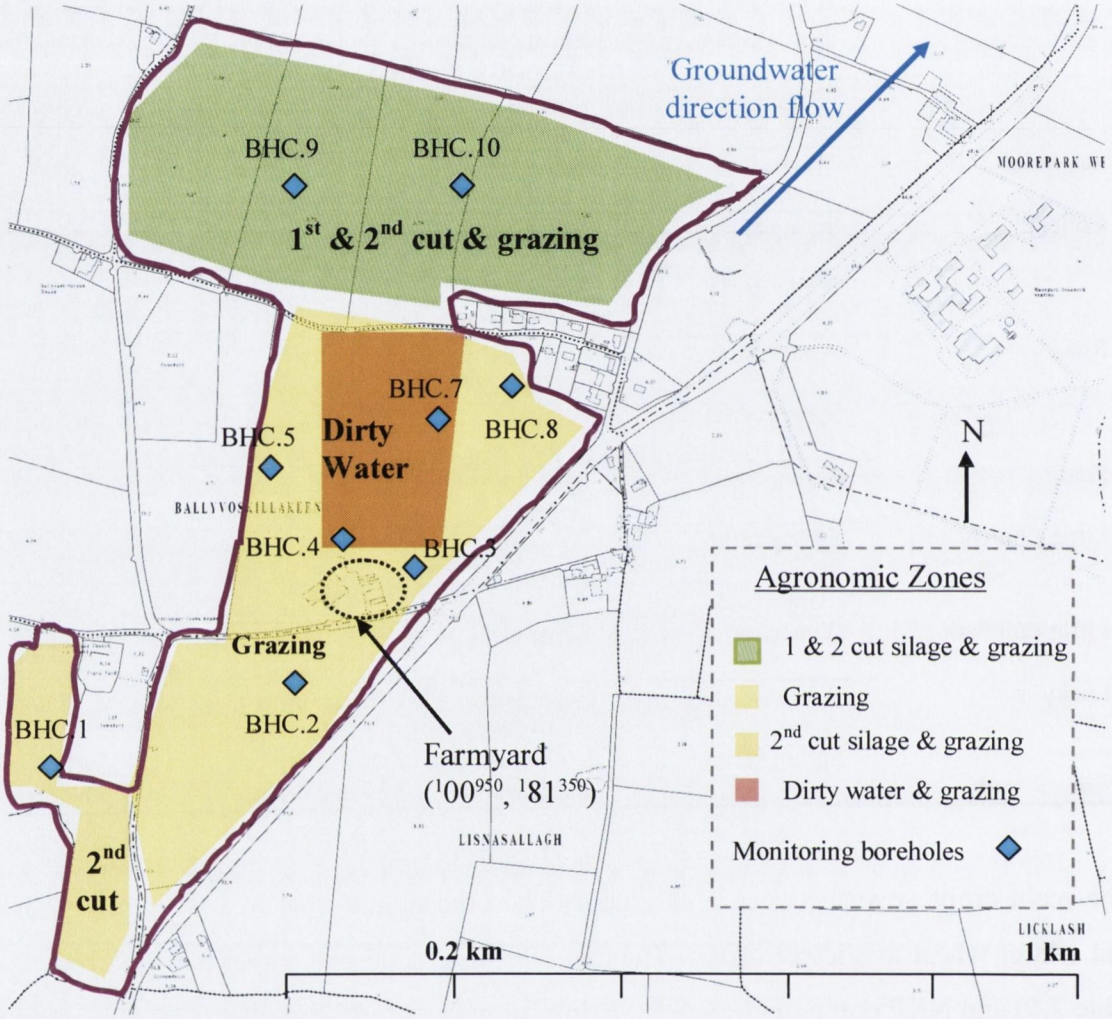


Table 3.10: Calculated annual total nitrogen application rates for each nitrogen source for each management zone at Curtin's farm between 2001 and 2003 (Adapted from Bartley, 2003). *(rates are reported in kg N/ha/year)*

Agricultural management zone	Total inorganic N	Recycled organic N			
		Total organic N	Contributor to total organic N		
			Grazing animals	*Dairy wastewater*	*Slurry*
October 2001 – September 2002					
Grazing only	295	179	*179*	*None*	*None*
Dairy wastewater & grazing	290	378	*198*	*180*	*None*
One-cut silage & grazing	285	230	*138*	*None*	*92*
Two cut silage & grazing	340	194	*98*	*None*	*96*
October 2001 – September 2002					
Grazing only	290	165	*165*	*None*	*None*
Dairy wastewater & grazing	248	471	*211*	*260*	*None*
One-cut silage & grazing	298	256	*121*	*None*	*135*
Two cut silage & grazing	310	263	*76*	*None*	*187*

Importantly, two sites, namely BHC.3 and BHC.4, were within 50 m of the farmyard, which includes a cattle house, a buried slurry tank, a buried dirty water tank, a manure pit and silage storage facilities. The fertiliser used in Moorepark RC was calcium ammonium nitrate (CAN) used for the fertiliser plots in section 3.3.1.

CHAPTER 4: METHODS

4.1 Design of field sampling programme

4.1.1 Choice of the study areas

- Saturated zone

The Barrow Valley aquifer was chosen as the main sampling area to test dual isotopic analyses in groundwater nitrate (in combination with chemical analyses) because it is a good example of a nitrate "hot spot" that needs to be better understood in order to address the nitrate problem in vulnerable and contaminated zones. Many supply wells have long yielded groundwater with nitrate levels over 25 mg/l NO_3^- (guide level set at in the old Drinking Water Directive - see section 2.1.4) or 50 mg/l NO_3^- (limit in the Drinking Water and also Nitrate Directives - see section 2.1.4). In addition to the geological and meteorological context that favours nitrate leaching, the choice of this specific area was motivated by the fact that several nitrogen sources coexist and can potentially contaminate groundwater. Early investigations in the Barrow Valley by Daly and Daly (1982) suggested that nitrate contamination was caused by organic point sources (farmyards and septic tanks), whereas other studies pointed out that diffuse fertiliser sources may have caused significant contamination in some areas (Coxon and Thorn, 1991). But the fact is that up to now, the origin of the contamination has remained unclear. The drilling of piezometers in Oak Park Research Centre at the edge of fields subjected to application of artificial fertiliser, and free of potential point sources (section 3.4), was intended to help investigate the influence of artificial fertiliser sources alone.

A second area located at Curtin's farm (Moorepark RC), and described in sections 3.2 and 3.4, was chosen because boreholes had been drilled as part of EPA ERTDI Project 2000-LS-2.3.1.3-M2 (Bartley, 2003) in a hydrogeological and land use context that are different from the Barrow Valley area. This limestone aquifer is deep, karstified and overlain by a thin soil cover, which are relevant to vulnerability described in section 2.1.5. The area is dominated by permanent grassland and dairy farming.

To summarise, the study areas were chosen to enable the testing of dual isotopic analyses in groundwater nitrate under several hydrogeological contexts favourable to nitrate

leaching, and in the presence of several types of organic and inorganic nitrogen sources. Besides, because most of the Barrow Valley sites had already been sampled in the late 1980's, this area provided a valuable opportunity to follow up the evolution of nitrate levels in groundwater over the last decade by comparing results with previous work (Coxon, unpublished data).

- Unsaturated zone

Several sites were selected for soil-water sampling in order to better understand the mechanisms involved during nitrate leaching through the unsaturated zone and the implications for $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values. Curtin's farm, at Moorepark RC was the main sampling site because of the presence of experimental plots exceptionally well instrumented with ceramic suction cups, which were originally installed, maintained and used by National University of Ireland Galway (NUIG) staff as part of EPA ERTDI Project LS 2.3.2 (see section 3.3.1). Nitrate leaching could be investigated under several treatments, application rates and depths. The high drainage capacity of soils was somewhat similar to conditions met in the Barrow Valley where most of the groundwater sampling took place. In addition, groundwater was also sampled at Moorepark, enabling the direct comparison between unsaturated and saturated zone results.
Experimental plots in Knockbeg (section 3.3.2), also installed with ceramic suction cups, were selected for sampling because soils are heavier, hence represented an opportunity to investigate dual isotopic analyses in soil water nitrate in a different context where denitrification was thought to be significant. Lysimeters set up in Johnstown Castle (section 3.3.3) were sampled because their soils originated from Oak Park Research Centre, where some boreholes were drilled for groundwater sampling.

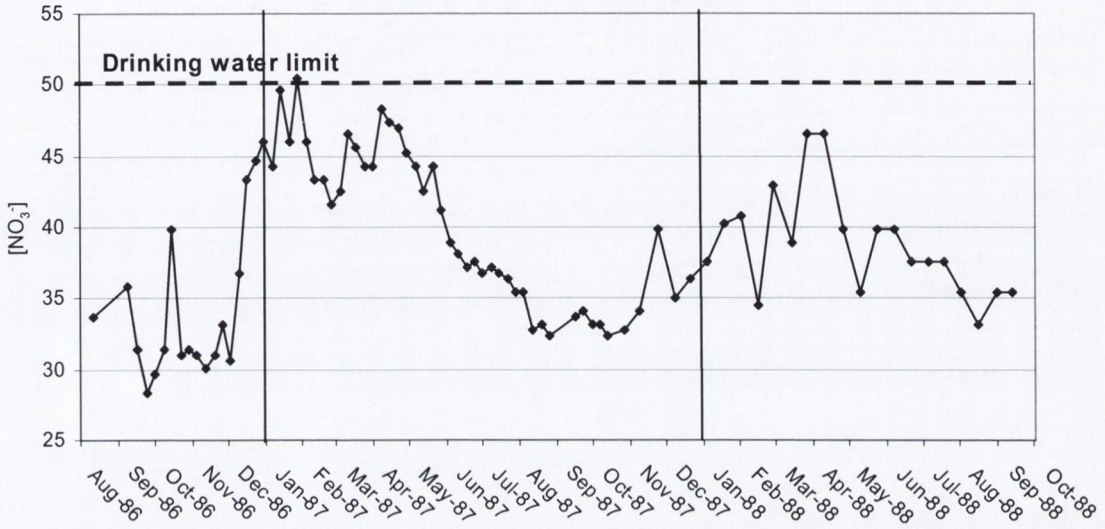
4.1.2 Choice of the sampling times

- Saturated zone

As discussed in section 3.2.6, groundwater recharge in the Barrow Valley generally occurs from November to April, and is at its minimum or null from May to October. If nitrate is present in soils at recharge time, and if the geological context is favourable (i.e. freely draining soils, unconfined and shallow aquifer), nitrate becomes available for leaching.

This can result in higher nitrate concentrations during winter and lower levels during summertime, as observed in figure 4.1 during the weekly monitoring of borehole O.11 at Oak Park House between 1986 and 1988.

Figure 4.1: Monitoring of nitrate concentration in borehole O.11 at Oak Park RC between August 1986 and September 1988 (Coxon, unpublished data). *(the dashed line represents the drinking water limit set at 50 mg/l NO_3^- in the drinking Water Directive)*



Between 2002 and 2004, groundwater sampling was carried out around February, June and September, which enabled the comparison of groundwater chemistry under winter recharge, and summer non-recharge, conditions, as described in figures 3.3 and 3.4.

- Unsaturated zone

The timing of unsaturated zone sampling was somewhat problematic due to a dependence on variable drainage conditions. Unlike groundwater, the supply of soil-water available from either suction cups or lysimeters is limited, and depends on what was intercepted or drained. Volumes collected from replicated cups also varied substantially within plots, some cups being almost dry while others were full, which may have being the result of variable drainage conditions. Furthermore, recharge conditions are rare or non-existent between May and October, which ruled out any soil-water sampling during summertime. This was further complicated by the fact that around 100 μmol of nitrate (i.e. 6.2 mg nitrate) was required from each sample for the nitrate extraction process (section 4.4.1). Table 4.1 shows amounts of nitrate contained in soil-water samples collected at Moorepark in April 2004. Sampling was made especially difficult in low nitrate plots, e.g. the control and the slurry treatments, because nitrate concentrations were generally very low and the

volumes collected inadequate for analyses. Another important reason for collecting most soil-water samples between March and May was that nitrate concentrations in soils reached a peak at this time of the year, as recorded by Gibbons *et al.* (2006).

Table 4.1: Amount of nitrate contained in soil-water samples collected at Moorepark in April 2004 at the aggregated depths of 1.0 m and 2.5 m (letter C means unfertilised control, letters L-M-H relate to the application rates low-medium-high and the second letters F-D-S stand for artificial fertiliser-dairy wastewater-slurry). *(nitrate concentration is reported in mg/l NO_3^-, volume in litre and amounts in mg)*

Suction cup	$[NO_3^-]$	Volume	Amount NO_3^-
C1.0	34.0	1.030	35
C2.5	25.7	0.130	3
HF1.0	136.3	0.810	110
HF2.5	136.3	0.950	129
MF1.0	115.0	1.050	121
MF2.5	89.2	1.030	92
HD1.0	108.8	0.980	107
HD2.5	56.4	0.900	51
MD1.0	48.4	1.050	51
MD2.5	63.4	1.350	86
HS1.0	7.4	1.020	8
HS2.5	19.3	0.340	7

4.2 Sample collection, treatment and storage prior to analysis

4.2.1 Soil water samples

Sixty-two soil-water samples were collected from Moorepark, Knockbeg and Oak Park soil lysimeter experiments (set at Johnstown Castle) between 2002 and 2004. The number of samples collected from each site is summarised in table 4.2 below with collection times, while the sampling procedure at each site is explained throughout this section.

Table 4.2: Number of soil-water samples collected between 2002 and 2004 in each sampling site.

Site	December 2002	June 2003	November 2003	March 2004	April 2004	May 2004
Moorepark RC	8	16	-	-	12	11
Knockbeg	-	-	-	9	-	-
Oak Park soil lysimeters	-	-	6	-	-	-

- Sample collection from suction cups in Moorepark RC

Forty-seven soil-water samples were collected between 2002 and 2004 from Moorepark suction cups installed in grassland plots. Two depth ranges were investigated for each plot: in this report, these are termed 1.0 m and 2.5 m. In reality, and because the volumes

collected were sometimes very small in conjunction with low nitrate concentrations, it was decided to combine samples collected for each experimental plot at 0.9 m, 1.0 m, 1.2 m and 1.5m depths, and label the resulting sample as 1.0 m depth. Equally, samples collected at depths of 2.0 m, 2.5 m and 3.0m were aggregated and the resulting sample was labelled as depth 2.5m. This was motivated by the fact that isotopic analysis on nitrate requires large quantities of nitrate, which were often not provided by a single ceramic cup at one depth.

Up to fourteen days prior to sample collection, a negative initial pressure of 40 mBar was applied to all cups in order to drain large enough volumes of water. Cups were then sampled by applying a positive pressure with a hand pump to a tube going down into the cup, water being pushed out into the tube going up and then collected at the outlet, as described in figure 4.2.

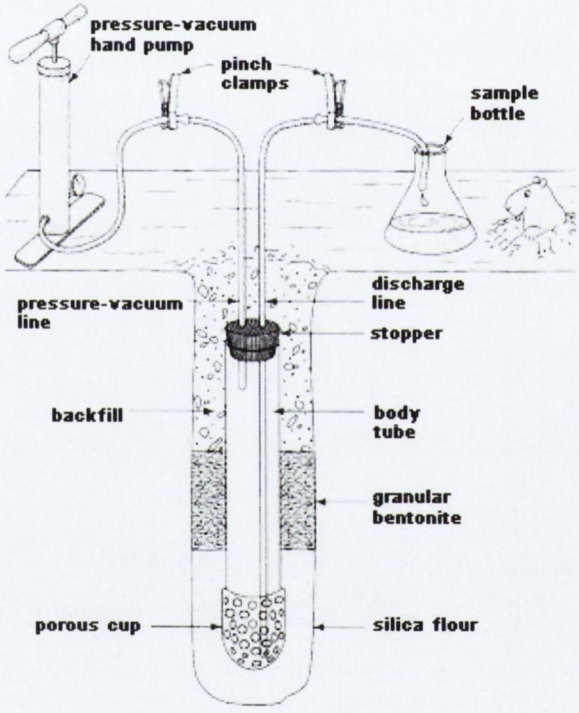


Figure 4.2: Schematic of the sampling procedure for pressure-vacuum suction cups in Moorepark RC (Fetter, 1999).

- Sample collection from suction cups in Knockbeg

Nine samples were collected on one occasion at the Knockbeg site in March 2004 from suction cups installed in fertilised winter wheat and spring barley plots. Because the volumes collected were sometimes very small in conjunction with low nitrate concentrations, it was decided to combine all replicated cups within each experimental plot into 1-litre polyethylene bottles. A week before sampling was scheduled, a negative initial

pressure of 50 mBar was applied by Teagasc staff to all cups. Samples were then collected from vacuum flasks into which soil-water was directly channelled. Although each of the four treatments was in triplicate (twelve plots in total), only nine plots could be sampled because one plot of the winter wheat low rate, and of the spring barley high and low rates did not provide enough water. Attempts were also made to sample plots in April 2004, but volumes collected were far too small for isotopic analysis.

- Sample collection from lysimeters

Six soil-water samples were collected on one occasion in November 2003 from unfertilised and fertilised Oak Park soil lysimeters set at Johnstown Castle where perennial ryegrass was grown. The sampling procedure was carried out by Teagasc staff and consisted of leaving a large container at the bottom of the lysimeters for several days where the leachate was collected. Attempts were also made to sample Elton and Castlecomer soil lysimeters on several occasions, but nitrate levels were always too low for isotopic analysis. Although all soils leached water, only Oak Park soils provided nitrate concentrations high enough to satisfy the nitrate extraction process (three control lysimeters and three high N rate lysimeters), other soils generally leaching nitrate levels below the detection limit.

- Soil water samples treatment and storage

Upon collection, all samples were immediately placed into cool boxes packed with ice packs for transport to the laboratory. They were then 0.45 μm nylon filtered on the evening of their collection and kept chilled at 4 °C overnight.

4.2.2 Groundwater samples

- Sample collection from monitoring boreholes

Thirty seven groundwater samples were collected from the intensive tillage fields in the Oak Park monitoring area, and thirty three groundwater samples were collected from the intensive dairy farm in Moorepark RC (table 4.3) between 2002 and 2004. The discrepancy between field trips in terms of sample number is explained by the fact that some wells were

dry on the sampling day, whereas one borehole from the Oak Park monitoring area could not be sampled in June 2004 because it had been damaged by some farming machinery.

Table 4.3: Number of groundwater samples collected between 2002 and 2004 from monitoring boreholes in Teagasc Research Centres of Oak Park and Moorepark.

Area	February 2002	December 2002	February 2003	June 2003	September 2003	February 2004	June 2004
Oak Park monitor.			8	8	7	8	6
Moorepark RC	9	8		9	7		

Groundwater samples were collected in Oak Park and Moorepark RC monitoring boreholes in a similar fashion. Prior to sample collection, each borehole was purged by removing three times the volume of standing water (peristaltic pump used at Oak Park, portable submersible pump at Moorepark RC). This volume was calculated by measuring the water table depth (with a dip-meter), the bottom of the borehole and the internal diameter of the casing.

- Sample collection from private wells

The Oak Park monitoring area aside, two hundred and forty-six groundwater samples were collected from the Barrow Valley aquifer between 2002 and 2004 (table 4.4), which represents a mixture of sites contaminated by diffuse agricultural N sources, point N sources, or both. The discrepancy between field trips in terms of sample number is explained by the fact that some wells could not be sampled for the following reasons: difficulty to gain access to the tap that was located inside a groundwater group scheme shed or the landowner's house, lack of cooperation from a few landowners.

Table 4.4: Number of groundwater samples collected between 2002 and 2004 from private wells in the Barrow Valley aquifer.

Area	February 2002	September 2002	February 2003	June 2003	September 2003	February 2004	June 2004
Castlemitchell	20	16	16	16	16	15	15
Ballyroe	10	9	8	8	8	8	7
Oak Park	12	-	13	13	12	12	12

Because private wells did not allow direct access to the aquifer, samples were collected directly from the closest tap to the well. The tap was turned on for up to five minutes in

order to purge and flush the pipe and to get water chemically and microbiologically representative of the underlying aquifer. In case the well was far away from the tap, as it was the case at a few locations, the tap was left on for a few more minutes. Each tap was also flamed or cleansed with some ethanol to avoid unwanted microbial contamination that would alter total and faecal coliform tests.

- Groundwater sample treatment and storage

Each monitoring and private well was sampled with four types of container:

- 1-litre polyethylene bottles for the measurement of NO_3^-, SO_4^{2-}, Cl^- and DOC concentrations, the remainder being used for the nitrate extraction process.
- 50-ml polyethylene vials for water intended for pH and alkalinity measurements.
- 50-ml glass vials with screw cap and rubber liner for water intended for $\delta^{18}O\text{-}H_2O$ and $\delta^2H\text{-}H_2O$ measurements.
- Sterilised glass bottles (in the autoclave at 130 °C for 30 min) or sterile polystyrene containers (from 250 ml to 1 litre) for total and faecal coliform tests.

In order to minimise cross-contamination, the same bottles were always used for each site. Prior to any sampling, each bottle was washed with tap water, then distilled water and air-dried in the laboratory. Once on site and after boreholes were purged or tap water was left running for a few minutes, each bottle was rinsed three times with some sample. Bottles were then filled up with no air space left in the bottleneck in order to minimise aerobic biochemical reactions. Samples were kept chilled in a cool-box filled with ice packs during transport to the laboratory. All water samples contained in 1 litre plastic bottles were then 0.45 μm nylon-filtered on the evening of their collection and kept chilled at 4 °C overnight. At the same time, approximately 50 ml of each filtered sample was transferred to 50-ml polyethylene vials where 0.4 ml of 10 % $LnCl_4$ was added. These subsamples were kept chilled at 4 °C for later measurement of cation concentrations (Na^+, K^+, Ca^{2+} and Mg^{2+}).

4.2.3 Inorganic fertilisers and farmyard wastes

The following artificial fertilisers, commonly used by farmers in counties Kildare and Carlow, were collected in Oak Park RC on April 2003: calcium ammonium nitrate (CAN),

Nitrosulphur, Super Net, 24-2.5-10 (N-P-K) and 10-10-20 (N-P-K). Such samples were ground and kept in a dessicator in the dark until isotopic analyses were carried out. In addition, ammonium nitrate used for the Oak Park soil lysimeter experiments in Johnstown Castle was collected in November 2003 and identically ground and put in a dessicator. Samples of farmyard organic wastes applied to the experimental fields in Moorepark RC were collected in Moorepark RC prior to their application. One sample of slurry was collected in April 2004, and sixteen samples of dairy wastewater in November 2003. Samples were first kept in a fridge at 4 °C before being frozen at -75 °C.

4.3 Conventional chemical analyses

All the laboratory equipment described in this section (i.e. glassware, spatulas, filters) was cleaned first with tap water and then with distilled water. Dilutions and standard solutions were prepared with distilled water. High quality distilled water was generated by an Elgastat Option 4 water purifier. Resistivity was typically higher than 5 MΩ-cm at 25 °C (Elga Ltd, 1993), and microorganisms were destroyed by ultra-violet light. To ensure that no contamination was caused by washed equipment, distilled water was regularly checked for several ion concentrations: nitrate, sulphate and chloride concentrations proved below detection with the ion chromatography.

4.3.1 Temperature and conductivity

Groundwater temperature (°C) and conductivity (μS/cm) were measured on site with a WTW Multiline P4 multimeter. Beforehand, conductivity was checked with a 0.01M KCl solution (1413 μS/cm at 25 °C).

4.3.2 pH and alkalinity

Alkalinity and pH were both measured within 12 hours following sample collection. The pH was measured with 25 ml of unfiltered sample using a Jenway 3030 pH meter calibrated with two Reagecon buffered solutions (pH_1 = 7 and pH_2 = 10). The sample was not stirred, and pH was recorded after a few seconds stabilisation (Clesceri *et al.*, 1989).

Subsequently, alkalinity was measured from the same 25 ml of unfiltered sample, with an automatic titrator Metrohm 715 Dosimat. The stirred sample was titrated in less than two min with a 0.01M H_2SO_4 solution until pH 4.50 was reached (Clesceri *et al.*, 1989). The volume of titrant (H_2SO_4 solution) was then recorded and alkalinity was calculated as follows in equation 4.1:

$$\text{Alkalinity (mg/l as } CaCO_3) = \text{x ml titrant} \times 40 \qquad \text{(Equation 4.1)}$$

4.3.3 Nitrate, sulphate and chloride concentrations

- Instrumentation

Nitrate, sulphate and chloride concentrations were measured within twenty-four hours following sample collection. Two methods were used:

- For the measurement of NO_3^- concentration (in fact $NO_3^- + NO_2^-$): automated cadmium reduction method (Clesceri *et al.*, 1989) was undertaken with a Bran & Luebbe Auto-Analyser AA3.
- For the measurement of SO_4^{2-} and Cl^- concentrations: ion chromatography method (Clesceri *et al.*, 1989) was undertaken with a Dionex 2010i system (electrochemical suppressed conductivity system with an anion exchange column). Nitrate concentration was measured for all samples collected after June 2003 and cross-checked with AA3 results for quality assurance (section 4.3.6).

- Procedure for the cadmium reduction method (Auto-Analyser AA3)

All samples were diluted ten fold with a Hamilton Microlab 500 series dilutor, and then run with the Auto-Analyser AA3 in twenty-nine batches. Most samples would have otherwise displayed nitrate concentrations higher than the drinking water limit of 11.3 mg/l NO_3-N (i.e. 50 mg/l NO_3^-), which was unsuitable for the AA3, which cannot measure concentrations that exceed 4 mg/l NO_3-N (i.e. 17.7 mg/l NO_3^-). A few samples with very low nitrate levels (i.e. below 5 mg/l NO_3^- undiluted) were re-run separately and undiluted afterwards. Because each sample run with the Auto-Analyser AA3 was triplicated, all nitrate concentrations referred to throughout this thesis represent the average value of these three measurements.

The calibration curve consisted of 5 points: 4, 2, 1, 0.5 and 0 mg/l NO_3-N (i.e. 17.7, 8.9, 4.4, 2.2 and 0 mg/l NO_3^-). Standards used for the calibration curve were prepared with a Reagecon certified 1000 mg/l NO_3-N stock solution. Each batch began with distilled water, followed by a blank sample in order to check that no contamination was generated by the procedure (section 4.3.6). Quality controls were inserted in each of the twenty-nine analytical runs, and data were corrected in regard of the QCs' mean calculated value (section 4.3.6). Because no nitrite had been detected with the ion chromatography, and because the AA3 Auto-Analyser measured total oxidised nitrogen (i.e. nitrate plus nitrite), it was established that concentrations measured were totally due to nitrate.

- Procedure for the ion chromatography method

At the time the AA3 was running, identically-treated and ten-fold-diluted samples were also analysed using ion chromatography for sulphate and chloride in twenty-four batches. Because of technical problems, nitrate concentration could only be measured after June 2003 in thirteen batches, to be compared with Auto-Analyser AA3 results as part of the quality assurance procedure described in section 4.3.6. Because sample analysis with ion chromatography was much slower than with the AA3, samples were not replicated.
The calibration curve for nitrate, chloride and sulphate consisted of five mixed standards made from three Reagecon certified 1000 mg/l stock solutions. In the first, second, third, fourth and fifth standard, chloride concentrations were of 50, 33.3, 20, 10 and 5 mg/l respectively, nitrate concentrations were of 25, 16.7, 10, 5 and 2.5 mg/l NO_3-N respectively (i.e 110.7, 74, 44.3, 22.1 and 11.1 mg/l NO_3^-), and sulphate concentrations were of 50, 33.3, 20, 10 and 5 mg/l SO_4-S respectively (i.e. 150, 100, 60, 30 and 15 mg/l SO_4^{2-}). Each batch began with distilled water, followed by a blank sample in order to check that no contamination was generated by the procedure (section 4.3.6). Mixed quality controls were inserted in each of the twenty-four analytical runs, and data were corrected in regard of the QCs' mean calculated value (section 4.3.6). It should be noted that no detectable peak ever appeared at the elution time of nitrite, which confirmed the absence of nitrite in every sample.

On a few occasions, analysis with the ion chromatography failed due to technical problems. This resulted in no measured chloride or sulphate concentrations for those samples. Thirteen groundwater samples were involved: three samples from the Barrow Valley sites and all ten samples collected from Moorepark boreholes in February 2002. It

also concerned twenty four soil-water samples, nine samples from Moorepark and all samples from Knockbeg and Oak Park soil lysimeters.

4.3.4 Sodium, potassium, calcium and magnesium concentrations

Sodium, potassium, calcium and magnesium concentrations were measured within less than four weeks following sample collection by atomic absorption (Clesceri *et al.*, 1989) using a Perkin Elmer 3100 spectrometer. Ten mixed standards were prepared from four Reagecon certified 1000 mg/l stock solutions (Na^+, K^+, Mg^{2+} and Ca^{2+}) to contain concentrations of sodium, potassium, magnesium and calcium ranging between 0.5 and 15 mg/l. The upper limits of detection for Na^+, K^+, Mg^{2+} and Ca^{2+} were 3 mg/l, 6 mg/l, 1.5 mg/l and 15 mg/l respectively. Calibration for each cation consisted then of three standards, and readjustment of the non-linear calibration curve was based on the middle one using a re-slope factor. In case samples exceeded the upper limit of detection, ten times-diluted samples (with auto-diluter Hamilton Microlab 500) were also prepared. If necessary, samples were further diluted to bring them into the instrument range. To ensure that the procedure was free of contamination, blank samples (see section 4.3.6) were run alongside real samples and checked for zero values.

4.3.5 Total and faecal coliform tests

Total and faecal coliform tests were performed using the standard membrane filter technique (Clesceri *et al.*, 1989). For each total and faecal coliform test, 100 ml of water sample was filtered through a sterile GN-6 Gelman filter and a sterilised magnetic funnel within 6 hours following sample collection. Filters were then incubated in two different sterile Petri dishes (with pad) loaded with TC media (MF Endo Broth) and a FC media (M-FC Broth) respectively. TC and FC dishes were incubated at 35 °C and 44.5 °C respectively for 24 hours. When a test was positive, total coliforms appeared as metallic purple colonies and faecal coliforms appeared as blue colonies. In case there was any doubt on the result, a dish would be incubated for 24 extra hours. All equipment was sterilised at 130 °C for 30 min with an autoclave Astell Scientific ASB230. To avoid contamination, filters were carefully handled with forceps cleaned with ethanol. To ensure that the procedure did not bring any contaminants, blank samples (see section 4.3.6) were run along real samples and checked for zero.

4.3.6 Quality assurance procedures for chemical analyses

- Blank samples

Blank samples were used during anion, cation and coliform analyses to ensure that no contamination was inadvertently generated by the laboratory procedure. These blank samples, consisting of distilled water (autoclaved for coliform tests), were handled like soil-water and groundwater samples and inserted in every analytical run.

- Calibration curves

Analyses with the AA3 Auto-Analyser (nitrate) or with the ion chromatography (nitrate, sulphate and chloride) were aborted if the correlation coefficient of the calibration curve was not better than 0.999. Standards would then be re-prepared until a satisfactory calibration curve was obtained. Analyses with the atomic absorption (sodium, potassium, calcium and magnesium) were performed with a non-linear calibration curve, where the readjustment of the calibration curve was based on the middle standard using a re-slope factor.

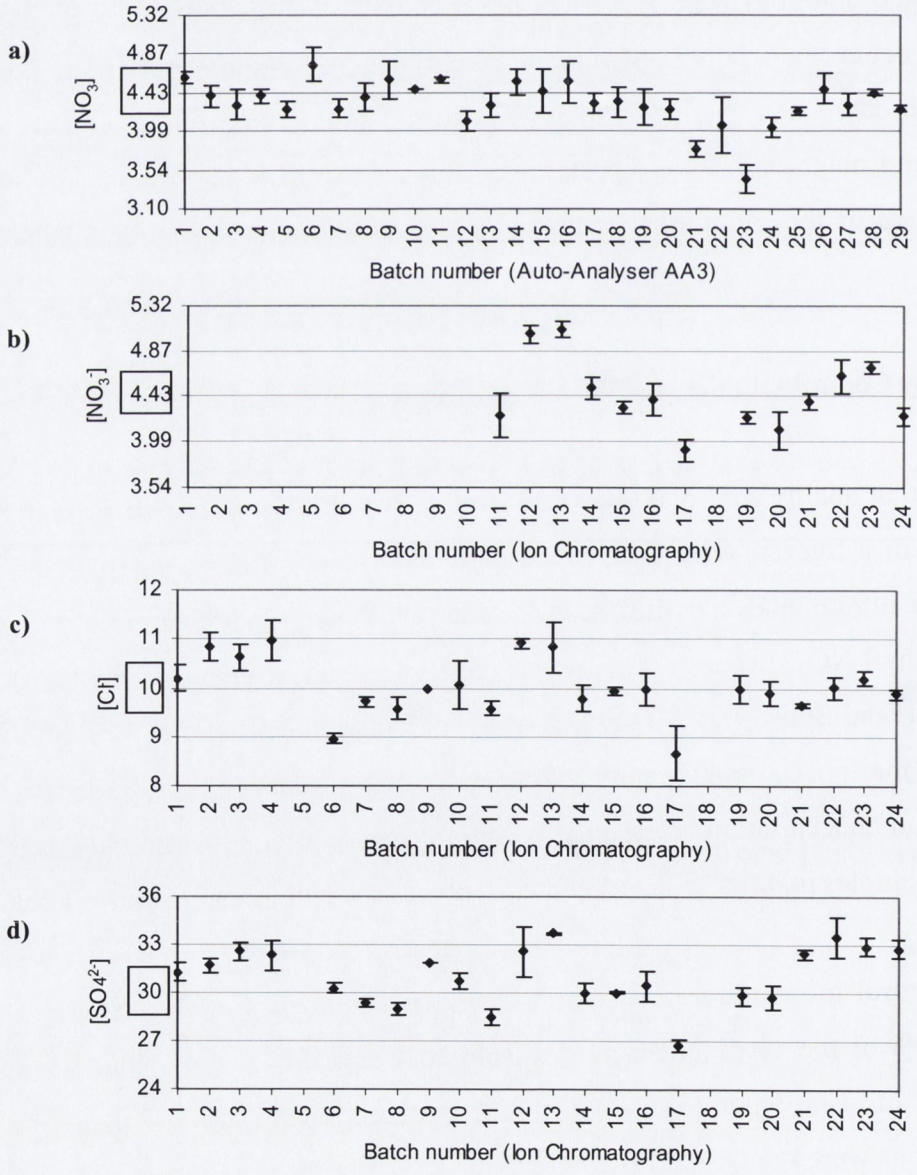
- Quality Control samples

Two different quality controls (QCs), prepared from salts by the laboratory staff and stored at -20 °C in a freezer, were used to validate anion concentration measurements (section 4.3.3). For nitrate analysis with the AA3 Auto-Analyser, QCs containing 1 mg/l NO_3-N (i.e. 4.43 mg/l NO_3^-) were inserted in each analytical run, whereas mixed QCs containing 10 mg/l Cl^- and SO_4-S (i.e. 30 mg/l SO_4^{2-}) and 1 mg/l NO_3-N (i.e. 4.43 mg/l NO_3^-) were used with the ion chromatography. No specific quality control assessment was used for major cation concentrations measured by atomic absorption. However, standards were run every ten samples in order to detect and correct for any drift in instrument readings.

Quality control mean nitrate concentrations measured with the Auto-Analyser AA3 fell within 10 % of the value given by the laboratory staff (4.43 mg/l NO_3^-) in all but two batches out of twenty-nine (figure 4.3a), with standard deviation better than 0.32. Only on two occasions were the QCs off by more than 10 %; but this was associated with technical problems that could not be solved at the time. Standard deviations smaller than 0.16 ruled

out erratic behaviour from the Auto-Analyser AA3, suggesting that the problem was consistent throughout both batches. Likewise, most of the thirteen batches run for nitrate with the ion chromatography saw their mixed QCs falling within 10 % of the 4.43 mg/l NO_3^- targeted value, with standard deviations better than 0.21 (figure 4.3b). During ion chromatography analyses, mixed QCs also displayed mean chloride and sulphate concentrations that were generally within 10 % of the values given by the laboratory staff (10 mg/l Cl^- and 30 mg/l SO_4^{2-}), with standard deviations for chloride and sulphate better than 0.6 and 1.6 respectively (figure 4.3c and figure 4.3d).

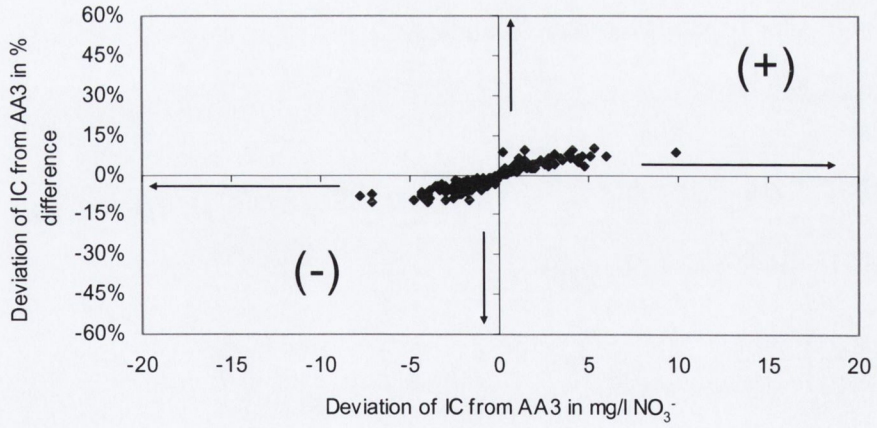
Figure 4.3: a) Nitrate mean concentrations and standard deviation for QCs analysed with the Auto-Analyser AA3 (targeted value = 4.43 mg/l NO_3^-); **b)** nitrate, **c)** chloride and **d)** sulphate mean values for mixed QCs analysed with the ion chromatography (targeted values for the mixed control = 4.43 mg/l NO_3^-, 30 mg/l SO_4^{2-} and 10 mg/l Cl^-). *(y-axis gridlines mark the 10 % deviations from targeted values)*



In order to be consistent with the corrections applied to the few batches where QC values deviated by more than 10 % from expected values, all batches were corrected for the small QC deviations observed. On the assumption that QCs were all identical and that their anion concentrations given by the laboratory staff were correct, all data were consequently corrected by a factor $QC_{theoretical}/QC_{measured}$.

Figure 4.4 shows how nitrate concentration measured with the ion chromatography compared with Auto-Analyser AA3 results over one hundred and eighty-seven water samples analysed. There was a good agreement between both analytical techniques. 93 % tested samples (174/187) being within 5 mg/l NO_3^- of the values measured by the Auto-Analyser AA3, whereas 60 % tested samples (112/187) were within 2 mg/l NO_3^-. In terms of percentage difference with Auto-Analyser AA3 results, figure 4.4 shows that 92 % tested samples (172/187) were within 10 % of the nitrate values measured by the Auto-Analyser AA3, whereas 61 % tested samples (114/187) were within 5 %. Finally, 97 % of tested samples (181/187) were either within 5 mg/l NO_3^- or 10 % of values that were measured with the Auto-Analyser AA3.

Figure 4.4: Deviation of nitrate concentration measured by the ion chromatography (IC) from nitrate concentration measured by the Auto-Analyser AA3 (in mg/l NO_3^-). *(x-axis represents the mathematical difference between IC and AA3 nitrate measurements, y-axis represents the deviation of IC measurements in % difference of AA3 results)*



It should be noted that no certified quality assurance samples were used during analyses. Nonetheless, all standards used for calibration curves were prepared from certified solutions and QCs were prepared independently from a different material (i.e. salts) in large quantities by the laboratory staff, which was deemed sufficient to ensure reliable results.

- Ion balance error calculation

The ion balance error is a useful calculation that helps detect errors in major ion concentrations in water samples. It was calculated for two hundred and sixty-one groundwater samples (see values in Appendix 3), after converting ion concentrations from mg/l to meq/l. The ion balance error (IBE) was then calculated as follows in equation 4.2:

$$IBE = (\text{cation sum} - \text{anion sum})/(\text{cation sum} + \text{anion sum}) \times 100 \qquad \text{(Equation 4.2)}$$

Ion balance error should be within at most ten percent, and preferably within five percent, although this does not guarantee that all analyses are correct because the IBE index is dominated by the major ions (generally Ca^{2+} and HCO_3^- in these samples) and errors in minor ions may remain undetected. These data displayed a median value of -2.3 % (mean of -2.6 %) and an interquartile range of 3.3. Less than three percent of these samples (seven samples) displayed IBE absolute values higher than 10 (and lower than 20), which may raise questions about which concentration(s) were wrongly measured. Nonetheless, nitrate concentration seemed beyond doubt, and it is reasonable to assume that occasional problems may have been caused by alkalinity, which proved sometimes difficult to measure. With most values around 300 mg/l $CaCO_3$, alkalinity accounts for most of the anion sum in equation 4.2, and a small overestimation (or underestimation) can then lead to a large IBE decrease towards negative values.

4.4 Isotopic analysis by CF-IRMS and sample preparation

4.4.1 Introduction to methods

- Sample preparation

$\delta^{15}N$ and $\delta^{18}O$ in water-dissolved nitrate can be measured by different means. Some of the most recent techniques involve reducing nitrate in solution into a gas that is then analysed by mass spectrometry. This can be achieved with a denitrifying bacteria, which is a technique described by Sigman *et al.* (2001) and Casciotti *et al.* (2002). The raw water sample is incubated for one day in a denitrifying medium loaded with denitrifying bacteria (*Pseudomonas chlororaphis* for measuring $\delta^{15}N\text{-}NO_3^-$ alone, or *Pseudomonas aureofaciens* for $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$). Emission of N_2O gas results from the bacterial

denitrification of the nitrate. This gas is isolated, purified, and analysed by on-line mass spectrometry for the measurement of $\delta^{15}N$ and $\delta^{18}O$. This technique is suitable for nitrate concentrations that do not exceed 0.064 mg/l NO_3^- (1 µmol/l). In case of higher concentrations, the samples must be diluted to be within range. This technique seems very reliable for $\delta^{15}N$ analyses on nitrate, but inconsistent for $\delta^{18}O$ analyses. In fact, both oxygen isotope fractionation (related to microbial nitrate reduction) and oxygen atom exchange (between N_2O and water) occur consistently during the incubation, which requires a mathematical correction.

As an alternative to the bacterial method, the chemical reduction of nitrate to nitrous oxide (prior to $\delta^{15}N$ and $\delta^{18}O$ analyses) can also be conducted by chemical means. McIlvin and Altabet (2005) described a technique that involves the use of spongy cadmium for the reduction of nitrate to nitrite, while further reduction to nitrous oxide necessitates the use of sodium azide in an acetic acid buffer.

Another method specific to the measurement of $\delta^{18}O\text{-}NO_3^-$ was described by Bräuer and Strauch (2000) and involve the use of guanidine hydrochloride. After addition to the water sample, it reduces nitrate and fixes the oxygen to CO_2. An advantage of guanidine hydrochloride is that it is a non-toxic and inexpensive reactant for tube combustion methods. The reproducibility for the guanidine method was 0.2 ‰ based on the tests carried out using KNO_3 (laboratory standard) and the IAEA-NO-3 reference material. The yield of the conversion of nitrate oxygen to CO_2 was 95–100 %.

A third method was used during this project. This technique described by Wassenaar (1995) and Silva *et al.* (2000) consists of extracting nitrate from water samples and converting it into solid silver nitrate ($AgNO_3$) that is analysed by CF-IRMS for $\delta^{15}N$ and $\delta^{18}O$. Theory behind this technique and procedure are then further described in section 4.4.2.

- Isotopic Ratio Mass Spectrometry measurements

For years, the off-line combustion and dual inlet methodology, which was described by Wassenaar (1995) and Silva *et al.* (2000) in the context of analyses on nitrate, has been successfully implemented at low temperature. For $\delta^{15}N$ and $\delta^{18}O$ analyses, the silver nitrate sample is respectively reduced to N_2 gas and combusted into CO_2 gas with the appropriate reagents. Sample and reagents are sealed into a quartz tube and put in a furnace at 850 - 860 °C for several hours. The subsequent N_2 and CO_2 gases are then analysed by IRMS

against internationally certified gas references that should have $\delta^{15}N$ and $\delta^{18}O$ values within the range of the sample.

The main problem lies in the time needed to prepare and then to combust the samples. According to Mayer *et al.* (2002), sample preparation requires at least 15 minutes and combustion at 860 °C takes 3 hours. Moreover, the machine cannot treat more than a few samples simultaneously. Nevertheless this technique has proved successful over the years with results often consistent: Silva *et al.* (2000) reported respective analytical precision of ±0.05 ‰ and ±0.5 ‰ for $\delta^{15}N$ and for $\delta^{18}O$ analyses of pure KNO_3 that was converted into silver nitrate. Furthermore many internationally certified gas references are available for these analyses.

Alternatively, a more recent technique was used during this project. This involved the on-line combustion with an elemental analyser under a continuous flow of helium, often referred as Continuous-Flow Isotopic Ratio Mass Spectrometry (CF-IRMS), which displays unquestionable advantages alongside some unfortunate drawbacks. This technique is further discussed in section 4.4.4.

On-line combustion can also be performed on liquids, especially water, to measure $\delta^{2}H$-H_2O and $\delta^{18}O$-H_2O, in place of the old equilibration technique. Gehre *et al.* (2004) or Sharp *et al.* (2001) detailed the analysis of raw water samples, whose procedure is described in section 4.4.4.

4.4.2 Nitrate extraction procedure for water samples

This step was completed within 48 hours following sample collection in order to minimise any isotopic fractionation that could be caused by sample alteration. High quality distilled water generated by Elgastat Option 4 water purifier (see comment in section 4.3) was used throughout this procedure for washing all equipment and glassware.

- Introduction to the nitrate extraction method

The technique consists of isolating nitrate from other N and O-bearing compounds and any kind of contaminant. This is achieved by passing a water sample through a column packed with highly selective anion exchange resin. Nitrate is eventually converted into solid $AgNO_3$ that is analysed by CF-IRMS for $\delta^{15}N$ and $\delta^{18}O$. The method is designed to ensure

that $AgNO_3$ samples ultimately show the same ^{15}N and ^{18}O isotopic composition as nitrate present in the original groundwater sample.

A plastic column was packed with 2 ml of resin Bio-Rad AG 1-X8 (200 - 400 mesh in chloride form, capacity of 1.2 meq/ml) that had been carefully washed with high quality distilled water. The column, which has a capacity of 2.4 meq (i.e. 2 ml × 1.2 meq/ml), can then potentially adsorb 2400 μmol of monovalent anion such as nitrate or chloride, or 1200 μmol of a bivalent anion like sulphate. The relative selectivity of this resin for common species found in groundwater is given by Bio Rad: 85 for HSO_4^-, 65 for NO_3^-, but only 22 for Cl^-, 6 for HCO_3^- and 5 for HPO_4^- (selectivity at equal concentrations). It should be noted that after packing each column, the resin was pre-conditioned by dripping through 4 ml of 1M HCl. The resin, which was kept constantly moist during the process, was subsequently rinsed with several increments of high quality distilled water.

Because suspended organic matter, DOC, phosphate, bicarbonate and sulphate are contaminants that can introduce extra N and O, which would alter the original isotopic composition of nitrates, their concentrations must be assessed beforehand. Suspended organic matter is easily removed by filtration, DOC and phosphate are often found at very low concentrations in groundwater, and bicarbonate has a very low affinity for the resin. So the main issue is sulphate, but this compound is readily precipitated and removed after addition of $BaCl_2$ before passing the sample through the resin.

The capacity of the column (2.4 meq) should never be exceeded, as overloading the column would cause the nitrate with higher $\delta^{15}N\text{-}NO_3^-$ values to exit and result in the sample being artificially depleted in ^{15}N. To prevent this, volumes of sample small enough to contain only 100μmol of nitrate are passed through the column, which also prevents DOC accumulation.Nitrate is then eluted from the resin by passing a solution of hydrochloric acid through it. The solution is neutralised after addition of a stoichiometric quantity of silver oxide Ag_2O (Silva *et al.*, 2000), and nitrate is converted to $AgNO_3$:

$$HNO_3 + Ag_2O + HCl \leftrightarrows AgNO_3 + AgCl + H_2O \qquad \text{(Equation 4.3)}$$

The reaction is exothermic and complete. This step must be completed swiftly since HNO_3 is volatile, which could cause some isotopic fractionation. A bath of ice is required to cool down the eluted solution in order to prevent volatilisation of HNO_3. After removing the

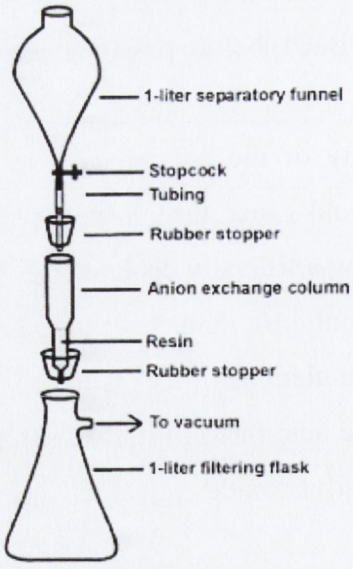
precipitate of AgCl, the solution is either freeze-dried or evaporated (Fukada *et al.*, 2003) until obtaining a solid sample of silver oxide. Ideally, this product should be white. It must be kept in the dark as it is photosensitive.

This protocol has also been successfully adapted to water samples with low nitrate concentrations and high DOC (Chang *et al.*, 1999; USGS, 2001). The main change involved the addition of a cation exchange resin column put before the anion exchange resin column in order to remove DOC with high molecular weight. The use of activated charcoal was also advised to remove low molecular weight DOC, but there is a risk that some nitrate may also be adsorbed, resulting in some isotopic fractionation (Silva *et al.*, 2000). An alternative method to clean samples was developed by Haberhauer and Blochberger (1999), and consisted of using water-insoluble polyvinylpyrrolidone polymer to adsorb and remove DOC. Panno *et al.* (2001) advised the use of a molecular sieve.

- Apparatus employed

Four sets of apparatus such as the one illustrated in figure 4.5 were used to extract nitrate from four different samples simultaneously.

Figure 4.5: Apparatus used by Silva *et al.* (2000) to extract nitrate from water samples.



Described from the top to the bottom, each apparatus consisted of:

- A 1-litre separatory funnel with a stopcock. The base of the funnel was fitted with a rubber stopper that was connected to the anion exchange resin plastic.

- A plastic column filled with 2 ml of anion exchange resin Bio-Rad AG 1-X8, 200-400 mesh in chloride form (exchange capacity of 2.4 meq, i.e. capable of adsorbing 2400 μmol of nitrate at most).
- A stopcock adapted to a rubber stopper, which was fitted the bottom of the anion exchange column and connected to the vacuum flask below (this was the only modification made to the apparatus described in figure 4.5).
- A 1-litre vacuum flask connected to a water jet filter pump.

- Procedure to extract nitrate from water samples

Because our groundwater samples were known to contain low DOC concentrations and high nitrate concentrations, it was decided to adopt the procedure described by USGS (2001) for high nitrate concentration (section 4.4.2). After nitrate and all major ion concentrations were measured, an aliquot of each sample containing 100 μmol of nitrate (i.e. 6.2 mg as NO_3^-) was portioned off into a glass container. Each aliquot would undergo five successive steps:

1. Addition of 4 ml of 1M $BaCl_2$, which can precipitate 384 mg of sulphate (along with phosphate), followed by storage at 4 °C overnight, and filtration through a 0.2 μm Whatman nylon membrane to remove the precipitate of $BaSO_4$.
2. Sample passed through the anion exchange resin column (2 ml Bio Rad AG1-X8, 200 - 400 mesh in Cl^- form) at a flow rate no faster than 1 litre/hour with great care taken to keep the resin wet at all times, resin subsequently rinsed with three increments of 5 ml of distilled water, and column eventually filled with 5 ml of deionised water before storage at 4 °C (storage for up to two years without any significant isotopic fractionation according to Silva *et al.*, 2000) until later elution.
3. Nitrate elution by passing five 3 ml increments of 3M HCl through the column (elutant kept chilled with ice bath to minimise volatilisation of HNO_3), each increment being kept in the column for at least 30 seconds before a light positive air pressure was applied to slowly blow the column dry, and subsequent rinsing with 3 ml of distilled water.
4. Immediate neutralisation of the elutant by slow addition of 6 g of Ag_2O until pH reaches 5 - 6 (checked with pH-paper), followed by filtration through a 0.2 μm Whatman nylon membrane to remove AgCl, and rinsing with distilled water.
5. The sample (about 40 ml) was frozen overnight at -75 °C, and then freeze-dried with a LabConco freeze-drier under 30 mbar and -48 °C in the collector room.

Steps 3 and 4 were completed as quickly as possible, protected from direct light. Each silver nitrate sample was then stored in a 2 ml amber vial, and placed in a dessicator in the dark for several days before analysis.

- Cleaning of silver oxide reagent Ag_2O

Cleaning the silver oxide was crucial as high grade Ag_2O purchased from Lancaster Synthesis Ltd (Morecambe, UK), at least 99 % pure, was heavily contaminated with nitrate. This problem was overcome by five successive washings of Ag_2O in a ratio 350 ml distilled water / 100 g silver oxide. The procedure adopted consisted of putting the silver oxide in a magnetic funnel fitted to a vacuum flask which was connected to a vacuum pump, filling up the funnel with distilled water, stirring for a few minutes and draining the water as far as possible. Drained water was tested for nitrate, and the washing was stopped when nitrate levels were below the detection limit of the AA3 Auto-Analyser and the ion chromatography. In addition, aliquots of drained water were also tested for sulphate and phosphate, which are O-bearing compounds. A few ml of 1M $BaCl_4$ were added to the solution to check that no (or little) precipitate was present. Once the silver oxide was deemed clean, it was oven dried at 50 °C for several days and kept in the dark.

4.4.3 Preparation of artificial fertilisers, organic wastes and water samples

Apart for silver nitrate, stable isotope ratios were also measured in other compounds. The preparation involved is described in this section.

- δ^{15}N-TN, δ^{15}N-NO_3^- and δ^{18}O-NO_3^- measurements in artificial fertilisers

A portion of each artificial fertiliser was finely ground with a pestle and mortar and desiccated for several days before δ^{15}N-TN measurement. At the same time, a portion of each artificial fertiliser that contained pre-formed nitrate (e.g. CAN) was dissolved in distilled water and nitrate was extracted as described in section 4.4.2. This step was undertaken to determine δ^{15}N-NO_3^- and δ^{18}O-NO_3^- in artificial pre-formed nitrate.

- δ^{15}N-TN measurement in slurry and dairy wastewater

Slurry and dairy wastewater samples were frozen at -75 °C before being freeze-dried.

- δ^{18}O-H_2O and δ^{2}H-H_2O measurement in water

Water samples destined for δ^{2}H and δ^{18}O analysis did not undergo any treatment. They were kept raw in their glass vials with screw cap and rubber liner in order to prevent exchange with atmospheric moist. Samples were then stored at 4 °C to minimise potential evaporation, which is the only process likely to generate isotopic fractionation.

4.4.4 CF-IRMS instruments and reference materials for solid and liquid sample analyses

- δ^{15}N-NO_3^- measurement on silver nitrate samples and other N-bearing materials

δ^{15}N analyses on solid samples (silver nitrate, fertilisers or organic wastes) were performed in Trinity College Dublin by laboratory staff with an elemental analyser Flash 1112 Series (CE Instruments, Milan, Italy) coupled to a ThermoFinnigan Delta^{Plus} isotopic ratio mass spectrometer (ThermoFinnigan MAT, Bremen, Germany) via a Conflow III Interface (ThermoFinnigan MAT). This technique, often referred to as 'flash combustion' causes the sample to be first oxidised in the reactor tube, and then reduced into N_2 gas in the reduction tube before being carried through a gas chromatography column (GC) to separate the lighter N_2 from heavier CO_2. The reactor quartz tubes, where sample oxidation takes place, were purchased from Elemental Microanalysis Ltd (Okehampton, UK) and self-packed by laboratory staff with quartz wool, copper oxide and silvered cobaltous. The only modification made from the original manufacturer's packing recommendations by the laboratory staff involved the replacement of chromic oxide by copper oxide in the oxidation tube (this is now recommended by ThermoFinnigan). In addition, porous liners were fitted inside the reactor tube to protect the oxidising reagents from residue accumulation. The reduction quartz tube was self-packed with quartz wool and reduced copper. Temperature was set at 900 °C in the reactor tube and at 650 °C for the reduction tube, whereas the post-reactor GC column was maintained at 40 °C. The run time set for each sample was 652 seconds.

An L-Alanine reference standard was run in blocks before, during, and after $\delta^{15}N$ analyses on solid samples. It was supplied by Oxford University (Palaeodiet and Stable Isotope Group, School of Archaeology) with an established $\delta^{15}N$ value of -1.66 ‰ (no standard deviation available), which was cross-checked by the laboratory staff with IAEA standards IAEA-NO-3 and IAEA-N2. High purity CP-grade nitrogen (BOC Gases Ireland, Dublin) was used as a reference gas (sometimes called monitoring gas) for the Delta^{Plus} and A-grade helium, which was also purified by an on-line Supelco filter, as a gas carrier. Data were processed using Isodat NT software, version 1.5 (ThermoFinnigan, Basel, Switzerland).

All $\delta^{15}N$ data initially measured against the N_2 gas reference were subsequently corrected to AIR using both L-Alanine measured and established $\delta^{15}N$ values (against the gas reference and AIR respectively) as described in section 4.4.5. It should be noted that all samples and standards were encapsulated in 4 × 6 mm silver boats (Santis Analytical), which were also inserted empty at the beginning of each batch for blank correction.

- $\delta^{18}O\text{-}NO_3^-$ measurement on silver nitrate samples

$\delta^{18}O$ analyses on solids (silver nitrate) were performed at QUESTOR Centre (Queen's University Belfast) by laboratory staff with a high temperature conversion elemental analyser (TC/EA) coupled to a Delta^{Plus} XP isotope ratio mass spectrometer via a Conflow III Interface (all ThermoFinnigan MAT). Samples were dropped with a Costech Zero-Blank solid auto-sampler (Pelican Scientific Ltd, Alford, UK) into the reactor where they were combusted. The product of the combustion to be analysed is carbon monoxide (CO), which is separated from the N_2 by-product by the GC column. The reactor tube consisted of an Alsint ceramic tube (Multi-Lab, Newcastle, UK) self-packed by laboratory staff with a glassy carbon tube (HTW GmbH, Thierhaupten, Germany), glassy carbon granules, silver and quartz wool. Reactor tubes were self-packed according to manufacturer's packing recommendations for solid sample analysis. Reactor temperature was set at 1350 °C while the post-reactor GC column was maintained at 95 °C. The run time set for each sample was 330 seconds.

Reference material IAEA-NO-3 (IAEA, Vienna, Austria), which established $\delta^{18}O$ value against V-SMOW has recently been adopted by the IAEA as 25.6 ±0.2 ‰ after being first reported by Böhlke *et al.* (2003), was run in blocks before, during, and after $\delta^{18}O$ analyses on silver nitrate samples. High purity carbon monoxide (CO) and helium gases, purchased from Air Products (Crewe, UK) and at least 99.995 % pure, were used for the Delta^{Plus} as

reference gas and gas carrier respectively. Data were also processed using Isodat NT software.

All $\delta^{18}O$ values, which initially measured against the CO gas reference, were subsequently corrected to V-SMOW using both IAEA-NO-3 measured and established $\delta^{18}O$ values (against the gas reference and V-SMOW respectively) as described in section 4.4.5. It should be noted that all samples and standards were encapsulated in 4 × 6 mm silver boats (Santis Analytical), which were also inserted empty at the beginning of each batch for blank correction.

- $\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O measurement on water samples

$\delta^{2}H$ and $\delta^{18}O$ analyses on liquids (water) were performed in Queen's University Belfast by laboratory staff using the same TC/EA Delta^{Plus} XP system. Samples were injected with a liquid auto-sampler (A200S, CTC, Switzerland) fitted with a 1.2 ml syringe in the reactor, where they were reduced into H_2 and CO gases and then carried through a GC column. Deviating from the manufacturer's instructions issued for solid analysis, no liner was used by the laboratory staff and the glassy carbon tube was filled with glassy carbon granules to 3-4 cm of its top. Reactor temperature was set at 1400 °C, and the GC was maintained at 85 °C.

Reference materials IAEA-OH-1 ($\delta^{2}H$-H_2O = -3.9 ‰ and $\delta^{18}O$-H_2O = -0.1 ‰) and IAEA-OH-4 ($\delta^{2}H$-H_2O = -109.4 ‰ and $\delta^{18}O$-H_2O = -15.3 ‰) were used as standards during all $\delta^{2}H$ and $\delta^{18}O$ analyses and were run before, during, and after the groundwater samples. High purity carbon monoxide (CO) and hydrogen (H_2), at least of 99.995 % purity, were used as reference gases for the Delta^{Plus} with helium as a gas carrier. Results were then corrected to $\delta^{18}O$ and $\delta^{2}H$ (V-SMOW) using the IAEA-HO-1 and IAEA-HO-4 values. Data were also processed using Isodat NT software.

4.4.5 Quality assurance procedures for CF-IRMS measurements

- Quality controls for $\delta^{15}N$ and $\delta^{18}O$ analyses and data correction

As $\delta^{15}N$ was initially measured against $\delta^{15}N$ of the N_2 gas reference, data needed to be corrected to $\delta^{15}N$ AIR, which was carried out owing to L-Alanine reference material that was inserted in blocks among solid samples (i.e. silver nitrate, fertiliser or organic wastes).

Data correction was conducted according to three steps that are described in equations 4.4 to 4.6.

While the standard true δ^{15}N-TN value against AIR is -1.66 ‰ (see section 4.4.4), L-Alanine mean δ^{15}N-TN values recorded against the N_2 gas reference for each of the seventeen batches varied between -2.1 ‰ and -1.5 ‰ (with standard deviations better than 0.1). The first step of the data correction, which is described in equation 4.4, consists of inverting the standard mean δ^{15}N-TN measured against the gas reference for each batch ($\delta^{15}N_{STD\text{-}REF}$) in order to obtain the gas reference δ^{15}N-TN value against the standard ($\delta^{15}N_{REF\text{-}STD}$).

$$\delta^{15}N_{REF\text{-}STD} = - [\delta^{15}N_{STD\text{-}REF} / (1 + \delta^{15}N_{STD\text{-}REF} /1000)] \quad \text{(Equation 4.4)}$$

In equation 4.5, the inverted value ($\delta^{15}N_{REF\text{-}STD}$) is then corrected to δ^{15}N AIR ($\delta^{15}N_{REF\text{-}AIR}$) using the standard true value against AIR ($\delta^{15}N_{STD\text{-}AIR}$) known as -1.66 ‰.

$$\delta^{15}N_{REF\text{-}AIR} = \delta^{15}N_{REF\text{-}STD} + \delta^{15}N_{STD\text{-}AIR} + (\delta^{15}N_{REF\text{-}STD} \times \delta^{15}N_{STD\text{-}AIR} / 1000)$$

(Equation 4.5)

Finally in equation 4.6, samples δ^{15}N values initially measured against the gas reference ($\delta^{15}N_{Sample\text{-}REF}$) are corrected to δ^{15}N AIR ($\delta^{15}N_{Sample\text{-}AIR}$) using the gas reference value against AIR ($\delta^{15}N_{REF\text{-}AIR}$).

$$\delta^{15}N_{Sample\text{-}AIR} = \delta^{15}N_{Sample\text{-}REF} + \delta^{15}N_{REF\text{-}AIR} + (\delta^{15}N_{Sample\text{-}REF} \times \delta^{15}N_{REF\text{-}AIR} / 1000)$$

(Equation 4.6)

Similarly, δ^{18}O data initially measured in solids against a CO gas reference was corrected to V-SMOW after applying equations 4.4 to 4.6. This required the insertion of IAEA-NO-3 reference material in blocks among silver nitrate samples, the standard mean δ^{18}O values recorded for each of the twenty analytical batches varying between 24.8 ‰ and 26.2 ‰ against the CO gas reference (standard deviations better than 1.2).

In equation 4.4, IAEA-NO-3 mean δ^{18}O value recorded against the gas reference ($\delta^{18}O_{STD\text{-}REF}$) is inverted in order to obtain the δ^{18}O value of the CO gas reference against the standard ($\delta^{18}O_{REF\text{-}STD}$). The application of equation 4.5 sees the inverted value ($\delta^{18}O_{REF\text{-}STD}$) being corrected to V-SMOW ($\delta^{18}O_{REF\text{-}VSMOW}$) using IAEA-NO-3 true δ^{18}O value ($\delta^{18}O_{STD\text{-}VSMOW}$) known as 25.6 ‰. Finally, the silver nitrate samples δ^{18}O-NO_3^- values are corrected to V-SMOW ($\delta^{18}O_{Sample\text{-}VSMOW}$) by inserting in equation 4.6 sample values

measured against the CO gas reference ($\delta^{18}O_{Sample\text{-}REF}$) and the calculated gas reference value against V-SMOW ($\delta^{18}O_{REF\text{-}VSMOW}$).

It should be noted that the literature refers to some differences between off-line and on-line in $\delta^{18}O\text{-}NO_3^-$ measurements. Révész and Böhlke (2002) showed that, whilst off-line and on-line techniques yield similar isotopic ratios for samples with $\delta^{18}O$ in the range of 21 to 25 ‰, differences become important for samples in the lower or higher range due to the oxygen isotope-exchange taking place in the off-line system. This caused confusion among isotopers when IAEA-NO-3 was used for calibration, as no $\delta^{18}O\text{-}NO_3^-$ value was internationally agreed. For instance, Révész *et al.* (1997) referred to 22.7 ±0.5 ‰ for this standard analysed by off-line combustion whereas Böhlke *et al.* (2003) referred to 25.6 ±0.2 ‰ with the on-line combustion, which is the value used in this thesis and now adopted by the IAEA. Although the difference is small, it introduces a problem for interlaboratory comparisons. On the other hand, both off-line and on-line methods agree for the $\delta^{15}N\text{-}NO_3^-$ value of IAEA-NO-3, which is reported to be of 4.72 ±0.13 ‰ (Böhlke and Coplen, 1995).

Groundwater samples analysed for $\delta^{18}O$ and $\delta^{2}H$ were run in a single batch during which IAEA-OH-1 and IAEA-OH-4 reference materials were inserted. $\delta^{2}H\text{-}H_2O$ and $\delta^{18}O\text{-}H_2O$ mean values recorded for IAEA-OH-1, whose true values are -3.9 ‰ and -0.1 ‰ respectively, were respectively measured at -3.0 ±1.6 ‰ and -0.5 ±0.2 ‰. In addition, $\delta^{2}H\text{-}H_2O$ and $\delta^{18}O\text{-}H_2O$ mean values recorded for IAEA-OH-4, whose true values are -109.4 ‰ and -15.3 ‰ respectively, were respectively measured at -107.4 ±1.7 ‰ and -15.2 ±0.3 ‰.

- Analytical precision of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{15}N$-TN measurement on solid samples

All samples were encapsulated in silver boats and duplicated. Silva *et al.* (2000) recommend the use of silver boats rather than tin boats as silver nitrate reacts with tin after several hours contact. Although some other studies recommend the addition of sucrose to sustain reduction and to improve the reproducibility (Silva *et al.*, 2000), each capsule contained only silver nitrate sample, typically around 0.8 mg. For the analysis of slurry, dairy wastewater and other N fertilisers, less than 2 mg of material was generally encapsulated. Each chromatograph was examined visually before processing, any data suspicion leading to the sample being rerun. L-Alanine standards were inserted among

duplicated samples to detect drift or analytical problems, which would have caused samples to be rerun until satisfactory and consistent $\delta^{15}N$ values were obtained.

Khayat *et al.* (2006) reported an analytical precision of ±0.1 ‰ for $\delta^{15}N$ analysis of silver nitrate samples. Results recorded for soil-water and groundwater nitrate (in Appendixes 2 and 4 respectively) conformed to this. During the analysis of three hundred and seventeen silver nitrate samples all run in duplicate, the standard deviations ranged from less than 0.001 to a maximum of 0.26, and they were less than 0.1 for 90 % of the samples (284/317). Similarly, the analysis of four silver nitrate samples resulting from the nitrate extraction process applied to four types of artificial fertilisers gave standard deviations that fell within the same range (see table 5.4). Except for one sample slightly outside that range, the standard deviation of $\delta^{15}N$-TN measurements (i.e. $\delta^{15}N$ for total nitrogen) in four dairy wastewater samples, one slurry and eight artificial fertilisers also fell within the pre-cited range of values, stretching between 0.03 and 0.24.

- Analytical precision of $\delta^{18}O$-NO_3^- measurement on silver nitrate samples

All samples were encapsulated in silver boats and duplicated. Typically, each capsule contained around 0.2 mg of silver nitrate sample. Similarly to $\delta^{15}N$ analyses, IAEA-NO-3 standards were inserted among duplicated samples to detect drifting or analytical problems. Each CO chromatograph was also examined visually and samples were rerun if necessary.

During $\delta^{18}O$ analyses of nitrate by CF-IRMS, the N_2 peak comes first and may become a nuisance if it trails and overlaps with the CO peak, which can considerably alter the $\delta^{18}O$-NO_3^- value measured from the CO peak. However, high precision (although lower than precision for $\delta^{15}N$ analysis) can generally be expected, as reported by Khayat *et al.* (2006) who observed an analytical precision of ±0.3 ‰ for measurement on silver nitrate. Again, similar standard deviations were also observed during this project. In Appendixes 2 and 4, the standard deviations for three hundred and five duplicated analyses out of three hundred and fifteen soil-water and groundwater nitrate sample measurements are reported (two samples analysed for ^{15}N were lost, and ten measurements could not be duplicated). It appears that the standard deviation varied from less than 0.001 to 2.15, and it was less than 0.5 for 79 % of the analysed samples (240/305). The standard deviations for the four silver nitrate samples of artificial fertiliser origin were within the same range, with values between 0.34 and 0.82 (see table 5.4).

- Precision of $\delta^{18}O\text{-}H_2O$ and $\delta^{2}H\text{-}H_2O$ measurement on water samples

All samples were run in triplicate, 0.36 ml being injected for each analysis. Similarly to other isotopic analyses, IAEA-OH-1 and IAEA-OH-4 standards were inserted among samples to detect drifting or analytical problems. Each chromatograph was also examined visually. $\delta^{2}H$ and $\delta^{18}O$ sample values were corrected in regard of IAEA-OH-1 and IAEA-OH-4 $\delta^{18}O$ values. During the triplicated measurement of $\delta^{2}H\text{-}H_2O$ in one hundred and fifty-seven groundwater samples, the standard deviation ranged between 0.07 ‰ and 2.46 ‰ (Appendix 4), and it was less than 1 ‰ for 86 % of the analysed samples (136/157). The triplicated measurement of $\delta^{18}O\text{-}H_2O$ of the same samples caused the standard deviation to vary between 0.01 and 1.36, and it was less than 0.2 for 91 % of the analysed samples (144/158). Similar analytical precisions were also reported by Gehre *et al.* (2004), who observed standard deviations better than 1 ‰ for $\delta^{2}H$ and about 0.1 ‰ for $\delta^{18}O$.

4.4.6 Quality assurance procedures for the nitrate extraction process

- Removal of sulphate and DOC from water samples (step 1)

Natural water samples contain some non-nitrate N and O-bearing compounds that, if found in silver nitrate samples, may compromise the reliability of the $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ measurements. These compounds are predominantly dissolved organic carbon (DOC) and sulphate, although the DOC level is typically low in most groundwaters.

Step 1 from the "Procedure to extract nitrate from water samples" in section 4.4.2 (i.e. the removal of SO_4^{2-}) was tested by checking the absence of sulphate in a solution of 100 mg/l SO_4^{2-} that had been treated with 4ml of 1M $BaCl_4$ and 0.45 μm nylon-filtered after three hours at 4 °C. This procedure proved highly effective as no detectable sulphate level was measured in the filtrate.

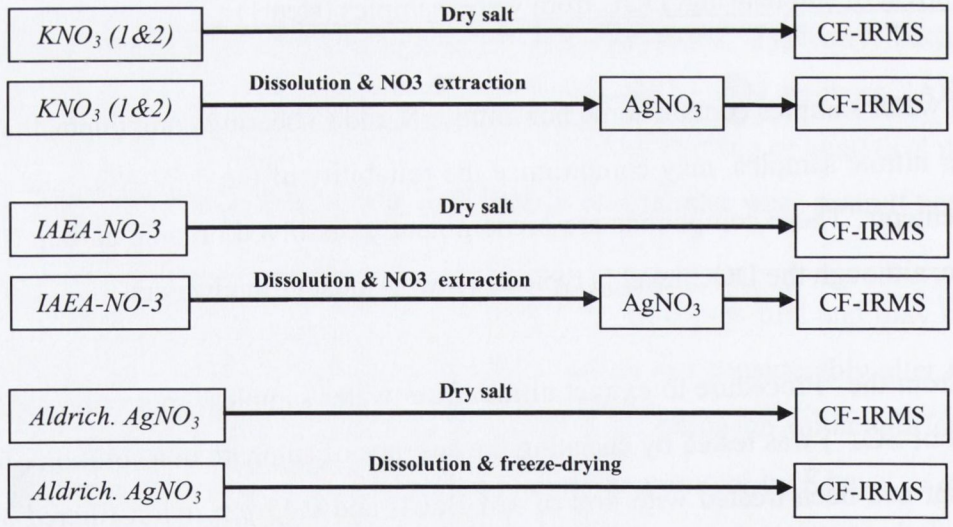
DOC is a more difficult compound to eliminate, because methods developed in the literature are either limited in their efficiency, or they cause isotopic fractionation of nitrate as a side effect. To overcome such potential problems, it was decided not to treat samples for DOC, but instead to rely on the filtration capacity of the anion exchange resin, and then to measure % C in all silver nitrate samples, which was provided by the elemental analyser

during $\delta^{15}N$ analyses. C concentration is an important parameter because it can indicate the presence of DOC that may have leaked along with nitrate during the elution of the anion exchange resin column. Hence it should be present in negligible quantities in samples free of DOC. C content was measured in two hundred and fourteen silver nitrate samples (see Appendix 2 for soil-water samples and Appendix 4 for groundwater samples), and % C was found to be higher than the detection limit in only eighteen of them. Nonetheless, % C in these samples only ranged between 1.6 and 2.5, which confirms that most silver nitrate samples were not contaminated by DOC.

- Testing of the nitrate extraction procedure (steps 2 to 5)

To ensure that no significant isotopic fractionation was occurring between sample collection and measurement, each major procedure involved in sample preparation and analysis was tested according to a plan described in figure 4.6.

Figure 4.6: Testing of the nitrate extraction procedure described in section 4.4.2.



Steps 2 to 4 from the "Procedure to extract nitrate from water samples" (section 4.4.2) were tested as follows. Three types of potassium nitrate (two commercial products taken from the shelf and an IAEA standard), whose dry salts exhibit different $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values, were dissolved in 125 ml distilled water (50 mg/l NO_3^- solutions) and converted to silver nitrate according to the protocol described in section 4.4.2. At the same time, sub-samples of these salts were desiccated for several days. The difference in $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values between KNO_3 dry salts and their converted $AgNO_3$ forms,

displayed in table 4.5, did not show any systematic trend and confirmed that little nitrate isotopic fractionation occurred during the extraction step. Conversion of KNO_3 (No.1) caused slight ^{15}N depletion and ^{18}O enrichment, conversion of KNO_3 (No.2) caused some ^{15}N enrichment and ^{18}O depletion, whereas conversion of IAEA-NO-3 showed both ^{15}N and ^{18}O depletion. Overall, the isotopic enrichment factor $\Delta_{AgNO3-\ KNO3}$ for ^{15}N varied between -0.71 ‰ and 0.08 ‰, whereas the range for ^{18}O was wider and stretched between -0.44 ‰ and 0.99 ‰. In addition, step 5, i.e. the freeze-drying step, was checked by comparing isotopic values from commercial silver nitrate and a subsample that had been dissolved and freeze-dried. The ^{15}N and ^{18}O isotopic enrichments Δ were recorded at -0.08 ‰ and -0.63 ‰ respectively. Finally, it should be noted that these test samples had been prepared with all three batches of silver oxide Ag_2O purchased from Lancaster Ltd (Dublin, Ireland) throughout this project. This was motivated by the fact that commercial silver oxide showed high levels of nitrate contamination and needed to be carefully washed with distilled water and oven-dried at 50 °C for several days prior to any use.

Table 4.5: Comparison of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values measured by CF-IRMS between reference materials (*in italic*) and converted products. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively; reference materials were dissolved in 125 ml of distilled water so that $[NO_3^-]$ = 50 mg/l)*

Type of material		$\delta^{15}N\text{-}NO_3^-$	$\delta^{18}O\text{-}NO_3^-$
KNO_3 (No.1)		*-20.36 ±0.16*	*13.41 ±0.93*
BATCH 1	Converted $AgNO_3$	-20.72 ±0.01	14.22 ±0.29
	Converted $AgNO_3$	-20.86 ±0.06	14.61 ±0.42
	Converted $AgNO_3$	-20.69 ±0.06	15.01 ±0.66
BATCH 2	Converted $AgNO_3$ *	-20.29 ±0.17	14.84 ±1.28
	Converted $AgNO_3$ *	-20.54 ±0.12	13.97 ±0.21
KNO_3 (No.2)		*-1.22 ±0.06*	*21.30 ±0.53*
Converted $AgNO_3$		-1.20 ±0.07	20.41 ±0.57
Converted $AgNO_3$		-1.08 ±0.12	21.32 ±0.23
IAEA-NO-3		*4.81 ±0.04*	*25.72 ±0.24*
Converted $AgNO_3$		4.10 ±0.23	25.38 ±0.71
Aldrich $AgNO_3$		*16.82 ±0.05*	*27.40 ±1.15*
Freeze-dried Aldrich $AgNO_3$		16.65 ±0.09	26.17 ±0.28
Freeze-dried Aldrich $AgNO_3$		16.83 ±0.22	ND

* % N ranged between 6.54 and 7.06
ND Not Determined

- Purity of silver nitrate samples

% N and % C in silver nitrate samples were measured by the elemental analyser during $\delta^{15}N$ analyses in solid samples, which provided a rough indication of each sample's purity.

Ideally, the assessment of the contamination level should be measured with % N and % O (or % N to % O ratio) in every silver nitrate sample. The comparison of both values would help determine the amount of non-nitrate oxygen present in every sample since pure silver nitrate holds 8.25 % N, 28.6 % O (i.e. 3.43 fold the mass percentage of N) and no C. Unfortunately, % O values could not be retrieved after analyses with the TC/EA ThermoFinnigan.

In accordance with the method described in section 4.4.5 for $\delta^{15}N$ and $\delta^{18}O$ data correction (see equations 4.4 to 4.6), % N and % C values were corrected to the true % N and % C values of the L-Alanine standards (15.73 % N and 40.44 % C) that were inserted during $\delta^{15}N$ analyses. It should be noted that the small standard deviations observed during L-Alanine measurements (better than 0.83 for % N and 2.16 for % C) confirmed that analyses were consistent within each of the seventeen batches.

As imperfect as this method may be in the absence of % O values, any major deviation from the ideal % N value of 8.25 may be indicative of contamination. While contaminants that contain neither N nor O do not interfere with the $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ measurements and are not a cause for concern, contamination caused by N and O-bearing compounds other than nitrate (e.g. DOC and sulphate) can be a serious issue for the measurement of reliable $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values. At the same time, deviation from the ideal % N value is also partially accounted for by the elemental analyser's accuracy and the uncertainty of each measurement.

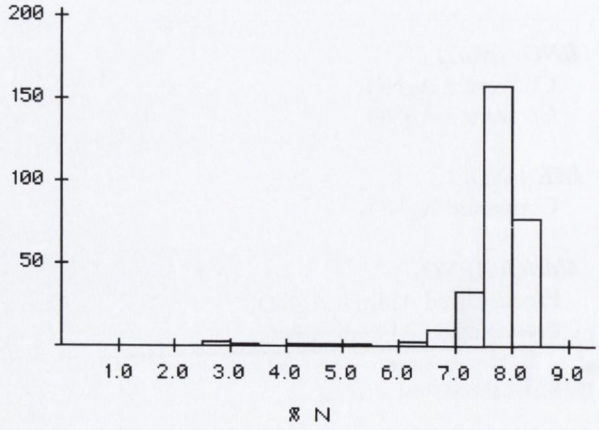


Figure 4.7: Distribution of % N in $AgNO_3$ samples prepared from water samples (n = 297).

The distribution of % N values (see Appendices 2 and 4 for soil-water and groundwater nitrate respectively) measured in two hundred and ninety seven out of three hundred and seventeen silver nitrate samples is displayed in figure 4.7. % N ranged from 1.7 to 8.3,

with a median value of 7.8 and an interquartile range of 0.4. The main body of % N values, which concerns ninety-one percent of these samples (270 out of 297), stretches between 7.0 and 8.3 and confirms that sample preparation was consistent. Conversely, five percent of the samples (16 out of 297) showed extreme outliers with low % N values below 6.3.

In the absence of DOC contamination, which was confirmed by the low C levels measured in $AgNO_3$ samples, all N accounted was assumed to be in nitrate form bound to silver. If the assumption is correct, it means that silver nitrate samples were on average ninety-five percent pure (median purity value corresponding to % N of 7.8). Unless % O is known, it may only be speculated what the nature of the impurities was, and whether or not they contain some non-nitrate oxygen. Nevertheless, % N values recorded from test samples in table 4.5 gave some evidence that any value lower than 8.25 does not necessarily affect $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ significantly. Two test samples whose mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values were of -20.41 ±0.19 ‰ and 14.40 ±0.90 ‰ respectively displayed % N ranging between 6.54 and 7.06. Nonetheless, their $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values differed only by -0.05 ‰ and 0.99 ‰ respectively from the original KNO_3 salt, which means that a substantial proportion of the impurities may only contain a small amounts of nitrogen or oxygen.

Interestingly, plotting % N against the inverse of the nitrate concentration results in a highly significant negative relationship (Spearman rank coefficient $r_s = -0.257$, $p < 0.0001$) as seen in figure 4.8. This provides evidence that samples were contaminated proportionally to the volume of original water sample that had been passed through the anion exchange resin to collect the required 100 μmol nitrate.

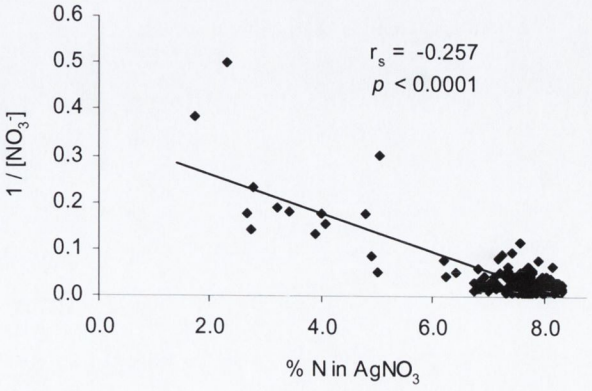


Figure 4.8: Variation of % N with $1/[NO_3^-]$. *(% N refers to AgNO3 samples; nitrate concentration refers to the original water sample and is reported in mg/l NO_3^-)*

4.5 Units and data analysis

4.5.1 Units

The metric system was used in this thesis. All concentrations were reported in mg/l. Unless stated otherwise, nitrate and sulphate concentrations were in mg/l NO_3^- and mg/l SO_4^{2-} respectively. Nitrogen, oxygen and hydrogen stable isotope ratios, which were referred to as $\delta^{15}N$, $\delta^{18}O$ and $\delta^{2}H$ respectively, were reported in permil (symbol ‰) against their respective references AIR (for $\delta^{15}N$) and V-SMOW (for $\delta^{18}O$ and $\delta^{2}H$) (see Isotope fundamentals in section 2.6.1). The following notations were used in this thesis: $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ for $\delta^{15}N$ and $\delta^{18}O$ in nitrate, $\delta^{15}N$-TN for $\delta^{15}N$ in Total Nitrogen, $\delta^{18}O\text{-}H_2O$ and $\delta^{2}H\text{-}H_2O$ for $\delta^{18}O$ and $\delta^{2}H$ in water.

4.5.2 Strategy for soil-water and groundwater data analysis

- Soil-water analysis

Analysis of soil-water chemistry and soil-water nitrate isotopic composition was undertaken in chapter 5, where i) treatment, ii) application rate and iii) depth effects were studied (see description of soil-water experiments in section 3.3). Therefore, soil-water samples were classified according to three parameters prior to data analysis:

- Type of applied nitrogenous material (no fertilisation, artificial fertiliser or animal organic wastes).
- Application rates (for Moorepark RC and Knockbeg experiments only).
- Sampling depths (for Moorepark RC experiments only).

- Groundwater analysis

Analysis of groundwater chemistry was undertaken in chapter 6 as a preliminary step towards the analysis of stable isotope data in chapter 7. The limitations of water chemistry analysis as a tool to identify nitrate sources in groundwater, and the needs for new techniques, were highlighted after comparing hydrochemical data with sites spatial characteristics, which were discussed earlier in section 3.4.2.

First groundwater chemistry was analysed alone for the Barrow Valley, groundwater sampling sites being classified according to different classes based on the exceedance of some contamination thresholds set for several chemical parameters. Exceedance of these thresholds indicated abnormal concentrations that were related, whenever possible, to either artificial fertiliser applications or organic point source contamination (farmyard and septic tank effluents), which are the two main N sources present in the study areas (section 3.2.7). The second step consisted of comparing the outcome of the chemical classification with site spatial characteristics discussed in section 3.4.2, which linked each sampling site with the % tillage within a 300 m radius, and also with N sources present within a 100 m and 300 m radius.

In chapter 7, groundwater isotopic results were analysed first in relation to site spatial characteristics. The isotopic composition of groundwater nitrate was then compared with groundwater chemistry discussed in chapter 6, where samples were classified according to the exceedance of some contamination thresholds used to characterise artificial diffuse from organic point contamination. Finally, the isotopic composition of groundwater nitrate where the origin of the contamination was well established, i.e. where spatial characteristics and hydrochemistry converged, was scrutinised as an ultimate step to test the usefulness of stable isotope tool in this complex context of mixed diffuse and point N sources.

4.5.3 Statistical analysis

Descriptive statistics were carried out on continuous variables, which included the calculation of means and standard deviations, medians, 25^{th} and 75^{th} percentile values, ranges with minimum and maximum values. Sometimes, boxplots were used to present the distribution of data around the median (explanation of the components of the boxplots in figure 4.9). Coefficients of variation (CV), which are the ratio of the standard deviation to the mean, were displayed whenever necessary.

Tests of association between chemical and/or isotopic variables were performed using Spearman's rank correlation coefficients rather than Pearson product-moment correlation coefficients because some variables were highly skewed. Regression analyses were used to check the statistical significance (p value) of such relationships, compared with thresholds set at 0.05, 0.01, 0.005 and also 0.001 levels. Regression analysis was sometimes used to

evaluate the relationships, i.e. to calculate the slope, which is an important parameter for studying denitrification.

In order to carry out statistical parametric tests, continuous variables used for the groundwater investigation had to be tested for Gaussian distribution. Normal probability plots were checked visually to spot any deviance from a straight line. Such deviance generally occurred for potassium and sodium concentrations, which were found to be extremely skewed. Usually, a log-transformation was adequate to achieve approximately normal distributions.

In order to investigate the effect of categorical independent variables on continuous dependent variables, a number of analyses of variance (ANOVA) were performed with Data Desk version 6.0 (Data Description Inc, Ithaca, USA). Where significant effects were found, LSD *Post-hoc* tests (Least Significant Difference) were used to make pairwise comparisons. Homogeneity of variance between categories of independent variables, which is a more serious assumption than that of normality according to Quinn and Keough (2003), was checked by calculating the ratio of the largest to smallest variance. Ideally, this ratio should be 1:1, and deviance by many folds can lead to either Type I (reject null hypothesis when true) or Type II error (accept null hypothesis when false).

Figure 4.9: Explanation of the components of boxplots.



The star represents a very extreme outlier

The circle represents extreme values

The horizontal bar of the "T" (whiskers) is the 75th %tile (percentile) + 1.5 × interquartile range (IQR)
The top of the box is the 75th %tile

The horizontal bar in the box is the median (the shaded area represents the 95 % confidence interval around the median)
The base of the box is the 25th %tile

The horizontal bar of the inverted "T" (whiskers) is the 25th %tile – 1.5 × IQR

CHAPTER 5: UNSATURATED ZONE INVESTIGATION: HYDROCHEMISTRY, ISOTOPE RESULTS, AND DISCUSSION

5.1 Introduction

As already mentioned in section 4.2.1, sixty-two soil-water samples were collected between 2002 and 2004 from Moorepark RC and Knockbeg sampling sites, where experimental plots were subjected to different types of fertilisation, and from lysimeters of Oak Park soil monoliths at Johnstown Castle. Chemical analyses were carried out on the water samples to measure nitrate, chloride and sulphate concentrations, whereas isotopic analysis involved the measurement of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in nitrate that had been extracted and converted into silver nitrate. In addition, isotopic analyses were also carried out on artificial fertilisers and organic N wastes used to fertilise experimental plots. Because the central aim was to investigate and understand the isotopic response of leaching nitrate to the application of artificial N fertiliser or organic N wastes, the following effects on soil-water nitrate isotopic composition were studied for each sampling site:

- Treatment effect was examined by comparing soil-water nitrate isotopic response to the application of artificial N fertiliser and organic N wastes.
- N rate effect was examined by comparing soil-water nitrate isotopic response to increasing N application rates for each treatment.
- Depth effect was examined by comparing soil-water nitrate isotopic response at two depths for each treatment at the Moorepark RC sites.

5.2 Overview of anion concentrations and nitrate isotopic composition

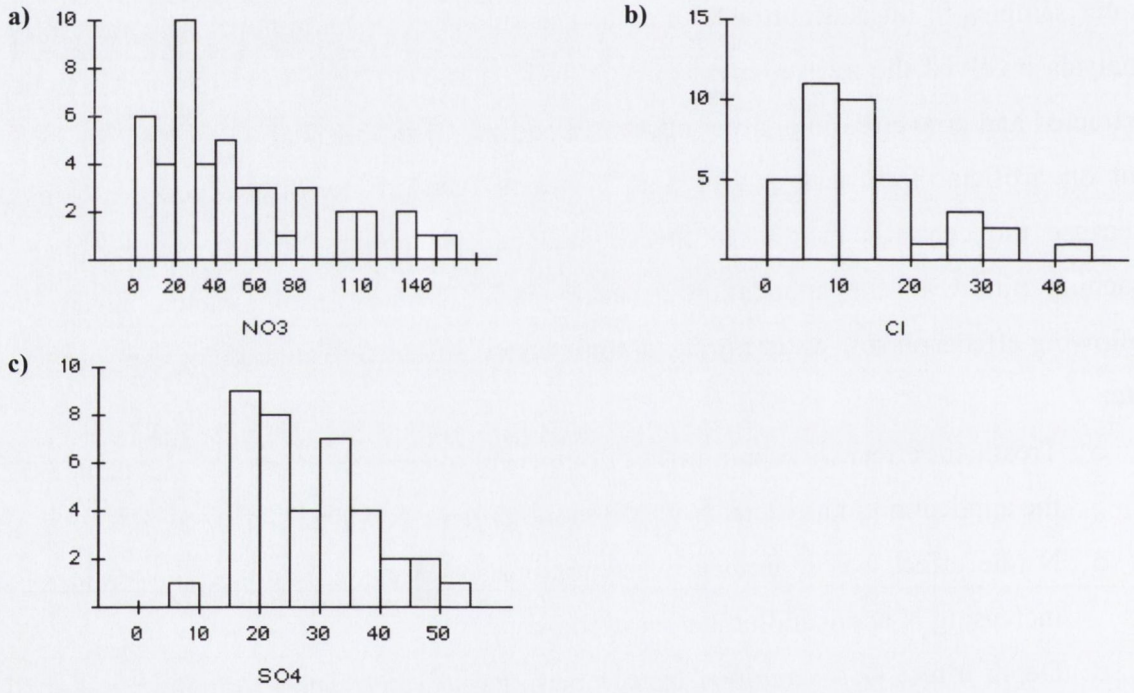
5.2.1 Nitrate, chloride and sulphate concentrations in soil-water samples

- Moorepark RC experiments

Forty-seven soil-water samples were collected between December 2002 and June 2004 from the nine grassland experimental plots in Moorepark RC where three treatments

(artificial fertiliser, dairy wastewater and slurry) and three application rates (high, medium and low) were investigated at the aggregated depths of 1.0 m and 2.5 m along with a control plot. Experimental conditions are detailed in section 3.3.1, while all the chemical data are tabulated in Appendix 2, where details for each sample include the anion concentrations, the collection date, the depth, the treatment and the application rate. The overall distributions of nitrate, chloride and sulphate concentrations measured are displayed below in figures 5.1a, 5.1b and 5.1c.

Figure 5.1: Overall distribution of **a)** NO_3^- concentrations (n = 47), **b)** Cl^- concentrations (n = 38) and **c)** SO_4^{2-} concentrations (n = 38) for Moorepark RC plots. *(on the x-axis are reported nitrate concentration in mg/l NO_3^-, chloride concentration in mg/l Cl^- and sulphate concentration in mg/l SO_4^{2-}; the frequency is reported on the y-axis)*



Overall, concentrations showed a very large range of values, which indicate that the different treatments and application rates induce highly variable leaching rates. Nitrate levels ranged from 3.5 to 150 mg/l NO_3^-, chloride concentrations ranged between 2.7 and 41.8 mg/l Cl^-, and sulphate concentrations between 7.6 and 51.4 mg/l SO_4^{2-}. It should be noted that nine chloride and sulphate results were not available due to technical problems.

Table 5.1 details how nitrate concentrations were distributed between application rates and depths within each treatment, whereas tables 5.2 and 5.3 below display the distribution between treatments of chloride and sulphate concentrations respectively.

Table 5.1: Central values and spread of nitrate concentrations in soil-water samples at Moorepark RC across the control and treatment plots at each application rate and aggregated depth (CTL for control, SLR for slurry, DW for dairy wastewater and FERT for artificial fertiliser - urea but mostly CAN). *(nitrate concentration is reported in mg/l NO_3^-, and application rates are in kg N/ha/year)*

Group	n	Application rate	Mean	SD	Median	25th %tile	75th %tile	Min	Max
CTL	**8**		25.6	5.1	24.6	21.6	29.2	19.7	34
1.0 m	4		27.1	6.6	27.2	21.6	32.7	20.1	34
2.5 m	4		24	3.2	24.6	21.6	26.3	19.7	27
SLR	**11**								
Low rate	4	53 *	7.5	6.4	4.5	3.7	11.5	3.5	17
Medium rate	2	105 *	23	9.9	23	16	30	16	30
High rate	5	160 *	12.4	8.1	7.4	6.8	20.2	5.2	22.9
1.0 m	6		7.2	4.6	6.3	4	7.4	3.5	16
2.5 m	5		19	8.9	19.3	14.2	24.7	5.7	30
DW	**12**								
Medium rate	6	171 *	43.7	18.9	49.0	21	59.9	20	63.4
High rate	6	343 *	62.7	28.3	58.4	49.9	76.2	24.2	108.8
1.0 m	6		49.8	36.2	36.3	21	76.2	10	108.8
2.5 m	6		56.6	5.7	58.1	49.9	60.5	49.7	63.4
FERT	**16**								
Low rate	2	174	35.6	11.0	35.6	27.9	43.4	27.9	43.4
Medium rate	8	286	73.2	27.4	79.4	48.4	89.7	35.4	115
High rate	6	387	130.1	18.8	136.3	112.2	143.7	101.9	150
1.0 m	8		82.9	48.4	76.9	40.15	125.6	27.9	150
2.5 m	8		96.7	33.3	89.7	79.4	124.2	43.4	143.7

* Rates estimated in section 3.3.1 from the TN concentration in dairy wastewater and slurry samples, and volumes applied

It can be seen that the lowest nitrate concentrations were not recorded in the control, but in the slurry plots, while conversely, much higher concentrations were measured in the dairy wastewater and fertiliser plots. These findings, including the surprising results for the control, are discussed in section 5.2.4. Nitrate concentrations measured in the slurry plots were at most within the range of the control. With the exception of two samples collected under medium and high rates, which matched the range of 20 to 34 mg/l NO_3^- observed in the control, all other samples from the slurry plots displayed nitrate concentration below 20 mg/l NO_3^- and as low as 3.5 mg/l NO_3^-.

Distinctively, samples from the dairy wastewater plots showed much higher nitrate concentrations. It should be noted that no sample was collected from the dairy wastewater low rate plot. With the exception of three soil-water samples (two from the medium rate and one from the high rate) for which nitrate concentrations were measured within the range of the control, all other samples from the dairy wastewater plots had nitrate concentrations above 48 mg/l NO_3^-. One sample from the high rate plot measured above 100 mg/l NO_3^-. On average, soil-water nitrate concentration in the dairy wastewater plots

was found to be higher under the high application rate than the medium rate by 10 to almost 20 mg/l NO_3^-, as reflected in median and mean values in table 5.1.

In comparison with other treatments, the artificial fertiliser plots showed the highest nitrate concentrations. Although two soil-water samples (one from the low rate plot and one from the medium) showed concentrations that were within and slightly above the range displayed by the control, concentrations measured in the other fourteen soil-water samples from the fertiliser plots were much higher. Similarly to the dairy wastewater plots, nitrate concentrations were found to increase along with increasing rates of artificial fertiliser. In fact, nitrate levels were much higher in the high rate plot, all nitrate concentrations being recorded above 100 mg/l NO_3^- and culminating at 150 mg/l NO_3^-. Most concentrations measured from the medium rate plot varied between 48 and 90 mg/l NO_3^-, and were on average lower than in the high rate plot by almost 60 mg/l NO_3^-, as seen in table 5.1.

Apart from the control plot, mean and median nitrate concentrations were found to be higher at 2.5 m than at 1.0 m. But such increase (or decrease for the control) was not necessarily meaningful. In all treatments except slurry application, the difference in nitrate concentration between both depths was much smaller than the standard deviations associated with each depth.

Similarly to what was witnessed for nitrate, higher application rates of slurry, dairy wastewater and artificial fertiliser caused higher chloride concentrations to be measured in soil-water samples, but such increases were generally moderate. Concentrations at 1.0 m and 2.5 m were very similar, differences in mean or median values between both aggregated depths being generally less than 2 mg/l. For these reasons, it was decided not to include applications rates and depths in table 5.2.

Table 5.2: Central values and spread of chloride concentrations in soil-water samples at Moorepark RC across treatment plots and the control (CTL for control, SLR for slurry, DW for dairy wastewater and FERT for artificial fertiliser). *(chloride concentration is reported in mg/l Cl^-)*

Group	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
CTL	6	7.2	1.6	7.6	6.5	8.1	4.4	9.1
SLR	5	9.4	6.9	6	4.1	16.6	2.7	17.1
DW	12	23.7	9.2	22.9	18.9	29.5	8.9	41.8
FERT	15	8.9	3.1	10.3	5.6	11.1	3.7	12.8

Little difference was observed between the control, the artificial fertiliser and the slurry treatment plots. Soil-water samples from the fertiliser plots had chloride levels that were closely matching the range of 4 to 9 mg/l seen in the control. Although concentrations measured in the slurry plots were slightly higher, which was mainly due to samples from plots with high rates of slurry application where the maximum recorded concentration reached 17 mg/l, values were still quite low. In fact, the most obvious difference was observed with the dairy wastewater treatment for which the highest chloride levels were recorded, although two samples showed low concentrations almost in the range of the control. These two samples aside, the remaining ten soil-water samples from the dairy wastewater plots showed values ranging between 19 mg/l and 31 mg/l, with an extreme high value of 42 mg/l.

Similarly to the preceding table, table 5.3 does not include application rates and depths for each treatment because results were quite homogeneous and only small differences were observed between categories. A systematic pattern was only observed for the fertiliser plots, where a higher application rate was linked to higher concentrations.

Table 5.3: Central values and spread of sulphate concentrations in soil-water samples at Moorepark RC across treatment plots and the control (CTL for control, SLR for slurry, DW for dairy wastewater and FERT for artificial fertiliser). *(sulphate concentration is reported in mg/l SO_4^{2-})*

Group	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
CTL	6	24.4	7.1	24.4	17.5	31.6	15.4	32.8
SLR	5	25	11.6	28.2	17.9	31.1	7.6	39.3
DW	12	30.5	12.3	30.6	19.3	40.4	15.4	49.5
FERT	15	29	10.5	24.6	20.4	36.8	16.3	51.4

The results show that soil-water samples from the slurry plots had sulphate concentrations very similar to values recorded from the control, which ranged between 15 and 33 mg/l SO_4^{2-}. Central values were similar in the dairy wastewater and fertiliser plots, but ranges of concentrations were wider, with maximums of around 50 mg/l SO_4^{2-}. It should be acknowledged that the missing data mentioned earlier may have introduced some bias in chloride and sulphate results. Indeed, six of the nine missing results for those two parameters affected the slurry plots alone. Hence, comparisons between slurry plots and other treatments for chloride and sulphate concentrations should be made with caution.

- Knockbeg experiments

Nine soil-water samples were collected on one occasion in March 2004 from nine tillage experimental plots in the Knockbeg site: two winter wheat plots with low application rate of CAN (187.5 N/ha/year), three winter wheat plots with high application rate of CAN (225 kg N/ha/year), two spring barley plots with low application rate of CAN and NPK compounds (105 N/ha/year) and two spring barley plots with high application rate of CAN and NPK compounds (137.5 N/ha/year). Experimental conditions are detailed in section 3.3.2, while all chemical data are available in Appendix 2, which details concentrations along with corresponding cropping system and fertiliser application rate for each sample.

Similarly to Moorepark experiments, the overall nitrate concentrations ranged from low to very high values, i.e. from 13.2 to 152.2 mg/l NO_3^-. But unlike Moorepark experiments, higher application rates were not necessarily associated with higher nitrate concentrations. In fact, the highest nitrate levels were seen in both low fertiliser application rate plots of spring barley, with concentrations of 129.5 and 152.2 mg/l NO_3^-. This apparent anomaly is discussed in section 5.2.4. The two other low rate plots, where winter wheat had been sown, exhibited concentrations slightly below or above the drinking water limit. These were lower than concentrations measured for the two high fertiliser application rate plots of winter wheat, which were around 70 mg/l NO_3^-. However, the lowest value recorded from the third high rate plot of winter wheat was 13 mg/l NO_3^-.

Across the area, soil-water nitrate levels were found to be higher in the spring barley plots than in the winter wheat plots, despite the former being subjected to lower fertiliser application rates. All spring barley soil-water samples displayed nitrate concentrations above 80 mg/l NO_3^-, whereas the highest concentration from the winter wheat samples was 71 mg/l NO_3^-.
Chloride and sulphate levels were not available because of a technical problem that affected the ion chromatography.

- Oak Park soil lysimeters experiments

Six soil-water samples were collected on one occasion in November 2003 from six Oak Park soil lysimeters set in Johnstown Castle, where grassland was subjected to a high application rate of ammonium nitrate (350 kg N/ha/year) in three lysimeters, whereas the

other three lysimeters were unfertilised controls. Experimental conditions are detailed in section 3.3, while all chemical data are available in Appendix 2, which details concentrations along with corresponding treatments for each sample. Overall, nitrate concentrations ranged between 2.6 and 60.5 mg/l NO_3^-. But important differences were observed between the controls and fertilised lysimeters. All three soil-water samples from the controls had very low nitrate concentrations (maximum was 11.4 mg/l NO_3^-) with a mean concentration of 6.8 mg/l NO_3^-, whereas fertilised lysimeters had nitrate levels between 30 and 60 mg/l NO_3^-, with a mean concentration of 52.8 mg/l NO_3^-.

5.2.2 Nitrogen and oxygen isotopic composition in N sources used for experimental plots

Nitrogen and oxygen isotope ratios were measured in eight artificial N fertilisers commonly used by Teagasc and farmers across Ireland, along with two types of organic N wastes collected and used in Moorepark RC experimental intensive dairy farm. Urea, CAN, dairy wastewater and slurry were used for the Moorepark experiments, whereas CAN and NPK compounds were used for the Knockbeg sites and ammonium nitrate for the Oak Park soil lysimeters. The chemical characteristics of such forms of N-bearing materials were discussed earlier in sections 2.3.2 and 2.3.3. $\delta^{15}N$ was measured for total nitrogen in all artificial N fertilisers and organic N wastes (slurry and dairy wastewater), as well as in the nitrate fraction extracted from artificial fertilisers (other than urea). Because most nitrogen in dairy wastewater and slurry is in non-nitrate form (i.e. organic or ammonium form according to table 2.6), no nitrate could be extracted. Therefore $\delta^{18}O$ was only measured in the nitrate fractions extracted from those artificial fertilisers containing nitrate (no $\delta^{18}O$ could be measured where there was no nitrogen in nitrate form). Results of these analyses are shown in table 5.4 below.

$\delta^{15}N$-TN measured in total nitrogen of collected fertilisers ranged between -2.4 and 2.0 ‰. The nitrate fraction of four of these fertilisers gave $\delta^{15}N$-NO_3^- values that were recorded within at least 1.9 ‰ of the value for total nitrogen. $\delta^{18}O$-NO_3^- values measured in the nitrate fraction of four fertilisers ranged between 17.2 and 20.2 ‰. The measurement of nitrogen isotope ratios in dairy wastewater collected in November 2003 yielded $\delta^{15}N$-TN value of 3.8 ‰, i.e. higher than that recorded from artificial fertilisers. In comparison, the average nitrogen isotope ratio was considerably higher in the slurry sample collected during April 2004, which had a $\delta^{15}N$ value of 10.2 ‰.

Table 5.4: $\delta^{15}N$ and $\delta^{18}O$ values measured in total nitrogen (TN) or nitrate of some organic wastes and artificial fertilisers. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively, plus or minus the standard deviation of duplicated measurements)*

N source	$\delta^{15}N$ ±SD	$\delta^{18}O$ ±SD
ARTIFICIAL FERTILISERS		
Artificial Urea (TN)	-0.4 ±0.1	N/A
CAN (TN)	-1.5 ±0.1	N/A
CAN (NO_3^- fraction)	0.4 ±0.2	18.5 ±0.3
Super Net (TN)	0.1 ±0.1	N/A
Super Net (NO_3^-fraction)	0.3 ±0.2	18.2 ±0.7
Nitro Sulfur (TN)	-1.0 ±0.2	N/A
Nitro Sulfur (NO_3^-fraction)	-0.9 ±0.2	ND
10-10-20 compound (TN)	0.3 ±0.1	N/A
10-10-20 compound (NO_3^-fraction)	-0.4 ±0.1	17.2 ±0.4
24-2.5-10 compound (TN)	2.0 ±0.1	N/A
24-2.5-10 compound (NO_3^-fraction)	ND	20.2 ±0.4
18-6-12 compound(TN)	0.2 ±0.5	N/A
18-6-12 compound (NO_3^-fraction)	ND	ND
NH_4NO_3 (TN)	-2.4 ±0.1	N/A
NH_4NO_3 (NO_3^-fraction)	ND	ND
ORGANIC ANIMAL WASTES		
Dairy wastewater (TN)	3.8 ±0.2	N/A
Slurry (TN)	10.2 ±0.2	N/A

N/A Not Applicable
ND Not Determined

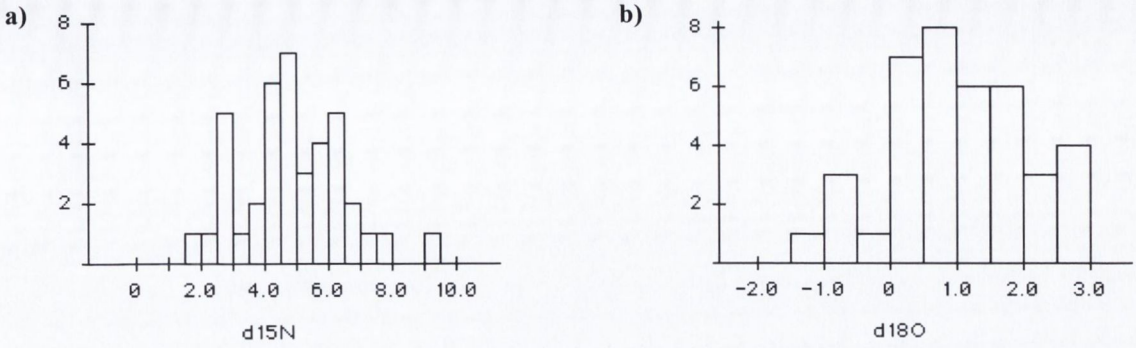
5.2.3 Nitrogen and oxygen isotopic composition in soil-water nitrate

- Moorepark RC experiments

Nitrate extraction for isotopic analyses was carried out on forty soil-water samples collected in Moorpark RC. Seven other soil-water samples, for which anion concentrations were measured, could not be processed because they did not contain enough nitrate. All isotopic data are available in Appendix 2, along with chemical data described in section 5.2.1. The resulting silver nitrate was then analysed for $\delta^{15}N$ and $\delta^{18}O$. One oxygen result was not available due to a technical problem. Figures 5.2a and 5.2b display the overall distribution of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values for all Moorepark soil-water nitrate samples.

$\delta^{15}N\text{-}NO_3^-$ showed an overall range of 7.4 ‰, from 1.8 to 9.2 ‰, whereas $\delta^{18}O\text{-}NO_3^-$ showed a narrower range of 4.3 ‰, from -1.4 to 2.9 ‰. Further description of these results for each treatment, application rate and depth is provided in sections 5.3, 5.4 and 5.5 respectively.

Figure 5.2: Overall distribution for Moorepark RC samples of **a)** $\delta^{15}N\text{-}NO_3^-$ (n = 40) and **b)** $\delta^{18}O\text{-}NO_3^-$ (n = 39). *(on the x-axis are reported $\delta^{15}N$ and $\delta^{18}O$ in ‰ against AIR and V-SMOW respectively; the frequency is reported on the y-axis)*



- Knockbeg experiments

All nine soil-water samples collected from Knockbeg yielded enough nitrate to be converted into silver nitrate. All isotopic data are presented in Appendix 2, and all chemical data are described in section 5.2.1. The range of isotopic values was much wider for oxygen isotopic ratios than in the Moorepark experiments. The overall range of $\delta^{15}N\text{-}NO_3^-$ values was 7 ‰, stretching between –0.4 and 6.6 ‰, whereas the range for $\delta^{18}O\text{-}NO_3^-$ was 16.3 ‰, varying between 0.7 and 17 ‰.

- Oak Park soil lysimeter experiments

All six soil-water samples collected from the Oak Park soil lysimeters located at Johnstown Castle yielded enough water for nitrate extraction and conversion into silver nitrate, although one oxygen result could not be retrieved due to a technical problem. All isotopic data are presented in Appendix 2, along with chemical data described in section 5.2.1. The overall range of $\delta^{15}N\text{-}NO_3^-$ values was 2.5 ‰, stretching between 0.4 and 2.9 ‰, whereas the range for $\delta^{18}O\text{-}NO_3^-$ was 6.6 ‰, varying between -1.2 and 5.4 ‰.

5.2.4 Discussion of anion concentrations in soil-water

The results described in section 5.2.1 highlight the fact that high application rates of artificial fertiliser (from 174 to 387 kg N/ha/year to grassland, from 105 to 225 kg N/ha/year to tillage) or dairy wastewater (from 171 to 343 kg N/ha/year to grassland) on

freely-draining soils can generate high nitrate leaching, hence the necessity of a technique that permits identifying the contamination source.

Overall, nitrate concentrations measured in soil-water samples collected from plots or lysimeters where artificial fertiliser was applied were consistently above the nitrate GL (guide level) of the 1980 Drinking Water Directive set at 25 mg/l NO_3^-, and up to three times higher than the nitrate drinking water limit set at 50 mg/l NO_3^- in the Drinking Water Directive (Council of the European Communities, 1998). Noticeable differences were nonetheless observed between sites, grass cover on Oak Park soil yielding nitrate concentrations that ranged between the GL and slightly above the drinking water limit, despite having one of the highest application rates. The most obvious reason is that those Oak Park soil-water samples were collected in November, which might have been too early in the recharge season to measure high nitrate levels, whereas samples from Moorepark and Knockbeg were collected after March, when nitrate had time to reach greater depths. Conversely, Knockbeg plots showed among the highest nitrate concentrations under application rates similar to Teagasc standard recommendations for tillage, which are much lower than recommendations for grassland (DE and DAFF, 1996). This feature was similarly witnessed by Hooker (2005). This is consistent with studies from the literature that often show high nitrate leaching from tillage areas (see section 2.5.2) where soils are sparsely covered by vegetation and the crop rooting system is not as extensive as in permanent grassland, so nutrient uptake is less efficient.

Although application of dairy wastewater in Moorepark was not associated with as much nitrate leaching as with artificial fertiliser, nitrate levels in soil-water samples were also consistently above the GL and up to more than twice the drinking water limit. If it is considered that dairy wastewater applied contained between 257 and 430 mg /l N (Gibbons *et al.*, 2006), then the total N inputs in the high and medium rate plots were about 343 and 171 kg N/ha/year respectively, which is less than in the high and medium rate artificial fertiliser plots. However, it should be remembered that dairy wastewater is mainly water, which induces high drainage and may consequently induce high nitrate leaching. In addition, it contains a large fraction of NH_4^+ (Gibbons *et al.*, 2006) readily available for nitrification.

High nitrate concentrations in fertiliser and dairy wastewater plots contrasted with values measured in unfertilised control plots and lysimeters, where nitrate levels were consistently around the GL or well below it. Yet, the control plot in Moorepark exhibited nitrate levels

above those from control lysimeters of Oak Park soils by more that 15 mg/l NO_3^- on average, higher than what would have been expected. As explained earlier, this could be attributed to the fact that Oak Park soil lysimeters were sampled earlier in the recharge season than Moorepark suction cups. In addition, the control lysimeters of Oak Park soils, unlike the Moorepark experimental plots, were set about fifteen years ago and probably already nitrified and leached out any of the original anthropogenic N inputs. In the case of Moorepark experiments, Gibbons *et al.* (2006) witnessed a constant decrease in nitrate leaching from the control during their monitoring period, which indicates possible continued nitrification and leaching of N applied prior to the experiment (the plots were originally in the grazing area of Moorepark RC until May 2001, i.e. a year and a half before the first sampling event of December 2002). Of initial surprise was the fact that the application of slurry (between 1.5 and 4.5 mm applied) appeared to have no influence on nitrate leaching. Gibbons *et al.* (2006) reported TN content of 3548 mg/l N in the slurry sample, which means that the application rates ranged between 53 and 160 kg N/ha/year. Yet, nitrate concentration in soil-water samples was in the range of values from unfertilised controls. The reason might be that slurry contains mainly organic nitrogen that may undergo slow mineralisation, hence low nitrate leaching.

In the Moorepark experiments only, it was also observed that increasing rates of artificial fertiliser or dairy wastewater application were associated with higher nitrate concentrations in soil-water samples. Table 5.1 displays means, medians, 25^{th} and 75^{th} percentiles that all increased with higher application rates. Increments of nearly 100 kg N/ha/year in artificial fertiliser application rate were associated with mean and median nitrate concentration increases of 40 to 60 mg/l NO_3^-. As for dairy wastewater plots, a similar increment in application rate was linked with an average increase in nitrate concentration of 10 to 20 mg/l NO_3^-. It should be noted that chloride concentrations also increased moderately with higher application rates for both types of treatment. In the Knockbeg plots where artificial fertiliser was applied, no clear pattern was observed, the highest nitrate concentration (above 120 mg/l NO_3^-) being recorded in two low rate - spring barley plots subjected to 105 kg N/ha/year. Such a trend was also witnessed by Hooker (2005) in the context of a large scale sampling at the same location. In comparison with Moorepark experimental conditions, the fertiliser application rates were much lower and the increment from low to high rate was only of 30 - 40 kg N/ha/year. Hooker suggested several explanations for these unexpected results. The first one was that lower fertiliser inputs may have caused less efficient use of soil derived N (Vinten *et al.*, 1991), which could have resulted in reduced

crop uptake in the low rate plots. Another assumption is based on the fact that nitrate losses tend to increase in proportion to N fertiliser inputs only when the optimum rate is exceeded (Shepherd *et al.*, 1993). In Knockbeg, the high application rates for both spring barley and winter wheat matched Teagasc recommendations given in the Code of Good Agricultural Practice (DE and DAFF, 1996), whereas low rates were below the recommended values. In comparison, application rates of artificial fertiliser at Moorepark were quite high when compared with Teagasc recommendations (DE and DAFF, 1996) for one cut silage (140 kg N/ha/ in May/June), or for grazed swards with stocking rate of 2.1 LU/ha (100 kg N/ha/year), grass being removed once a year from the plots around April.

The last factor of interest was the soil-water sampling depth, which was investigated in Moorepark only (table 5.1). Excluding the control plot, nitrate concentrations measured at the aggregated depths of 1.0 m and 2.5 m were found to be higher by 7 to 18 mg/l NO_3^- on average (difference between means or medians at both depths). Apart from the January application of urea to the fertiliser plots, all other applications of CAN / dairy wastewater / slurry took place after March (see section 3.3.1). Because almost all soil-water sampling was undertaken between April and June, it is likely that most of the newly applied nitrogen and nitrate did not have time to reach the sampled depths of 1.0 m nor 2.5 m at the time of collection. Rather, the nitrate sampled at these depths may have originated from the previous fertilisation, explaining higher concentrations at 2.5 m than at 1.0 m, which would reflect the nitrate migration front movement. Excluding slurry plots for which nitrate levels were very low, the average increase of 7 to 18 mg/l NO_3^- in nitrate level between both depths is nonetheless not necessarily meaningful in the view of high concentrations found in fertiliser and dairy wastewater plots.

5.2.5 Discussion of the isotopic composition of N source materials

δ^{15}N-TN and δ^{15}N-NO_3^- measured in the TN and nitrate fractions of artificial fertilisers used for the soil-water experiments (table 5.4 and section 5.2.2) showed values similar to those given in the literature for synthetic N fertiliser (section 2.6.2). δ^{15}N in TN or nitrate was measured between -2.4 ‰ and 2.0 ‰, which falls with the -4 to 4 ‰ range often found to describe the isotopic characteristics of artificial fertiliser nitrogen and nitrate (Wassenaar, 1995; Kendall and Aravena, 2000). As for δ^{18}O-NO_3^-, which can only be measured if the artificial fertiliser contains a nitrate fraction (e.g. CAN, but not urea), it

was recorded between 17.2 and 20.2 ‰ in three different fertilisers. Such values agreed with the range of 18 and 22 ‰ given by Amberger and Schmidt (1987) for oxygen isotopic ratio in the nitrate fraction of artificial fertilisers, which reflects the atmospheric origin of these synthetic compounds.

The δ^{15}N-TN measurement of 10.2 ‰ in a slurry sample collected in April 2004 agreed with the typical range of 8 to 20 ‰ reported in the literature for TN in animal solid wastes (Wassenaar, 1995; Krapac *et al.*, 2002; Karr *et al.*, 2003), although it was not exceptionally high. This might be caused by the fact that Moorepark slurry, like dairy wastewater, was stored in closed tanks, which inhibits ammonia volatilisation and decreases the consequent isotopic fractionation that can lead to slurry with higher δ^{15}N-TN values.

δ^{15}N-TN in dairy wastewater was found to be much lower than that of slurry with a value of 3.8 ‰ for samples collected in November 2003. This was higher than values recorded from artificial fertilisers described above, but it is not as high as what is generally referred to in the literature for animal wastes (section 2.6.2), although, Gormly and Spalding (1979) recorded lower δ^{15}N-TN for cow and pig excrements ranging between 1.7 and 4.8 ‰. The explanation may lie in the composition of dairy wastewater which does not only contain faeces, but also urine and milk residues. As already mentioned in section 2.6.2, urine originally displays low δ^{15}N-TN around -3 ‰, which is likely to stay low if there is little ammonia volatilisation. As for milk, typical δ^{15}N-TN values are reported between 3.5 and 5 ‰ (Kornexl *et al.*, 1997; Knobbe *et al.*, 2006) Considering the type of storage in Moorepark RC, the mixture of ^{15}N-depleted materials may explain why dairy wastewater displayed low δ^{15}N-TN values.

5.2.6 Preliminary discussion on soil-water nitrate isotopic composition

Results and interpretations of soil-water nitrate isotopic composition analysis are presented in detail in the following sections of this chapter. Treatment, application rate and depth effects on nitrate δ values are dealt with in sections 5.3, 5.4 and 5.5 respectively. Nonetheless, some preliminary comments can be made when comparing the distributions of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values in soil-water nitrate (section 5.2.3) with the isotopic composition of artificial fertilisers described above (see also table 5.4 in section 5.2.2). The range of soil-water δ^{15}N-NO_3^- values, which stretched between -0.4 and 9.2 ‰ for a total

of fifty five samples, nearly covers the range displayed in table 5.4 by artificial fertiliser and animal organic wastes or by soil organic nitrogen (range of 4 and 9 ‰, according to Heaton (1986)). In comparison, $\delta^{18}O\text{-}NO_3^-$ showed less variation. If two samples from the low rate - spring barley plots in Knockbeg, for which soil-water nitrate isotopic ratio measured was above 15 ‰, are excluded, $\delta^{18}O\text{-}NO_3^-$ values for the other fifty-one soil-water samples only ranged between -1.4 and 7.4 ‰. This encompasses the range of 0 to 5 ‰ generally given for nitrification by Durka *et al.* (1994), but it does not match values for the nitrate fraction of artificial fertilisers discussed above and displayed at around 20 ‰ in table 5.4.

5.3 Treatment effect on the isotopic composition of soil-water nitrate

5.3.1 Comparison between soil-water nitrate and N sources

- Moorepark RC experiments

Table 5.5 reviews the isotopic composition of N sources listed in table 5.4 that were used in each Moorepark treatment.

Table 5.5: $\delta^{15}N$ and $\delta^{18}O$ values for N sources of Moorepark RC experimental treatment plots (CTL for control, SLR for slurry, DW for dairy wastewater and FERT for artificial fertiliser). *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*

Treatment	Main N source	$\delta^{15}N$	$\delta^{18}O$
CTL	Soil organic N	4 to 9 *	N/A
SLR	slurry	10.2	N/A
DW	dairy wastewater	3.8	N/A
FERT	Urea	-0.4	N/A
	CAN (TN)	-1.5	N/A
	CAN (NO_3^-)	0.4	18.5

N/A Not Applicable

* $\delta^{15}N$ value widely adopted in the literature (see subsection for soil organic matter in section 2.6.2)

It should be noted that with the exception of CAN, none of these N sources contain any nitrate (or too little in the case of organic wastes), hence the absence of $\delta^{18}O$ values for these N-bearing materials in the table 5.5. Because non-nitrate forms of nitrogen are destined to undergo nitrification once present in soils, which is a process that was discussed in detail in section 2.4.1, $\delta^{18}O\text{-}NO_3^-$ values measured in soil-water nitrate

originating from the dairy wastewater / slurry / control plots were then compared with the range of values given in the literature for nitrification (see nitrification in section 2.6.3). This range was estimated by Durka *et al.* (1994) between 0 and 5 ‰ in the event of percolating water with $\delta^{18}O\text{-}H_2O$ values between -10.5 and -3 ‰, which matches the range of $\delta^{18}O\text{-}H_2O$ values measured in the Barrow Valley study area (see section 7.2.2).

The isotopic response to the application of such N-bearing materials is displayed in tables 5.6 and 5.7 in terms of soil-water nitrate isotopic composition, where $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ median and mean values are given along with range and other measures of spread.

Table 5.6: Central values and spread of $\delta^{15}N\text{-}NO_3^-$ in soil-water nitrate at Moorepark RC across treatment plots and the control (CTL for control, SLR for slurry, DW for dairy wastewater and FERT for artificial fertiliser). *($\delta^{15}N$ is reported in ‰ against AIR)*

Group	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
CTL	5	6.2	0.8	5.9	5.7	6.9	5.1	7.2
SLR	7	6.3	1.3	6.0	5.7	6.2	5.1	9.2
DW	12	5.3	1.0	4.9	4.5	6.1	4.3	7.6
FERT	16	3.4	0.9	3.7	2.6	4.1	1.8	4.9

Table 5.7: Central values and spread of $\delta^{18}O\text{-}NO_3^-$ in soil-water nitrate at Moorepark RC across treatment plots and the control (CTL for control, SLR for slurry, DW for dairy wastewater and FERT for artificial fertiliser). *($\delta^{18}O$ is reported in ‰ against V-SMOW)*

Group	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
CTL	5	0.9	0.7	0.7	0.4	1.6	0.0	1.6
SLR	7	0.8	1.1	0.7	0.1	1.7	-1.0	2.3
DW	12	1.0	0.9	1.1	0.4	1.6	-0.6	2.8
FERT	15	1.0	1.3	0.8	0.1	2.1	-1.4	2.9

The fertiliser plots, where 82 % of nitrogen input was applied as CAN and 18 % as urea (see table 3.4 in section 3.3.1), yielded soil-water nitrate with $\delta^{15}N\text{-}NO_3^-$ values ranging between 1.8 and 4.9 ‰, which was at least 1.4 ‰ higher than the highest value measured for CAN at 0.4 ‰ (and at most 4.5 ‰ higher). Meanwhile, $\delta^{18}O\text{-}NO_3^-$ in soil-water nitrate from the fertiliser plots was recorded between -1.4 and 2.9 ‰, which was more than 15 ‰ lower than that measured in the nitrate fraction of CAN. Soil-water nitrate from the dairy wastewater plots, with a $\delta^{15}N\text{-}NO_3^-$ range of 4.3 to 7.6 ‰, was ^{15}N-enriched relative to the dairy wastewater source (3.8 ‰) by at least 0.5 ‰ (by 3.8 ‰ at most). $\delta^{18}O\text{-}NO_3^-$ was found between -0.6 and 2.8 ‰, which overlapped with the lower end of the expected range generally given in the literature for nitrification. $\delta^{18}O\text{-}NO_3^-$ values from the dairy wastewater plots were in fact very similar to those from the fertiliser plot. The slurry plots, whose N source had a mean measured $\delta^{15}N\text{-}TN$ value of 10.2 ‰, yielded soil-water nitrate

with $\delta^{15}N\text{-}NO_3^-$ values between 5.1 and 9.2 ‰, which was lower than the TN value from the source by at least 1.0 ‰, and by a maximum of 5.1 ‰. $\delta^{18}O\text{-}NO_3^-$ ranged between -1.0 and 2.3 ‰, which was similar to nitrate from fertiliser and dairy wastewater plots, and once again, overlapped with the lower end of the expected range expected for nitrification. The source of nitrogen for the control plot, which was not analysed for isotopic composition, is organic soil nitrogen originating from the biomass decay, assuming no residual nitrogen effect from previous applications or grazing. In reality, the field where experimental plots were installed had been grazed until May 2001 and the input of animal faeces and urine should be acknowledged in result interpretation. It is generally established, from the extensive literature review discussed in section 2.6.2, that $\delta^{15}N$-TN in soil organic matter (coming from biomass decomposition) ranges between 4 and 9 ‰. Based on this information, $\delta^{15}N\text{-}NO_3^-$ measured in soil-water nitrate from the control was found to be within the same range, stretching between 5.1 and 7.2 ‰. As for $\delta^{18}O\text{-}NO_3^-$, it varied between 0 to 1.6 ‰, which was also very similar to the other treatment plots and fell within the lower end of the range expected for nitrification.

- Knockbeg experiments

Table 5.8 refers to the overall mean and median δ values measured in soil-water nitrate sampled in the Knockbeg experimental plots (along with ranges and measures of spread). Comparisons are made with nitrogen and oxygen isotopic compositions of CAN (for winter wheat plots), NPK compounds and Super Net (for spring barley plots) applied for the experiments and summarised in table 5.4.

Table 5.8: Central values and spread of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in soil-water nitrate at Knockbeg for fertilised plots (n = 9). *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*

Parameters	$\delta^{15}N\text{-}NO_3^-$ (‰)	$\delta^{18}O\text{-}NO_3^-$ (‰)
Mean	3.0	6.1
SD	2.4	6.0
Median	3.5	3.8
25th %tile	1.4	1.4
75th %tile	4.5	9.3
Range	-0.4 to 6.6	0.7 to 17

Isotopic values $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ measured in soil-water nitrate varied according to a much wider range than that observed in Moorepark fertiliser plots. The extent of the range was such that it actually overlapped the range of δ values measured in the applied

fertilisers, for which $\delta^{15}N$ (in TN or the nitrate fraction) was between -1.5 and 2 ‰ and $\delta^{18}O$ between 17.2 and 20.2 ‰. In fact, this overlap was mainly attributable to two samples taken from the two low application rate plots of spring barley. Both samples displayed $\delta^{15}N\text{-}NO_3^-$ of -0.4 ‰ whereas $\delta^{18}O\text{-}NO_3^-$ was measured at 15.1 and 17 ‰, which is only 0.2 ‰ lower than the lowest value recorded for the nitrate fraction of artificial fertilisers (see NPK fertiliser 10-10-20 in table 5.4). The other six soil-water nitrate samples exhibited $\delta^{15}N\text{-}NO_3^-$ values between 2.0 and 6.6 ‰, which are higher than the -1.5 to 2.0 ‰ range measured in total nitrogen and nitrate fraction of CAN, NPK compounds and Super Net by a maximum of 4.6 ‰. $\delta^{18}O\text{-}NO_3^-$ for these six samples was found to range between 0.7 to 7.4 ‰, which was lower than the lightest nitrate-fertiliser fraction by at least 10 ‰.

- Oak Park soil lysimeter experiments

Tables 5.9 and 5.10 exhibit $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ mean values and ranges recorded in soil-water nitrate sampled from fertilised and unfertilised Oak Park soil lysimeters. The isotopic composition of ammonium nitrate, which was the only type of N fertiliser applied to the fertilised lysimeters, is given in table 5.4 for $\delta^{15}N\text{-}TN$ only. Similarly to Moorepark experiments, $\delta^{18}O\text{-}NO_3^-$ values from the control lysimeter are compared with the 0-5 ‰ range of values taken from the literature for naturally nitrified nitrate (see nitrification subsection of section 2.6.3).

Table 5.9: $\delta^{15}N\text{-}NO_3^-$ values for soil-water nitrate in fertilised lysimeters (FERT) and control lysimeters (CTL) in Oak Park soil experiments at Johnstown Castle (n = 6). *($\delta^{15}N$ is reported in ‰ against AIR)*

Group	n	Mean	SD	Min	Max
CTL	3	2.6	0.3	2.3	2.9
FERT	3	0.6	0.4	0.4	1.1

Table 5.10: $\delta^{18}O\text{-}NO_3^-$ values for soil-water nitrate in fertilised lysimeters (FERT) and control lysimeters (CTL) in Oak Park soil experiments at Johnstown Castle (n = 6). *($\delta^{18}O$ is reported in ‰ against V-SMOW)*

Group	n	Mean	SD	Min	Max
CTL	3	-0.2	1.5	-1.2	1.5
FERT	2	5.2	0.4	4.9	5.4

Similarly to Moorepark and Knockbeg experiments, fertilised lysimeters of Oak Park soil produced soil-water nitrate with higher $\delta^{15}N\text{-}NO_3^-$ values than that of applied ammonium nitrate. $\delta^{15}N\text{-}NO_3^-$ in the fertilised lysimeters was within a narrow range of between 0.4

and 1.1 ‰, which is at least 2.0 ‰ higher than that observed for total nitrogen in the ammonium nitrate fertiliser (-2.4 ‰). Soil-water nitrate leached out of the fertilised lysimeters exhibited $\delta^{18}O\text{-}NO_3^-$ values between 4.9 and 5.4 ‰, which were lower than that expected for the ammonium nitrate fertiliser itself. The nitrate fraction of ammonium nitrate was not analysed, but if the assumption is made that $\delta^{18}O$ is somewhere within the 18 to 22 ‰ range given by Amberger and Schmidt (1987) for artificial fertilisers, then soil-water nitrate from the fertiliser lysimeters displays $\delta^{18}O\text{-}NO_3^-$ values that were almost 13 ‰ lower than that of the N source.

Unlike the Moorepark experiments, soil-water nitrate from the control showed $\delta^{15}N\text{-}NO_3^-$ values that were below the range of 4 to 9 ‰ expected for organic soil N by more than 1 ‰. But similarly to the Moorepark control plot, $\delta^{18}O\text{-}NO_3^-$ values from the control lysimeter were centred on 0 ‰, which overlapped with the lower end of the 0 to 5 ‰ range expected for naturally nitrified nitrate.

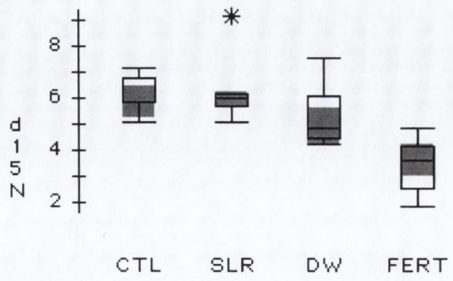
5.3.2 Comparison between treatments

This section aims to identify the impact of treatments on soil-water nitrate $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values. To do so, values are compared between treatments and control plots or lysimeters at Moorepark and Oak Park soil lysimeter experiments. This cannot apply to Knockbeg because all plots were subjected to similar applications of artificial fertilisers and there was no unfertilised control.

- Moorepark RC experiments

Figures 5.3 and 5.4 show how $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ measured in soil-water nitrate in the Moorepark experiments are distributed around the median for each treatment and the control. While the preceding section dealt with differences in isotopic composition between soil-water nitrate and predicted values for the source of N applied to the experimental plots, the following figures and comments focus on isotopic differences between treatments.

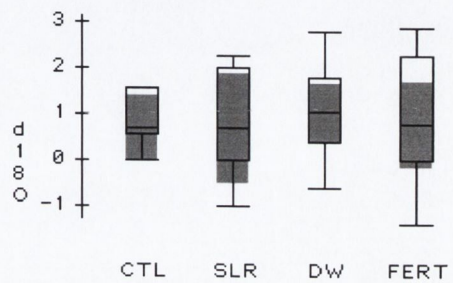
Figure 5.3: Distribution of $\delta^{15}N\text{-}NO_3^-$ values measured in soil-water nitrate from the following Moorepark treatments: control plot (CTL, n = 5), slurry plots (SLR, n = 7), dairy wastewater plot (DW, n = 12) and artificial fertiliser plots (n = 16). *($\delta^{15}N$ is reported in ‰ against AIR)*



Although the range of $\delta^{15}N\text{-}NO_3^-$ values was consistently lower in the fertiliser plot than in other treatments and the control, an overlap was observed between 4 and 5 ‰ with the lower end of the range of values from the dairy wastewater treatments. This overlap was attributed to two samples collected from the low rate fertiliser plot that showed $\delta^{15}N\text{-}NO_3^-$ values of 4.4 and 4.9 ‰, whereas the lowest value from the dairy wastewater plots was recorded at 4.3 ‰. These two samples were also associated with the lowest nitrate concentrations reported in the fertiliser treatment plots, of 28 and 43 mg/l NO_3^- (section 5.2.1). Conversely, the high fertiliser rate plots, which were associated with the highest nitrate concentrations (102 to 150 mg/l NO_3^-, see section 5.2.1), exhibited all but one of the lowest $\delta^{15}N\text{-}NO_3^-$ values of Moorepark experiments, within a 2.4 to 2.9 ‰ range.

Figure 5.3 also highlights the fact that slurry and control $\delta^{15}N\text{-}NO_3^-$ values were encompassed within the dairy wastewater treatments range (4.3 - 7.6 ‰), with the exception of one outlier from the slurry plots. Yet, eight of the twelve soil-water nitrate samples from the dairy wastewater treatments displayed $\delta^{15}N\text{-}NO_3^-$ values confined between 4.3 and 5.1 ‰, edging towards the lower end of the range of control values. Soil water nitrate from slurry treatments displayed $\delta^{15}N\text{-}NO_3^-$ values that were even more closely matched by the control plot. All values, except for one outlier, were seen within the range of the control, i.e. between 5.1 and 7.2 ‰. This was observed regardless of the slurry application rate, no soil-water sample from the slurry plots having nitrate concentrations higher than in the control (section 5.2.1).

Figure 5.4: Distribution of $\delta^{18}O\text{-}NO_3^-$ values measured in soil-water nitrate from the following Moorepark treatments: control plot (CTL, n = 5), slurry plots (SLR, n = 7), dairy wastewater plot (DW, n = 12) and artificial fertiliser plots (n = 15). *($\delta^{18}O$ is reported in ‰ against V-SMOW)*

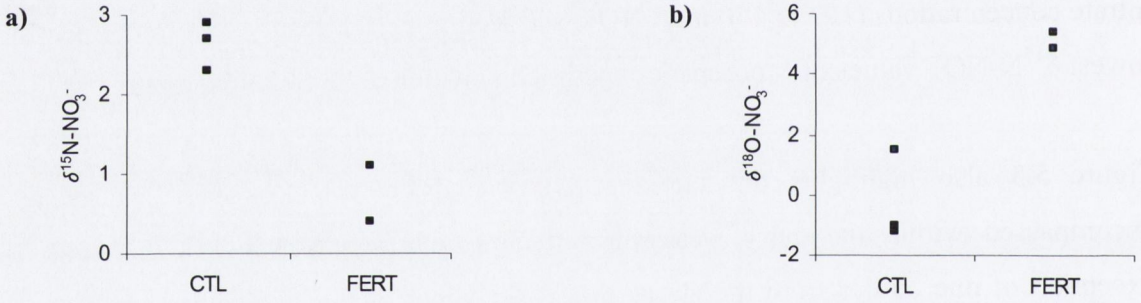


δ^{18}O-NO_3^- values followed a different pattern to δ^{15}N-NO_3^- values. Figure 5.4, which gives an overview of the distribution within and between treatments, shows that all values were within the range displayed by soil-water nitrate from the fertiliser treatments, i.e. between -1.4 and 2.9 ‰. Even the high fertiliser rate plot did not show any distinctive values. In fact δ^{18}O-NO_3^- values from this plot were recorded between 1.2 and 2.9 ‰, which is a range that widely overlaps with values from all dairy wastewater, slurry and control plots.

- Oak Park soil lysimeter experiments

Figures 5.5a and 5.5b show how δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values measured in soil-water nitrate are distributed in the fertilised lysimeter and the control.

Figure 5.5: Distribution of **a)** δ^{15}N-NO_3^- (n = 5) and **b)** δ^{18}O-NO_3^- values (n = 5) in fertilised lysimeters (FERT) and control lysimeters (CTL) in Oak Park soil experiments at Johnstown Castle. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*



Some contrast was observed between the fertilised lysimeters and the unmanaged controls. Soil-water nitrate from the fertilised lysimeters displayed the lowest δ^{15}N-NO_3^- along with the highest δ^{18}O-NO_3^- values. δ^{15}N-NO_3^- value from fertilised lysimeters culminated at 1.1 ‰, which was 1.2 ‰ lower than the lowest value recorded from the controls (2.3 ‰). At the same time, δ^{18}O-NO_3^- values from the fertilised lysimeters ranged between 4.9 and 5.4 ‰, i.e. at least 3.4 ‰ higher than the highest value from the controls. Importantly, soil-water nitrate from the fertilised lysimeters was associated with nitrate concentrations that were three to times higher than in the control lysimeters. Nitrate levels in the fertilised lysimeters ranged between 30 and 60 mg/l NO_3^-, whereas levels in the control were found to be only between 2.6 and 11.4 mg/l NO_3^- (section 5.2.1).

5.3.3 Correlation between soil-water nitrate δ variables and anion concentrations

This section presents relationships between isotopic and chemical variables for different treatments (application of artificial fertiliser, organic waste and unfertilised controls) using the Spearman's rank correlation coefficients. While these coefficients cannot be taken as a definite guide to relationships, owing to correlations forced by outliers or the possibility of non-linear relationships (which can be the case with isotopes - see Equation 2.14), they provide a useful first indication of the main inter-variable relationships worthy of further exploration. Such relationships are further explored in section 5.4.1, where application rate effects are discussed.

- Application of artificial fertilisers

Tables 5.11 and 5.12 display Spearman's rank correlation coefficients in correlation matrices that include nitrate concentrations and nitrate isotopic composition, along with other anion concentrations, for (artificial) fertiliser treatment plots in Moorepark and Knockbeg respectively. Oak Park soil lysimeters results are not included in this section because not enough samples were collected.

Table 5.11: Correlation matrix of Spearman's rank r_s values between soil-water dependent variables within fertiliser treatment plots in Moorepark RC sampling site ($p \leq 0.05$ in bold, $p \leq 0.01$ in bold and single-underlined, $p \leq 0.001$ and double-underlined).

	$[NO_3^-]$	$\delta^{15}N\text{-}NO_3^-$	$\delta^{18}O\text{-}NO_3^-$	$[SO_4^{2-}]$	$[Cl^-]$
$[NO_3^-]$	1				
$\delta^{15}N\text{-}NO_3^-$	**-0.886**	1			
$\delta^{18}O\text{-}NO_3^-$	**0.691**	**-0.755**	1		
$[SO_4^{2-}]$	**0.767**	**-0.629**	0.403	1	
$[Cl^-]$	**0.699**	**-0.586**	**0.551**	0.472	1

Table 5.12: Correlation matrix of Spearman's rank r_s values between soil-water dependent variables within fertilised plots in Knockbeg sampling site ($p \leq 0.05$ in bold, $p \leq 0.001$ and double-underlined).

	$[NO_3^-]$	$\delta^{15}N\text{-}NO_3^-$	$\delta^{18}O\text{-}NO_3^-$
$[NO_3^-]$	1		
$\delta^{15}N\text{-}NO_3^-$	**-0.946**	1	
$\delta^{18}O\text{-}NO_3^-$	**0.8**	**-0.711**	1

Among the Moorepark fertiliser plots and the Knockbeg site, all but two correlations between dependent variables were significant ($p \leq 0.05$), with the absolute values of Spearman's rank correlation r_s values ranging between 0.551 and 0.946. In both Moorepark

and Knockbeg fertiliser plots, nitrate concentrations in soil-water were negatively correlated with $\delta^{15}N\text{-}NO_3^-$ (r_s = -0.886 and -0.946 respectively, $p \leq 0.001$) while positively correlated with $\delta^{18}O\text{-}NO_3^-$ (r_s = 0.691 and 0.8 respectively, $p \leq 0.05$). In other words, the higher the nitrate concentration, the more ^{15}N-depleted (low $\delta^{15}N\text{-}NO_3^-$) and the more ^{18}O-enriched (high $\delta^{18}O\text{-}NO_3^-$) soil-water nitrate was.

In Moorepark fertiliser plots, the regression lines drawn from the plotting of nitrate concentration (y coordinate) against $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ (x coordinates) have slopes of -38 and 21.7 respectively. In comparison, relationships involving the same variables for the Knockbeg plots gave regression slopes of -15.6 and 6 respectively. At the same time, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were negatively correlated in both Moorepark and Knockbeg fertiliser plots (r_s = -0.755 and -0.711 respectively, $p \leq 0.05$), which is a feature not seen in any other treatment. The linear regression lines for Moorepark and Knockbeg had slopes of -1.13 and -2.1 respectively, which is further discussed in section 5.4.1.

Chloride and sulphate concentrations, measured in Moorepark only, were positively correlated with nitrate concentrations ($p \leq 0.01$) and behaved with $\delta^{15}N\text{-}NO_3^-$ like nitrate did, showing significant negative correlations ($p \leq 0.05$). The plotting of chloride and sulphate concentrations against $\delta^{15}N\text{-}NO_3^-$ yielded linear regression slopes of -2.16 and -6.8.

- Application of organic waste N

Tables 5.13 and 5.14 show Spearman's rank correlation coefficients in correlation matrices that include nitrate concentrations and nitrate isotopic composition, along with other anion concentrations, for Moorepark dairy wastewater and slurry treatment plots respectively.

Table 5.13: Correlation matrix of Spearman's rank r_s values between soil-water dependent variables within dairy wastewater treatment plots in Moorepark RC sampling site ($p \leq 0.05$ in bold).

	$[NO_3^-]$	$\delta^{15}N\text{-}NO_3^-$	$\delta^{18}O\text{-}NO_3^-$	$[SO_4^{2-}]$	$[Cl^-]$
$[NO_3^-]$	1				
$\delta^{15}N\text{-}NO_3^-$	-0.194	1			
$\delta^{18}O\text{-}NO_3^-$	0.098	**0.672**	1		
$[SO_4^{2-}]$	-0.147	-0.134	0.186	1	
$[Cl^-]$	**0.629**	0.304	**0.607**	-0.07	1

Table 5.14: Correlation matrix of Spearman's rank r_s values between soil-water dependent variables within slurry treatment plots in Moorepark RC sampling site (no correlation with $p \leq 0.05$).

	$[NO_3^-]$	$\delta^{15}N\text{-}NO_3^-$	$\delta^{18}O\text{-}NO_3^-$	$[SO_4^{2-}]$	$[Cl^-]$
$[NO_3^-]$	1				
$\delta^{15}N\text{-}NO_3^-$	0.214	1			
$\delta^{18}O\text{-}NO_3^-$	-0.679	-0.286	1		
$[SO_4^{2-}]$	0.7	1*	-1*	1	
$[Cl^-]$	0.7	1*	-1*	0.7	1

* Concerns only two samples

Unlike artificial fertiliser applications, the application of organic waste N in Moorepark RC, in the form of dairy wastewater and slurry, was not associated with strong correlations between nitrate δ values and anion concentrations. Among Moorepark dairy wastewater and slurry plots, only three correlations were significant ($p \leq 0.05$), all from the dairy wastewater treatment (table 5.13). Distinctively from the fertiliser plots, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ variables in the dairy wastewater plots were positively correlated ($r_s = 0.672$, $p \leq 0.05$) with a regression slope of 0.63. This relationship is further discussed in section 5.4.2 and linked to the application rate of wastewater. The other significant correlations concerned chloride, which was positively correlated with nitrate concentration ($r_s = 0.629$, $p \leq 0.05$) and $\delta^{18}O\text{-}NO_3^-$ ($r_s = 0.607, p \leq 0.05$).

- No fertilisation

Table 5.15 displays Spearman's rank correlation coefficients in correlation matrices that include nitrate concentrations and nitrate isotopic composition, along with other anion concentrations, for the Moorepark control plot.

Table 5.15: Correlation matrix of Spearman's rank r_s values between soil-water dependent variables within control plot in Moorepark RC sampling site (no correlation with $p \leq 0.05$).

	$[NO_3^-]$	$\delta^{15}N\text{-}NO_3^-$	$\delta^{18}O\text{-}NO_3^-$	$[SO_4^{2-}]$	$[Cl^-]$
$[NO_3^-]$	1				
$\delta^{15}N\text{-}NO_3^-$	-0.667	1			
$\delta^{18}O\text{-}NO_3^-$	0.051	0.553	1		
$[SO_4^{2-}]$	-0.086	0*	0.5	1	
$[Cl^-]$	0.429	-0.866	-0.5	0.314	1

* Relationship between three samples

The control plot exhibited no significant correlations between any of the variables, which may be attributed to the small number of samples involved (between three and six). In order to establish the significance of some correlations with high r_s values (e.g. $r_s = 0.866$ between chloride concentration and $\delta^{15}N\text{-}NO_3^-$), a greater number of samples is necessary.

It is nonetheless interesting to note that $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in the control plot, despite being not significant (p = 0.334) for reasons explained above, showed a trend associated with a positive r value and a slope of 0.4. This point is expanded in section 5.4.3.

5.3.4 Introduction to discussion on treatment effect

Before discussing the results presented in sections 5.3.1 to 5.3.3, it is useful to recall briefly some features related to these N-bearing materials and to the nitrification process in order to understand what can be expected from the application of artificial fertilisers or animal wastes in terms of soil-water nitrate isotopic composition. The fate of organic N contained in organic wastes is to undergo nitrification once in the soil, and this is also the fate of the non-nitrate fraction of artificial fertilisers (i.e. artificial ammonium and urea). Like most microbial reactions, nitrification generates products (i.e. nitrate) ^{15}N-depleted relative to the substrate (remaining ammonium). Isotopic fractionation may be initially large, but it declines progressively as nitrification goes on (see section 2.6.3). Consequently, $\delta^{15}N\text{-}NO_3^-$ of nitrified nitrate becomes similar to the initial isotopic composition of its source after some time. Because soil-water samples were collected during this project a few weeks to a few months after fertilisation events, isotopic fractionation associated with nitrification is not thought to be a problem. Therefore, $\delta^{15}N\text{-}NO_3^-$ may then be similar to $\delta^{15}N$ values displayed by fertilisers, dairy wastewater or slurry, which all proved noticeably different from one another in table 5.4. From the $\delta^{18}O$ point of view, the situation is quite different. Because, nitrification in soil is thought to consist of nitrogen oxidation by incorporation of oxygen from soil H_2O and O_2 (see section 2.6.3), all nitrogenous materials nitrified in soil are expected to display $\delta^{18}O\text{-}NO_3^-$ values within the same range. In other words, dairy wastewater and slurry-derived nitrate should show ^{18}O content similar to that of artificial fertiliser ammonium / urea-derived nitrate, generally between 0 and 5 ‰ (Durka *et al.*, 1994). The implications for artificial fertilisers are quite drastic. Nitrate fractions extracted from CAN and different NPK compounds used in Moorepark, Knockbeg and Johnstown Castle (Oak Park soils) showed $\delta^{18}O\text{-}NO_3^-$ values between 17.2 and 20.2 ‰, which reflects the atmospheric origin of the fertiliser nitrate-oxygen. But these artificial fertilisers also contain some ammonium that will undergo nitrification under the same conditions as organic waste nitrogen. Consequently, the application of ammonium nitrate is expected to generate soil-water nitrate with $\delta^{18}O\text{-}NO_3^-$

around 10 ‰ only (Mengis *et al.*, 2001), i.e. an intermediate value between nitrified and artificial pre-formed nitrate. For the same reasons, CAN, which contains a higher proportion of synthetic nitrate, should give rise to heavier soil-water nitrate with $\delta^{18}O\text{-}NO_3^-$ around 15 ‰. In reality, things are complicated by the fact that leached nitrate ultimately originates from a combination of natural and managed sources (see section 2.3). In addition, some reactions may alter nitrate isotopic composition during leaching (see section 2.6.3).

5.3.5 Discussion of the comparisons between soil-water nitrate and N sources

Table 5.4 showed earlier that artificial fertilisers, dairy wastewater and slurry applied to experimental plots and lysimeters during this project had different isotopic compositions with respect to their ^{15}N content. With a -2.4 to 2 ‰ range, artificial fertilisers (total nitrogen and nitrate fraction) had the lowest $\delta^{15}N$ values, whereas dairy wastewater had slightly higher $\delta^{15}N$ with a mean value of 3.8 ‰, and slurry displayed the greatest ^{15}N-enriched material of all with $\delta^{15}N$ of 10.2 ‰. Results displayed in section 5.3.1 reveal that soil-water nitrate collected from plots at Moorepark, Knockbeg and from Oak Park soil lysimeters poorly reflected the original ^{15}N content of the above nitrogenous sources that had been applied. First, soil-water nitrate collected from plots subjected to applications of artificial fertilisers was found to be consistently ^{15}N-enriched (by up to 4.6 ‰) in comparison with the fertiliser. Only two samples from Knockbeg actually fell into the range of the applied fertiliser, with low values both recorded at -0.4 ‰. With dairy wastewater applications, the range of $\delta^{15}N\text{-}NO_3^-$ in soil-water was likewise slightly higher than $\delta^{15}N$-TN of dairy wastewater itself (by up to 3.8 ‰). In contrast, soil-water from the slurry treatment plots contained $\delta^{15}N\text{-}NO_3^-$ lower than $\delta^{15}N$-TN in slurry (by up to 5.1 ‰). These findings strongly suggest that soil organic matter also contributed to the overall nitrate leaching. As often referred to in the literature, $\delta^{15}N$-TN values for soil organic nitrogen often range between 4 and 9 ‰ (see section 2.6.2 and Heaton (1986)), which is higher than values from table 5.5 measured in artificial fertilisers or dairy wastewater but lower than in slurry. Nitrification of soil organic matter would thus be expected to display $\delta^{15}N\text{-}NO_3^-$ values similar to this reported soil $\delta^{15}N$-TN range. If substantial quantities of soil organic matter are available for nitrification, then $\delta^{15}N\text{-}NO_3^-$ values elevated from the applied N source would be expected in artificial fertiliser and dairy wastewater plots, whilst $\delta^{15}N\text{-}NO_3^-$ values decreased from source would be expected in the slurry plots.

The experiments in Moorepark confirmed the assumptions made about soil organic nitrogen as the control plot yielded nitrate with $\delta^{15}N\text{-}NO_3^-$ values ranging between 5.1 and 7.2 ‰. Values from Oak Park soil controls were slightly lower (between 2.3 and 2.9 ‰), but these values, which are not unusual according to Fogg *et al.* (1998), were still higher than that measured in ammonium nitrate applied to fertilised lysimeters.

It should be noted that denitrification alone cannot explain the increase of $\delta^{15}N\text{-}NO_3^-$ in the artificial fertiliser and dairy wastewater plots. Because denitrification is more likely to occur where liquid animal wastes have been applied (due to the abundance of available carbon and possible water-logging) than in the artificial fertiliser plots, the associated isotopic enrichment of soil-water nitrate is also more likely to be significant in the slurry and dairy wastewater plots than under artificial fertiliser application. Results from the slurry treatment plots contradict this assumption since $\delta^{15}N\text{-}NO_3^-$ values in soil-water nitrate were lower than $\delta^{15}N$-TN measured in slurry.

The results in section 5.3.1 also reveal that except for two samples, $\delta^{18}O\text{-}NO_3^-$ values measured in soil-water nitrate collected from experimental plots or lysimeters subjected to applications of artificial fertilisers were all within a range of values similar to that expected for nitrification. In other words, most soil-water nitrate samples from artificial fertiliser treatments showed values far below what could have been expected from direct leaching of fertiliser. Moorepark fertiliser plots yielded nitrate with $\delta^{18}O\text{-}NO_3^-$ values between -1.4 and 2.9 ‰, whereas most of the applied fertiliser was CAN (some urea was also applied every January), which has the potential to lead to values around 15 ‰. In Oak Park soil lysimeters, $\delta^{18}O\text{-}NO_3^-$ was measured around 5 ‰, despite all applied fertiliser being ammonium nitrate, which could have led to values around 10 ‰. Similarly, all but two samples from Knockbeg plots yielded soil-water nitrate with $\delta^{18}O\text{-}NO_3^-$ between 0.7 and 7.4 ‰, whereas the fertilisers used were NPK compounds and CAN, which can potentially lead to values above 10 ‰. On the other hand, soil-water nitrate collected from controls (at Moorepark and Oak Park soil lysimeters), dairy wastewater and slurry treatment plots showed a very narrow range of $\delta^{18}O\text{-}NO_3^-$ values, between -1.2 and 2.8 ‰, which overlaps the expected lower range of the 0 to 5 ‰ given by Durka *et al.* (1994) for nitrification.

Several factors mentioned earlier in section 2.6.4 may contribute to explaining why applications of artificial fertilisers did not generate soil-water nitrate with higher $\delta^{18}O\text{-}NO_3^-$ values. Roadcap *et al.* (2002) suggested that pre-formed nitrate contained in artificial

fertilisers is rapidly taken up by plants, which might leave fertiliser-derived ammonium available for nitrification in soils, hence the absence of high $\delta^{18}O\text{-}NO_3^-$ values in soil-water nitrate. Although this hypothesis may have credence, it was dismissed by Mengis *et al.* (2001) who postulated that pre-formed nitrate is probably too mobile an anion to be entirely taken up by plants. In addition, fertiliser-derived ammonium is preferentially adsorbed by soil particles and subjected to ammonia volatilisation, which is why it does not qualify for being the main source of leached fertiliser-derived nitrate. The alternative hypothesis of Mengis *et al.* (2001) was that, in the event of artificial fertiliser applications (fertiliser containing some pre-formed nitrate), low $\delta^{18}O\text{-}NO_3^-$ values should be observed along with low $\delta^{15}N\text{-}NO_3^-$ values if Mineralisation-Immobilisation Turnover processes (MIT) occurred (see sections 2.4.1, 2.6.3 and 2.6.4). The occurrence of MIT, which would mask the original $\delta^{18}O\text{-}NO_3^-$ values without much affecting $\delta^{15}N\text{-}NO_3^-$ values, sounds plausible. As detailed by Addiscott *et al.* (1991), very little artificial nitrate applied on soils remains in its inorganic form for long, but is instead likely to be immobilised by bacteria in the topsoil and then mineralised and nitrified again if the C/N ratio is favourable.
Finally, it could also be assumed that in the case of Moorepark fertiliser plots, some soil-water nitrate that was collected may originate from the nitrification of urea that was applied in January when grass biological requirements are very low at a time of higher recharge and potential leaching. Nonetheless, the quantity of urea applied to each artificial fertiliser plot only accounts for 18 % of the total N input, which seems unlikely to account alone for the above results.

Interestingly, the two soil-water nitrate samples from Knockbeg that showed distinctly low $\delta^{15}N\text{-}NO_3^-$ values (-0.4 ‰ each) were the same samples that also showed high $\delta^{18}O\text{-}NO_3^-$ values (15.1 and 17 ‰). Both samples originated from the two low rate- spring barley plots (plots K7-Lsb and K57-Lsb in figure 3.10), which were associated with nitrate concentrations above 120 mg/l NO_3^- (see section 5.2.1), the highest nitrate levels measured in Knockbeg, and among the highest measured during the whole project. Such high nitrate leaching, associated with soil-water nitrate isotopic composition close to that of artificial nitrate, can only be explained by the direct leaching of artificial fertiliser (20-0-15 NPK compound and Super Net). This point is further discussed in section 5.4.3, after the effect of artificial fertiliser application rate was analysed in section 5.4.1.

5.3.6 Discussion of the comparison between treatments

Although the soil-water nitrate $\delta^{15}N\text{-}NO_3^-$ values poorly reflected the isotopic signature of what was applied to soils, which would have enabled nitrate of synthetic origin to be easily identified, it was still observed that plots and lysimeters subjected to applications of artificial fertiliser leached nitrate with lower $\delta^{15}N\text{-}NO_3^-$ than in other treatments or controls. Studies featuring artificial fertiliser-derived nitrate that has lower $\delta^{15}N\text{-}NO_3^-$ than animal waste-derived nitrate have often been reported (Fogg *et al.*, 1998). But differences between artificial-derived nitrate and nitrate derived from soil organic matter have been less commonly observed in the literature because both types of nitrate seemed to overlap values in many studies (Fogg *et al.*, 1998; Kendall and Aravena, 2000). In the Oak Park soil experiments for instance, the range of $\delta^{15}N\text{-}NO_3^-$ in the fertilised lysimeters was lower than in unfertilised controls, but the gap was small (1.2 ‰) and hence not necessarily meaningful. In Moorepark, the gap between values from fertiliser plots and the control was overall even smaller (0.2 ‰), though without overlap. Nevertheless, increasing application rates of artificial fertiliser seemed to widen this gap by lowering $\delta^{15}N\text{-}NO_3^-$ values in leached nitrate, which is an important point described and discussed in section 5.4.1.

Quite distinctly from fertiliser plots, $\delta^{15}N\text{-}NO_3^-$ values from dairy wastewater, slurry and control plots were higher and in a similar range, which would make it virtually impossible to differentiate one source from another. It is in fact little wonder that soil-water nitrate values from the dairy wastewater plot and the control were alike, since $\delta^{15}N\text{-}TN$ in dairy wastewater was already edging towards the lower end of the range given in the literature for soil organic nitrogen. What was initially surprising was to find $\delta^{15}N\text{-}NO_3^-$ values from the slurry plots unusually low and so different from values generally given in the literature, with nitrate around farmyards or other organic point sources generally measured between 10 and 22 ‰ (Nadelhoffer and Fry, 1994; Kendall and Aravena, 2000). Around point sources, soils are continuously soaked with animal organic wastes, which constitute a large pool of nitrogen (and carbon) available for nitrification and leaching. Under such conditions, ammonia volatilisation and denitrification are expected to cause severe isotopic fractionation. In the Moorepark slurry plots, slurry is used as a diffuse source of nitrogen that was applied only twice a year, which probably provided a much more limited supply of nitrogen that was less likely to cause extensive isotopic fractionation and very high $\delta^{15}N\text{-}NO_3^-$ values.

Unlike $\delta^{15}N\text{-}NO_3^-$, $\delta^{18}O\text{-}NO_3^-$ values from the artificial fertiliser plots varied very little when compared with other treatments and controls. This was more striking in the Moorepark experiments where all samples from the artificial fertiliser plots fell within a narrow range of -1.4 to 2.9 ‰, which happens to be similar to that displayed by soil-water samples from the control or from other plots subjected to applications of animal organic wastes. This result supports the idea that most fertiliser nitrate applied to soils was immobilised and remineralised through the MIT processes, which is consistent with comments made in section 2.5.3 (i.e. very little nitrate fertiliser stays in its inorganic form). $\delta^{18}O\text{-}NO_3^-$ values from the fertilised Oak Park soil lysimeters were higher than the range from the Moorepark fertiliser plots by 2 ‰ at least. Linked with the fact that the $\delta^{15}N\text{-}NO_3^-$ values from these lysimeters were lower than in Moorepark, this may mean that there was a higher proportion of nitrate leaching directly from the artificial fertiliser.

Despite the fact that differences in soil-water nitrate isotopic composition are limited between experimental plots subjected to applications of artificial fertiliser and organic N, the results described in this section should be seen in the more global context developed in section 5.4. There, evidence is presented indicating that the isotopic composition of soil-water nitrate may be influenced by artificial fertiliser application rate under certain conditions.

5.3.7 Discussion of correlations

Correlation matrices of Spearman's rank coefficients in section 5.3.3 highlight how soils responded differently to applications of artificial fertiliser and organic wastes. First, most relationships between isotopic and chemical variables under the artificial fertiliser treatments were highly significant. This attests to the impact that synthetic fertilisers had on soil-water quality and nitrate leaching, which makes sense considering the high solubility in water of such compounds, and the consequent rapid release of ions within soils, especially the highly mobile nitrate anion. This contrasts with organic waste treatments where most relationships were not significant.

Another difference between the application of artificial fertiliser and organic wastes, more especially dairy wastewater, arose from the plotting of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$. The positive correlation in the dairy wastewater plots is probably indicative of denitrification if

one compares the 0.63 slope found when plotting $\delta^{15}N\text{-}NO_3^-$ against $\delta^{18}O\text{-}NO_3^-$ with the 0.5 to 0.77 range that is generally given in the literature for microbial denitrification (see sections 2.6.3 and 2.6.4). A possible stimulus for denitrification is the fact that dairy wastewater application also brings in carbon, which is a suitable electron donor for nitrate reduction, and high soil moisture content, which favours the anaerobic conditions necessary for denitrification (Whitehead, 1996). In comparison, artificial fertiliser applications do not provide any additional carbon to the existing soil pool and do not change the soil moisture content. The fact that $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in the control plot were also positively correlated with a regression slope of 0.4 could have likewise been indicative of denitrification had the relation between both variable been significant. In this case, a greater number of samples would have been necessary to further test this assumption.

In the Moorepark and Knockbeg artificial fertiliser plots, nitrate concentration was negatively correlated with $\delta^{15}N\text{-}NO_3^-$ while positively correlated with $\delta^{18}O\text{-}NO_3^-$. In other words, the higher the nitrate concentration, the lower the $\delta^{15}N\text{-}NO_3^-$ and the higher the $\delta^{18}O\text{-}NO_3^-$, which is consistent with the leaching of an increasing proportion of pre-formed nitrate coming directly from the fertiliser. This could mean that nitrate leaching in the fertiliser plots is not only controlled by the leaching of fertiliser-derived nitrate, but also by the direct leaching of synthetic nitrate coming from the artificial fertilisers applied (this point is further developed in section 5.4 from the perspective of application rates). One consequence of the relationship between nitrate concentration and soil-water nitrate δ variables is that $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were negatively correlated. Indeed, if A is negatively correlated with B, and B is positively correlated (or proportional) with C, then A and C are expected to be negatively correlated. This outcome is interesting because it contrasts with the positive correlation observed between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in the dairy wastewater plots.

Some differences were observed between fertiliser sites. In the Moorepark fertiliser plots, the regression lines drawn from the plotting of nitrate concentration (y coordinate) against $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ (x coordinates) had slopes almost twice those of the Knockbeg site. This indicates that for the same variation in $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ (decrease in the former and an increase in the latter), the increase in nitrate concentration for Moorepark fertiliser plots was twice that observed at Knockbeg. This suggests that Knockbeg cropping systems leached out a higher proportion of nitrate coming directly from the fertiliser than

the Moorepark grassland system did, despite lower application rates. This is consistent with grass and its dense rooting system being much more efficient than tillage crops at taking up nutrients, such as nitrate, from soil. But it should also be considered that the significance of the relationship and the slope at the Knockbeg site might have been forced by two outliers from the low application rate - spring barley plots (see figures 5.12). In this context, more samples would have been welcome to confirm the above assumptions.

5.4 N application rate effect on nitrate isotopic composition

5.4.1 Artificial fertiliser rate effect

- Moorepark RC fertiliser experiments

Figures 5.6a and 5.6b show the distribution of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in Moorepark fertiliser treatment plots for each application rate, and highlight the differences in soil-water nitrate isotopic composition between the low, medium, high fertiliser application rates and the control plot (application rate referred to as "none"). As a reminder of the experimental conditions described in chapter 3 and in table 5.1, the low rate corresponded to 174 kg N/ha/yr, the medium rate to 286 kg N/ha/yr and the high rate to 387 kg N/ha/yr, whereas the fertiliser applied consisted of several applications of CAN during the growing season following a single application of synthetic urea in January.

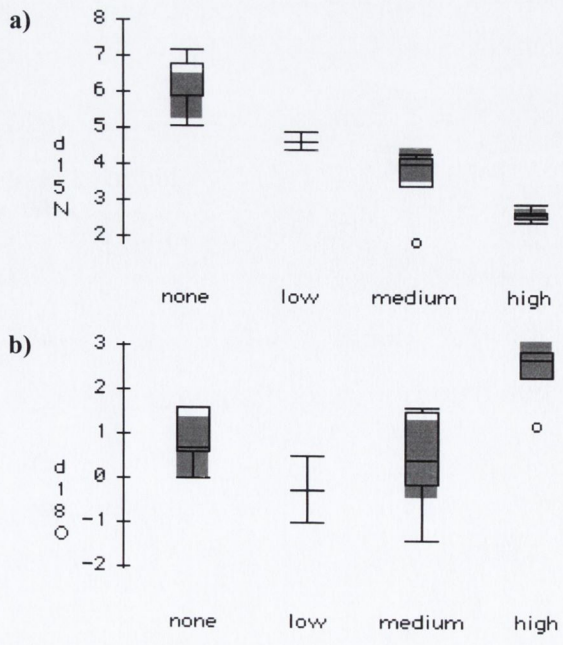


Figure 5.6: Distribution of **a)** $\delta^{15}N\text{-}NO_3^-$ (n = 16) and **b)** $\delta^{18}O\text{-}NO_3^-$ values (n = 15) for each application rate of fertiliser and the control in Moorepark RC. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*

Figure 5.6a shows that higher application rates of artificial fertiliser were consistently associated with lower $\delta^{15}N\text{-}NO_3^-$ values. In the low rate plot (n = 2), $\delta^{15}N\text{-}NO_3^-$ ranged between 4.4 and 4.9 ‰ with a median value of 4.6 ‰. In the medium rate plot (n = 8), whose N rate was higher by 112 kg N/ha/yr, $\delta^{15}N\text{-}NO_3^-$ dropped to range between 3.4 and 4.3 ‰, with a median value of 4 ‰. In the high rate plot (n = 6), whose rate was higher by 101 kg N/ha/yr, $\delta^{15}N\text{-}NO_3^-$ was only found to range between 2.4 and 2.9 ‰, with a median value of 2.6 ‰. In comparison, the $\delta^{15}N\text{-}NO_3^-$ in the unfertilised control (n = 5) ranged between 5.1 and 7.2 ‰, the median being 5.9 ‰, which is higher than the median value for the low rate plot by more than 1.3 ‰.

Simultaneously, higher application rates of artificial fertiliser were also associated with higher $\delta^{18}O\text{-}NO_3^-$ values in figure 5.6b, but the increase was made less obvious because values tended to overlap due to larger ranges. Nonetheless, the opposite trend to the one of $\delta^{15}N\text{-}NO_3^-$ was observed. $\delta^{18}O\text{-}NO_3^-$ in the low rate plot ranged between -1 and 0.5 ‰, with a median value of -0.2 ‰. It increased in the medium rate plot where it ranged between -1.4 to 1.6 ‰ (median of 0.4 ‰), and finally reached its peak in the high rate plot, ranging between 1.2 and 2.9 ‰ (median value of 2.7 ‰). In comparison, $\delta^{18}O\text{-}NO_3^-$ from the control plot ranged between 0 and 1.6 ‰, with a median value of 0.7 ‰, which was higher than that of the low rate plot by 0.9 ‰ and slightly higher than that of medium rate plot by 0.3 ‰.

Soil-water nitrate isotopic composition from the fertiliser plots is related to nitrate concentration in figures 5.7a and 5.7b, which display the plotting of nitrate concentration against $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ respectively (the regression lines and the associated Spearman's rank correlation coefficients r_s values referred to in table 5.11 are also exhibited). In addition, each plotted sample is linked to the application rate plot it belongs to. Samples from the control plot are not included here, but this point is discussed further on in this section.

Two main points may be drawn. First, higher application rates of artificial fertiliser are simultaneously associated with higher nitrate concentrations (see section 5.2.1 and table 5.1) and lower $\delta^{15}N\text{-}NO_3^-$ values in a systematic way. Second, higher application rates are also simultaneously associated with higher nitrate concentrations and higher $\delta^{18}O\text{-}NO_3^-$ values.

Figure 5.7: Variation of NO_3^- concentration with **a)** $\delta^{15}N\text{-}NO_3^-$ (n = 16) and **b)** $\delta^{18}O\text{-}NO_3^-$ (n = 15) in the artificial fertiliser treatment in Moorepark RC, and associated linear regression line with r_s and *p* values (high rate is marked with hollow rounds, medium rate with dots and low rate with crosses). *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively, nitrate concentration in mg/l NO_3^-)*

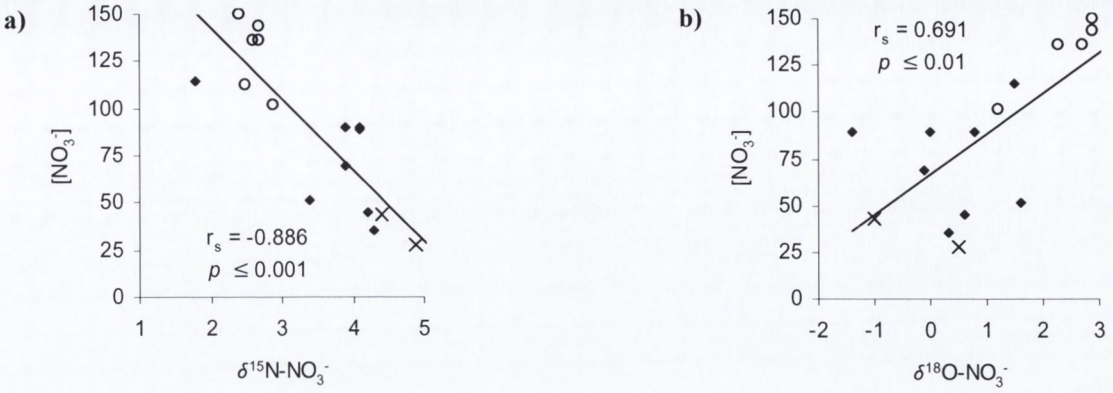
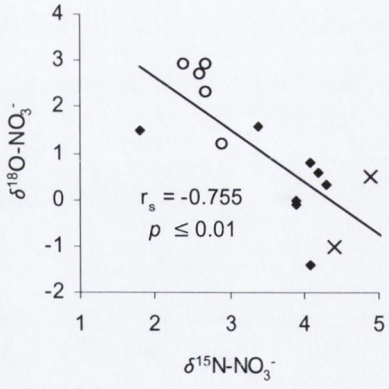


Figure 5.8 shows the above results from a different perspective with $\delta^{15}N\text{-}NO_3^-$ being plotted against $\delta^{18}O\text{-}NO_3^-$ (the regression line and the associated Spearman's rank correlation coefficient r_s value referred to in table 5.11 is also exhibited). This feature is important because every study from the literature that is related to nitrate isotopic composition in water refers to the plotting of $\delta^{15}N\text{-}NO_3^-$ against $\delta^{18}O\text{-}NO_3^-$ (sections 2.6.3 and 2.6.4).

Figure 5.8: Variation of $\delta^{15}N\text{-}NO_3^-$ with $\delta^{18}O\text{-}NO_3^-$ (n = 15) in the artificial fertiliser treatment in Moorepark RC, and associated linear regression line with r_s and *p* values (high rate is marked with hollow rounds, medium rate with dots, and low rate with crosses). *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*



It presents more directly what figures 5.7a and 5.7b already suggested, that higher application rates of artificial fertiliser are simultaneously associated with a shift of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ towards lower and higher values respectively.

It was already seen from table 5.11 that chloride and sulphate concentrations are strongly correlated with $\delta^{15}N\text{-}NO_3^-$ but not with $\delta^{18}O\text{-}NO_3^-$. Figure 5.9 shows the relationship with $\delta^{15}N\text{-}NO_3^-$ for chloride only (the regression line and the associated Spearman's rank correlation coefficient r_s value referred to in table 5.11 is also exhibited), and again, links

the variation in both variables with the application rate of artificial fertiliser. As a reminder, chloride and sulphate concentrations are discussed in section 5.2.1 (in tables 5.2 and 5.3 respectively).

Figure 5.9: Variation of $\delta^{15}N\text{-}NO_3^-$ with Cl^- concentration (n = 15) in the artificial fertiliser treatment in Moorepark RC, and associated linear regression line with r_s and *p* values (high rate is marked with hollow rounds, medium rate with dots, and low rate with crosses). *($\delta^{15}N$ is reported in ‰ against AIR, chloride concentration in mg/l Cl^-)*

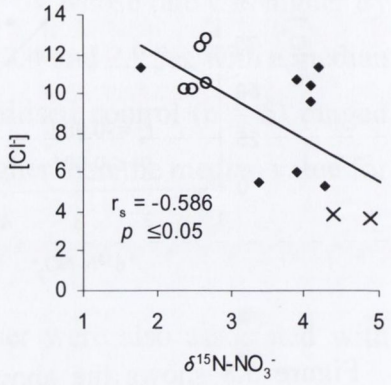
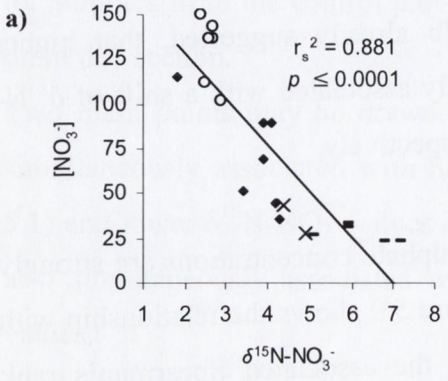
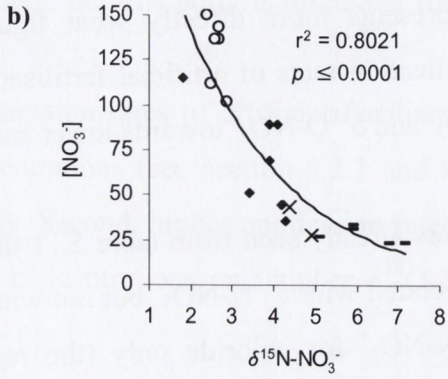


Figure 5.9 discloses a similar pattern to that observed with nitrate, i.e. that higher application rate of artificial fertiliser was concomitant with lower $\delta^{15}N\text{-}NO_3^-$ values and higher chloride concentrations.

Additionally to the previous results, figures 5.10a and 5.10b below are the result of a slightly different approach that consists of considering the control as an application rate plot of 0 kg N/ha/yr. Figures 5.10a and 5.10b present an updated version of figure 5.7a, i.e. the plotting of $\delta^{15}N\text{-}NO_3^-$ against nitrate concentration, which includes control results (n = 5) with the fertiliser plots dataset, and show how the relationship was impacted by displaying linear and exponential regression lines with r-squared values.

Figure 5.10: Variation of NO_3^- concentration with $\delta^{15}N\text{-}NO_3^-$ (n = 21) in Moorepark artificial fertiliser treatment and the control plots together, with **a)** linear and **b)** exponential regression lines (high rate is marked with hollow rounds, medium rate with dots, low rate with crosses, and control with hyphens). *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively, nitrate concentration in mg/l NO_3^-)*

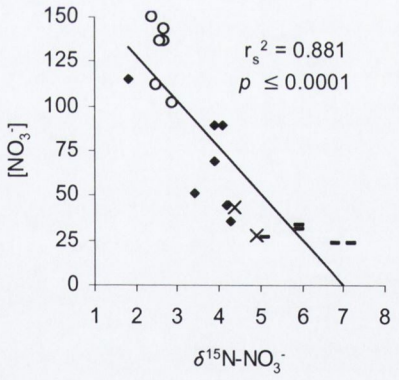




As already mentioned in table 5.11, the Spearman's rank r_s value for figure 5.7a, which describes fertiliser plots results alone, was -0.886. This implies a corresponding r_s-squared value of 0.785. In figure 5.10a, where control results were added to fertiliser plot results, the r_s-squared value increased to 0.881. Comparatively, the exponential regression shown in figure 5.10b displayed an r-squared value of 0.802, which is close to the linear fit. It appears then that the relationship between nitrate concentration and $\delta^{15}N\text{-}NO_3^-$ was strengthened by the addition of the control results.

Nonetheless, all other relationships given in table 5.11 for the fertiliser plots data alone were considerably weakened after adding control results. A typical example is displayed in figure 5.11, which plots $\delta^{15}N\text{-}NO_3^-$ against $\delta^{18}O\text{-}NO_3^-$ for the fertiliser treatment and the control plots together. This is in fact figure 5.8 plus the control plot data. Quite distinct from soil-water nitrate sampled in the fertiliser treatment plots, for which the regression line slope was -1.13, nitrate from the control plot did not follow the negative relationship, which explains why the overall relationship was weakened.

Figure 5.11: Variation of $\delta^{15}N\text{-}NO_3^-$ with $\delta^{18}O\text{-}NO_3^-$ in the artificial fertiliser plot (n = 21) and in the control (n = 5) in Moorepark RC, with dashed and plain lines as linear regression lines for the control and the fertiliser treatment plots data respectively (high rate is marked with hollow rounds, medium rate with dots, low rate with crosses, and control with hyphens). *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*

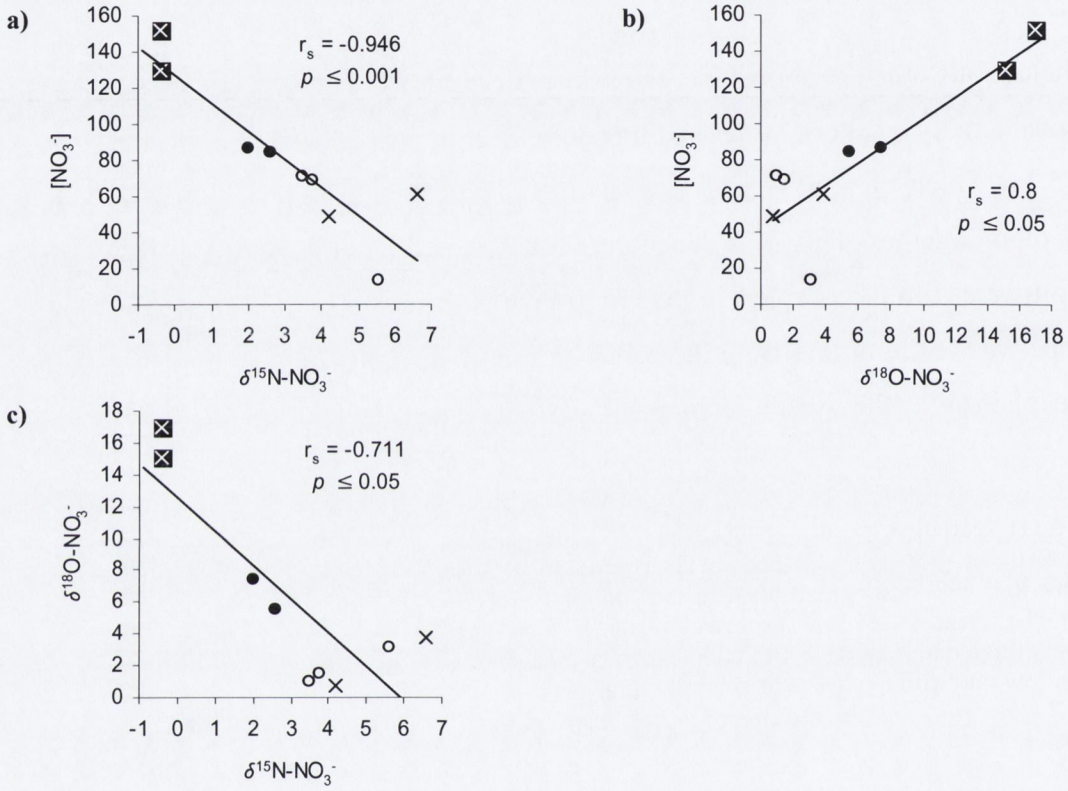


- Knockbeg experiments

Figures 5.12a and 5.12b show the variation of nitrate concentration with $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ respectively in Knockbeg experimental plots, while figure 5.12c displays the plotting of $\delta^{15}N\text{-}NO_3^-$ against $\delta^{18}O\text{-}NO_3^-$ (the regression lines and the associated Spearman's rank correlation coefficients r_s values referred to in table 5.12 are also exhibited). In all three figures, the link is made with the fertiliser application rate. As a reminder of experimental conditions detailed in section 3.3.2, winter wheat and spring barley plots were subjected to low artificial fertiliser application rates of 187.5 and 105 kg

N/ha/year respectively, and to high application rates of 225 and 137.5 kg N/ha/year respectively.

Figure 5.12: Variations of **a)** NO_3^- concentration with $\delta^{15}N\text{-}NO_3^-$ (n = 9), **b)** NO_3^- concentration with $\delta^{18}O\text{-}NO_3^-$ (n = 9) and **c)** $\delta^{15}N\text{-}NO_3^-$ with $\delta^{18}O\text{-}NO_3^-$ (n = 9) in the artificial fertiliser treatment in Knockbeg, and associated linear regression lines with r_s and p values (high rate is marked with rounds and low rate with crosses, shaded marks designate spring barley plot samples and other marks winter wheat plots). *(nitrate concentration is reported in mg/l NO_3^-, $\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*



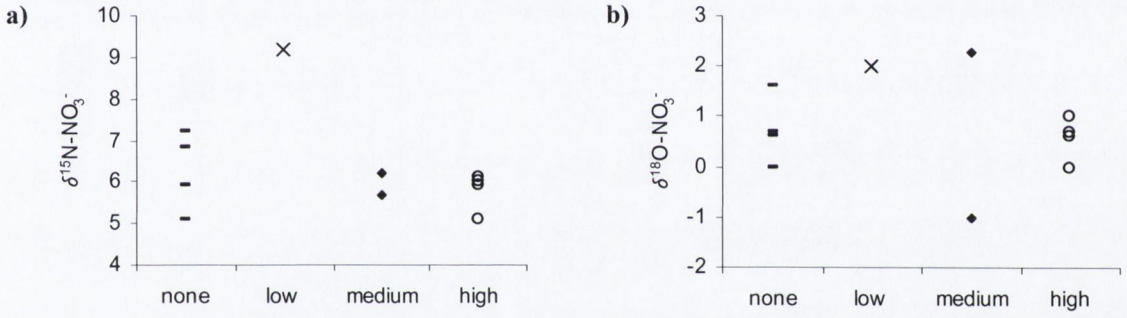
Unlike Moorepark, the application rates of artificial fertiliser in the Knockbeg tillage plots did not seem to relate to soil-water nitrate isotopic composition in a systematic and clear pattern. Figures 5.12a, 5.12b and 5.12c show that higher fertiliser application rate did not result in lower $\delta^{15}N\text{-}NO_3^-$ values and higher $\delta^{18}O\text{-}NO_3^-$ values, as was seen for the Moorepark fertiliser plots. Instead, the lowest $\delta^{15}N\text{-}NO_3^-$ values (-0.4 ‰) were measured in both spring barley plots subjected to low fertiliser application rates, which also corresponded with the highest $\delta^{18}O\text{-}NO_3^-$ values (15.1 and 17 ‰). In fact, nitrate δ values from these very plots proved to be the most extreme values recorded in the whole project, which is further discussed in section 5.4.3. Such combination of low $\delta^{15}N\text{-}NO_3^-$ and high $\delta^{18}O\text{-}NO_3^-$ values had only been measured in the nitrate fraction of some artificial fertilisers (table 5.4). In addition, those extreme δ values were associated with some of the highest nitrate concentrations, recorded at 130 and 152 mg/l NO_3^- (section 5.2.1).

5.4.2 Organic waste rate effect

- Moorepark RC slurry experiments

Figures 5.13a and 5.13b describe how $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ are distributed in the control and the slurry treatment plots under three application rates (control referred to as "none" rate). As a reminder of experimental conditions detailed in chapter 3 and table 5.1, the low, the medium and the high application rates consisted of approximately 53, 105 and 160 kg N/ha/year (based on the TN content of a single sample of slurry – see section 3.3.1).

Figure 5.13: Distribution of **a)** $\delta^{15}N\text{-}NO_3^-$ (n = 7) and **b)** $\delta^{18}O\text{-}NO_3^-$ values (n = 7) for each application rate of slurry and the control in Moorepark RC. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*

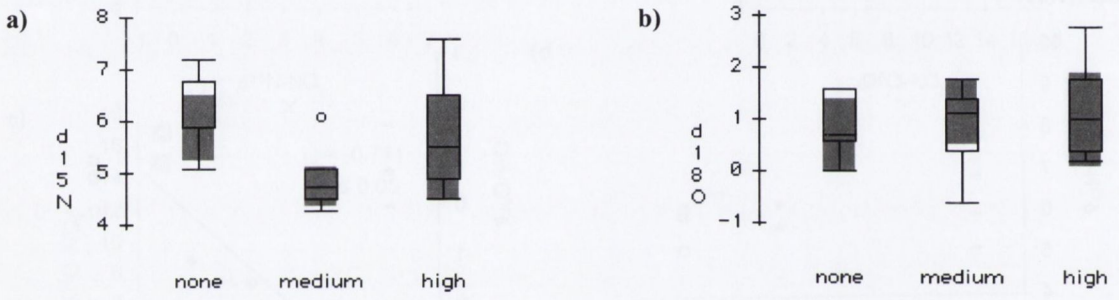


The three different slurry application rates did not influence soil-water nitrate isotopic composition in a systematic way. The only sample from the low rate plot showed the highest $\delta^{15}N\text{-}NO_3^-$ value at 9.2 ‰, whereas medium (n = 2) and high rate plots (n = 4) showed similar ranges, with values between 5.1 and 6.2 ‰. As for $\delta^{18}O\text{-}NO_3^-$, values from the high rate plot ranged between 0 and 1 ‰, whereas values from the low and medium rate were either lower or higher than this range by at least 1 ‰. Most soil-water nitrate samples were also found to display similar isotopic composition to those from the control plot (n = 5). All but one of the values were within less than 1 ‰ from the $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ ranges given by the control plot. These observations are made in a context that is very different from that of the fertiliser plots. In the case of the slurry plots, nitrate levels in soil-water samples were found to be lower than the concentration from the control (section 5.2.1 and table 5.1).

- Moorepark RC dairy wastewater experiments

Figures 5.14a and 5.14b display the distribution of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in the control (referred to as "none" rate), and in the dairy wastewater treatment plots under two different application rates. As a reminder of experimental condition detailed in chapter 3 and table 5.1, dairy wastewater plots sampled were subjected to two different application rates: a medium rate estimated at 171 kg N/ha/year and a high rate estimated at 343 kg N/ha/year (based on the TN contents of two dairy wastewater samples collected in November 2001 and May 2003 - see section 3.3.1)

Figure 5.14: Range of **a)** $\delta^{15}N\text{-}NO_3^-$ values (n = 12) and **b)** $\delta^{18}O\text{-}NO_3^-$ values (n = 12) for each application rate of dairy wastewater and the control in Moorepark RC. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*



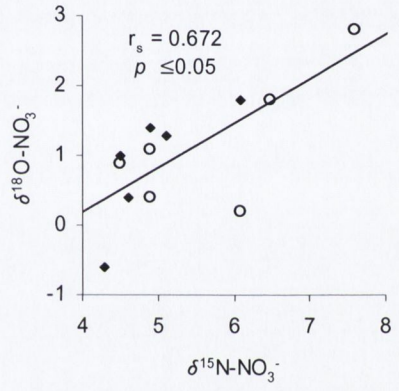
Unlike the slurry plots, the application of two different rates of dairy wastewater seemed to affect the isotopic composition of soil-water nitrate in a systematic way. As seen in figure 5.14a, the range of $\delta^{15}N\text{-}NO_3^-$ values increased from 4.3 - 5.1 ‰ (median value of 4.7 ‰) in the medium rate plot (n = 6), to 4.5 - 7.6 ‰ (median of 5.5 ‰) in the high rate plot (n = 6). Simultaneously, $\delta^{18}O\text{-}NO_3^-$ range in figure 5.14b increased from -0.6 - 1.8 ‰ (median of 1.1 ‰) in the medium rate plot to 0.2 - 2.8 ‰ (median almost unchanged at 1.0 ‰) in the high rate plot. $\delta^{15}N\text{-}NO_3^-$ values in the medium rate plot were also found to be lower than values from the control plot (n = 5), whose range was in fact within that of the high rate plot. $\delta^{18}O\text{-}NO_3^-$ values from the medium rate plot encompassed values from the control plot, whose range was slightly lower than that of the high rate plot.

Although there was no significant relationship found between nitrate concentration and $\delta^{15}N\text{-}NO_3^-$ or $\delta^{18}O\text{-}NO_3^-$ (see table 5.13), the increase in both nitrate δ values that was observed with higher dairy wastewater application rates was associated with higher nitrate concentration. Table 5.1 showed that nitrate levels in the high rate plot were, on average,

higher than in the medium rate plot by almost 20 mg/l NO_3^-. In addition, both medium and high rate plots had concentration much higher than the control.

Figure 5.15 below shows the plotting of $\delta^{15}N\text{-}NO_3^-$ against $\delta^{18}O\text{-}NO_3^-$ (the regression lines and the associated Spearman's rank correlation coefficients r_s value referred to in table 5.13 are also exhibited), and links the variation with the application rate of dairy wastewater. It highlights the limited, yet noticeable, contribution of the higher application rate of dairy wastewater to the increase of both nitrate δ values. Including values from the control plot caused the Spearman's rank correlation r_s value to decrease, from 0.672 to 0.519, although the correlation remained significant ($p \leq 0.05$).

Figure 5.15: Variation of $\delta^{15}N\text{-}NO_3^-$ with $\delta^{18}O\text{-}NO_3^-$ in dairy wastewater treatment plots in Moorepark RC, and associated linear regression line with r_s and p values (high rate is marked with hollow rounds and medium rate with dots). *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*



5.4.3 Discussion of the effect of artificial fertiliser application rate

Section 5.4.1 shows contrasting results between the Moorepark and Knockbeg experiments in relation to the influence of artificial fertiliser application rates on soil-water nitrate isotopic composition. Whereas $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ at Moorepark seemed to be related to the N input rate in a systematic way, no clear pattern was observed at Knockbeg. In the Moorepark low rate plot, soil-water nitrate had an isotopic composition in a similar range to that of nitrate from the control plot. The increase in CAN application rate resulted in soil-water nitrate $\delta^{15}N\text{-}NO_3^-$ decreasing markedly while $\delta^{18}O\text{-}NO_3^-$ simultaneously increased. This contrasts with the Knockbeg results where higher application rates were not reflected in soil-water nitrate isotopic signature. These isotopic results suggest then that in Moorepark (but not Knockbeg), a higher rate of fertiliser application resulted in more direct leaching of synthetic nitrate from artificial fertiliser. The similarity with nitrate concentration results displayed in section 5.2.1 is striking. Based on hypotheses developed in section 5.2.4, the assumption is then that artificial fertiliser application rate controls soil-

water nitrate isotopic composition and the amount of leached synthetic nitrate only if in exceedance of the plants' biological requirements. The Moorepark results, where application rates were high in regard of Teagasc recommendations (see section 5.2.4) and probably well above grass biological requirements, are supported by Barraclough *et al.* (1984) who observed that the increase in ammonium nitrate application rate to grassland from 250 to 900 kg N/ha/year (unrealistic rates in real agricultural systems but clearly above biological requirements) resulted in higher leaching of synthetic nitrate. In addition, exceedance of plant requirements at Moorepark may also be accompanied by the exceedance of bacterial capacity for nitrate immobilisation during MIT processes, which is supported by the slow increase in $\delta^{18}O\text{-}NO_3^-$ values with higher CAN application rates.

The situation at Knockbeg was radically different. Soil-water nitrate in both low rate - spring barley plots (plots K7-Lsb and K57-Lsb in figure 3.10) showed $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values close to the isotopic composition of artificial nitrate, in association with nitrate concentrations higher than 120 mg/l NO_3^-, which was not witnessed in the two high rate - spring barley plots. Because plots K7-Lsb and K57-Lsb are located in different areas of the field, and because Hooker (2005) observed similarly high nitrate leaching in the same plots during long-term monitoring, it can then be assumed that the direct leaching of artificial fertiliser in those two plots (evoked earlier in section 5.3.5) may be something systematic that is not due to a random event like a faulty bentonite joint or some exceedingly localised freely-draining soil. The fact that this outcome was not witnessed in the high rate - spring barley plots may accredit the hypothesis raised by Hooker (2005) (referred to in section 5.2.4) that low fertiliser inputs could result in reduced crop uptake, which could consequently enable some fertiliser nitrate to leach below the unsaturated zone.

A general observation can be made from scatterplots described in section 5.4.1. The significance of relationships between variables was assessed by measuring Spearman's rank correlation coefficients (see section 5.3.3), which are a measure of linear relationships. But variations in isotopic ratios are generally ruled by non-linear relationships (e.g. Rayleigh equation). One can imagine a hypothetical experiment where the application of artificial fertiliser goes from none to infinite. As the nitrate concentration increases, so does the percentage of artificial fertiliser leached. For an extremely high application rate, the percentage of pre-formed nitrate in soil-water would approach 100 %, without ever reaching this limit since there would still be a small amount of nitrate from

natural origin. At the same time, soil-water nitrate $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values would get closer and closer to the value of the artificial fertiliser applied, without reaching them: $\delta^{15}N\text{-}NO_3^-$ would decrease towards a fixed value as nitrate concentration goes up, and $\delta^{18}O\text{-}NO_3^-$ would also increase towards a fixed value. The plotting of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ against nitrate concentration should then theoretically lead to asymptotic exponential fit. However, the exponential fit, shown in figure 5.10b ($\delta^{15}N\text{-}NO_3^-$ versus nitrate concentration) after control plot results (i.e. the zero-application rate) were included with fertiliser data, matched slightly less than the linear fit showed in figure 5.10a. In addition, a reason for the exponential fit to display such a high r_s-squared value could be attributed to possible denitrification in the control plot, where low nitrate concentrations appeared to stretch towards greater δ values. This is reflected in the lower correlation between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ when control results are considered in the determination of an application rate effect, as seen in figure 5.11 for example.

5.4.4 Discussion of the effect of organic waste application rate

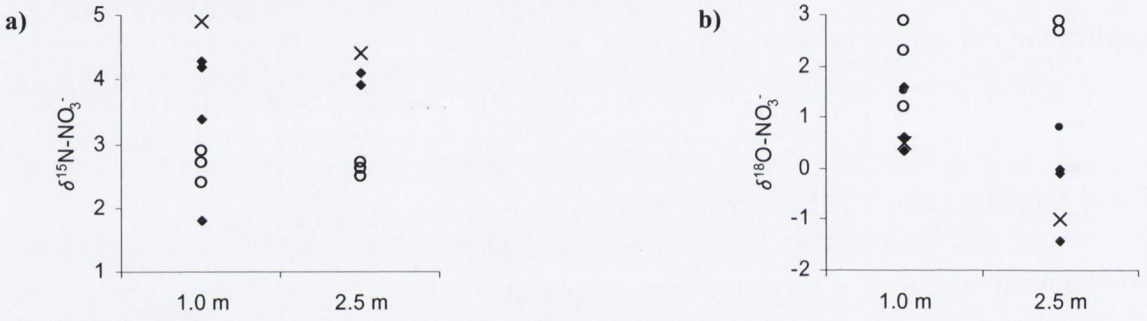
The application rate of slurry and dairy wastewater led to contrasting results in terms of influence on soil-water nitrate isotopic composition. Except for an outlier, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values from the slurry plots were in a similar range irrespective of the application rate. This may have been expected given that, in section 5.2.1, low rates of leaching are identified from slurry application in the Moorepark experiments. In contrast, both $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values from the dairy wastewater plots seemed to increase slightly with higher application rate. Medians in both medium and high rate plots were quite similar, but δ ranges shifted towards greater values with higher application rates. This suggests then that denitrification was influenced by the amount of dairy wastewater applied, which may reflect the inducement of conditions favourable to denitrification by wastewater application, i.e. higher soil moisture content and high inputs of carbon (i.e. electron donor that actively participates in nitrate reduction). Nonetheless, denitrification appears to be partial as soil-water nitrate isotopic composition did not reach the very high values typically described in the context of point organic sources. The fact that $\delta^{15}N\text{-}NO_3^-$ in the medium dairy wastewater plot was lower than in the control may be due to the fact that total nitrogen in dairy wastewater has lower $\delta^{15}N\text{-TN}$ value than in soil organic matter. Increasing the application rate from zero to 25 mm could cause an initial decrease in $\delta^{15}N\text{-}NO_3^-$, followed by an increase as denitrification proceeds.

5.5 Depth effect on nitrate isotopic composition (within treatments)

5.5.1 Depth effect within each treatment

Figures 5.16a & b and 5.17a & b show how $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were distributed within the Moorepark artificial fertiliser and dairy wastewater treatment plots respectively, over the aggregated depths of 1.0 m and 2.5 m. In addition, results are linked to application rates.

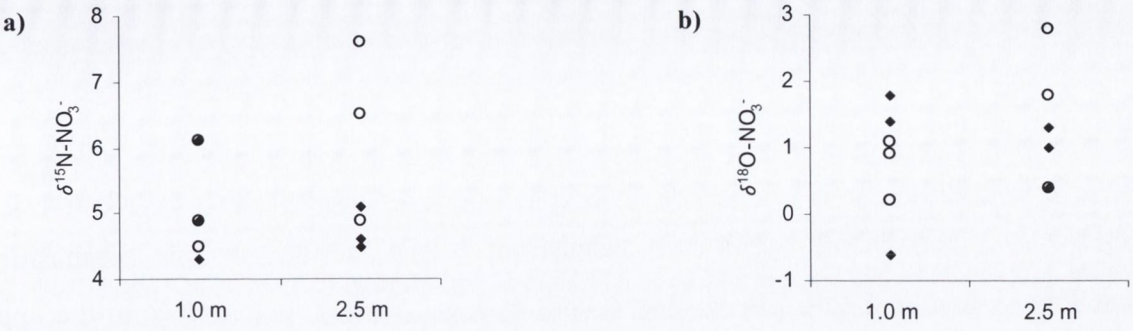
Figure 5.16: Distribution of **a)** $\delta^{15}N\text{-}NO_3^-$ (n = 16) and **b)** $\delta^{18}O\text{-}NO_3^-$ (n = 15) in the Moorepark artificial fertiliser treatment plots at depths 1.0 m and 2.5 m (high rate is marked with hollow rounds, medium rate with dots, and low rate with crosses). *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*



Overall, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ variables for the fertiliser plots fell within similar ranges at both depths. $\delta^{15}N\text{-}NO_3^-$ varied between 2 ‰ and 5 ‰, with mean values of 3.3 ‰ at 1.0 m and 3.5 ‰ at 2.5 m. $\delta^{18}O\text{-}NO_3^-$, which ranged between -1 ‰ and 3 ‰, showed mean values of 1.4 ‰ at 1.0 m and 0.6 ‰ at 2.5 m. In addition, no systematic depth effect was observed for each application rate. It should also be noted that nitrate concentrations were very similar at both depths, although slightly higher at 2.5 m than at 1.0 m (table 5.1).

Similar situations were also observed in the slurry plots and the control, where no obvious depth effect regarding soil-water nitrate isotopic composition was detected. With the exception of an outlier, $\delta^{15}N\text{-}NO_3^-$ in the slurry plots was within a narrow range of values at both depths, between 5.1 and 6.2 ‰. $\delta^{18}O\text{-}NO_3^-$ in the slurry plots was also found within a narrow range at both depths, between -1 and 2.3 ‰. This happened while nitrate concentrations were significantly higher at 2.5 m (table 5.1). As for the control, nitrate δ values were lower at 2.5 m than at 1.0 m, but the difference in means or medians for both variables was less than 0.4 ‰. In addition, nitrate concentrations were near-identical at 1.0 m and 2.5 m (table 5.1).

Figure 5.17: Distribution of **a)** $\delta^{15}N\text{-}NO_3^-$ (n = 12) and **b)** $\delta^{18}O\text{-}NO_3^-$ (n = 12) in the Moorepark dairy wastewater treatment plots at depths 1.0 m and 2.5 m (high rate is marked with hollow rounds and medium rate with dots). *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*



In figures 5.17a and 5.17b, both $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ variables from the dairy wastewater treatment plots appeared to shift slightly towards higher values with deeper samples. At 1.0 m, $\delta^{15}N\text{-}NO_3^-$ ranged between 4.5 and 6.1 ‰ (mean of 5.1 ‰), whereas at 2.5 m it ranged between 4.9 and 7.6 ‰ (mean of 5.5 ‰). At the same time, $\delta^{18}O\text{-}NO_3^-$ was measured between 0.2 and 1.1 ‰ at 1.0 m (mean of 0.8 ‰), while it ranged between 0.4 and 2.8 ‰ at 2.5 m (mean of 1.3 ‰). Nonetheless, such increase with depth in nitrate δ values was mainly due to the contribution of two samples from the high application rate plot collected at 2.5 m. Figures 5.17a and 5.17b also suggests that the depth effect was more important within the high rate plot alone, nitrate δ values being generally higher at 2.5 m than at 1.0 m. It should be noted that these soil-water nitrate isotopic compositions were in the context of similar concentrations at both depths, although concentrations were slightly higher at 2.5 m (table 5.1).

5.5.2 Discussion of the effect of depth

Depth seemed to have very little effect on the isotopic signature of soil-water nitrate, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ exhibiting similar ranges at 1.0 m and 2.5m, which suggests that between these two depths, soil-water nitrate underwent very little transformation. Deeper than the first few centimetres of soil where nitrification and MIT processes operate (see section 2.4.1), denitrification is the only other process with a large enrichment factor ϵ (see Equation 2.12) capable of influencing markedly soil-water nitrate isotopic composition (section 2.6.3). But if one considers that most of the microbial flora, which includes denitrifiers, is present in the top first metre of soil, then ^{15}N and ^{18}O-enrichment of soil-water nitrate caused by denitrification may be expected to be limited between 1.0 m and 2.5 m. Nonetheless, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values were slightly higher at 1.0 m than at

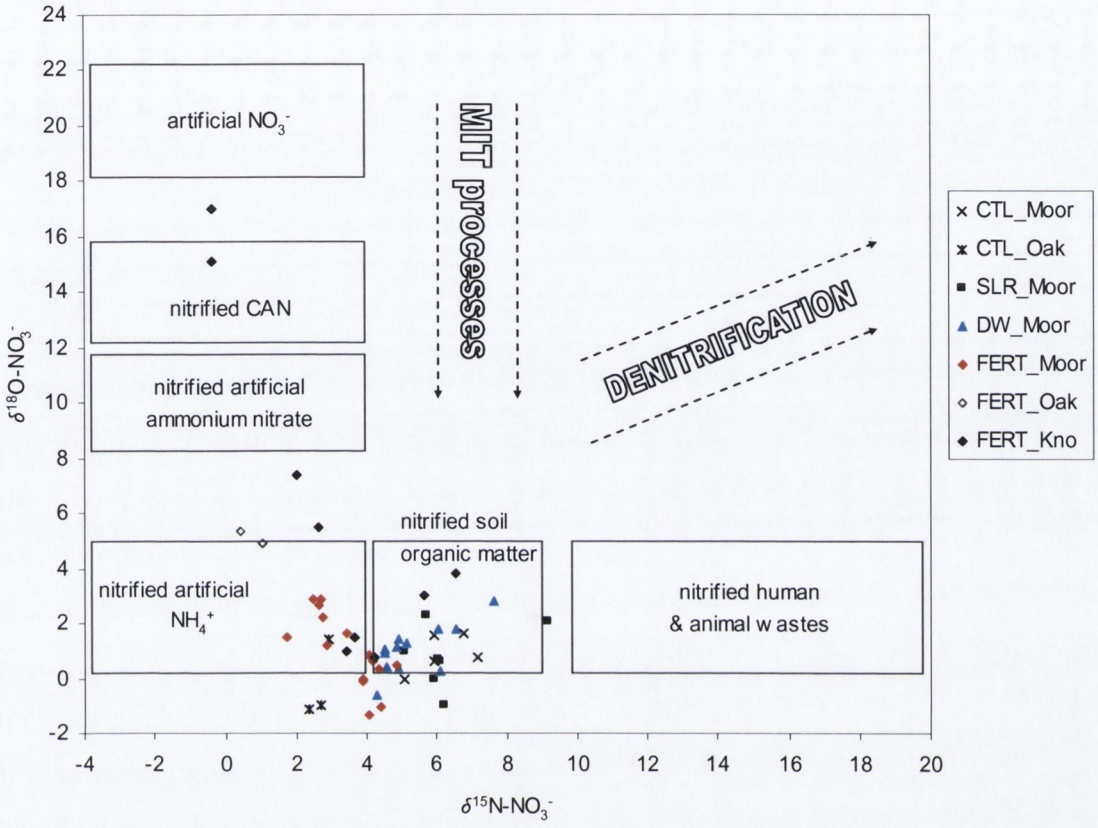
2.5 m in the high dairy wastewater plot (figures 5.17a and 5.17b), which may suggest the occurrence of denitrification between these depths due to higher concentrations of an electron donor like dissolved organic carbon.

A potential limitation to result interpretation may be attributed to the fact that suction cups generally sample the water in the soil matrix rather than the macropores. The occurrence of preferential flow has important implications for leached nitrate isotopic composition, because it could enable nitrate to bypass the microbial activity taking place in the upper part of the soil. This would result in the leached nitrate exhibiting the isotopic characteristics of the N source it originated from. Suction cups are unlikely to sample bypass flow (Gibbons *et al.*, 2006), or the nitrate within it, unless they happen to intersect a macropore, which could bias the results. So far, results from previous investigations at Moorepark or elsewhere in Ireland have provided contradictory evidence regarding the occurrence or the absence of preferential flow. While Gibbons *et al.* (2006) concluded on "the absence of macropore flow in the soil at the experimental site" of Moorepark RC, Bartley (2003) referred to the presence of preferential flow that suction cups could not relate to during tracing experiments. In a reference to the whole country of Ireland, Daly (2002) explained that bypass flow should not be expected below 0.5 m deep.

5.6 Conclusions

Because artificial fertiliser and organic waste-derived nitrates generally have distinctive isotopic compositions, the success of $\delta^{15}N$ and $\delta^{18}O$ analyses on nitrate as a tool to determine the origin of groundwater contamination depends on whether such differences are mirrored in the isotopic composition of leached nitrate. Experiments carried out on Moorepark, Knockbeg and Oak Park soils aimed to answer this question by investigating $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values measured in soil-water nitrate collected from plots that were subjected to application of either artificial fertilisers or dairy farm organic wastes. The results of all isotopic analyses for each treatment of the three sampling sites are displayed in figure 5.18 where $\delta^{15}N\text{-}NO_3^-$ is plotted against $\delta^{18}O\text{-}NO_3^-$. In order to facilitate conclusions, predicted values given from the literature in table 2.8 for nitrate derived from some artificial fertilisers and animal organic wastes, are also displayed on the scatterplot.

Figure 5.18: Scatterplot of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values measured in soil-water nitrate collected from Moorepark (Moor), Knockbeg (Kno) and Oak Park (Oak) soils subjected to applications of slurry (SLR), dairy wastewater (DW), artificial fertiliser (FERT) or no fertilisation (CTL); boxes delineate predicted values for nitrate derived from several N sources, and dashed lines represent the expected isotopic fraction caused by denitrification and MIT processes. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*



Several conclusions can be drawn from the results.

- Soil-water nitrate poorly mirrored the ^{15}N content of applied nitrogenous sources, which was probably due to the interference of soil-water nitrate derived from the nitrification of soil organic matter. Notwithstanding this, δ^{15}N-NO_3^- was found to be consistently lower where artificial fertiliser had been applied than in unfertilised controls and organic waste treatments, which suggests that δ^{15}N analysis can provide useful clues for the identification of diffuse inorganic sources if comparisons can be made with other types of N sources.
- Soil-water nitrate showed δ^{18}O-NO_3^- values that were consistently in the range expected for nitrification, even where artificial fertiliser was applied, which could be attributed to the occurrence of Mineralisation-Immobilisation Turnover processes that tend to level all δ^{18}O-NO_3^- values.
- Correlations between chemical and isotopic variables showed strong differences between artificial fertiliser application and other treatments. The most striking difference was related to the plotting of δ^{15}N-NO_3^- against δ^{18}O-NO_3^-. The negative

correlation under artificial fertiliser treatment appeared to be a direct consequence of the increasing influence synthetic nitrate had during the leaching process. The positive relationship in the dairy wastewater treatment was associated with the occurrence of denitrification.

- Where the plant biological requirements were exceeded, higher application rates of artificial fertiliser seemed to induce the leaching of more synthetic nitrate coming directly from the fertiliser.

Overall, it seemed that dual $\delta^{15}N$ and $\delta^{18}O$ analyses on soil-water nitrate are not a perfect tool to identify nitrate sources beyond doubt. Instead, isotopic analyses should be used along with the measurement of other physico-chemical and microbial parameters that, together, can provide clues as to the origin of leached nitrate. Nonetheless, this pessimistic conclusion should be seen under a positive light for several reasons. First, valuable information was obtained on nitrate dynamics and the occurrence of microbial processes. This contributes to a greater understanding of the nitrate problem and possible solutions. Second, the collection of two samples with $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values measured below 0 ‰ and above 15 ‰ respectively suggests that the direct leaching of synthetic nitrate is possible, although rarely, which could be identifiable in groundwater under favourable conditions, e.g. shallow water-table overlain by freely-draining soils. Finally, it should be borne in mind that all treatments were studied as diffuse sources. In the context of groundwater investigations in the Barrow Valley, animal wastes responsible for nitrate contamination originate predominantly from point sources (see section 3.4.2) that permanently soak soils, which may favour much higher isotopic fractionation due to long-term volatilisation (see sections 2.6.2 and 2.6.3). Consequently, the discrimination between artificial inorganic diffuse sources with organic point sources may be much easier than our unsaturated zone study suggests.

CHAPTER 6: SATURATED ZONE INVESTIGATION: HYDROCHEMISTRY RESULTS AND DISCUSSION

6.1 Introduction

As noted earlier in sections 1.2 and 4.1.1, this project focused mainly on the Barrow Valley in south Co. Kildare and north Co. Carlow, because the nitrate problem caused by varied N sources (i.e. artificial fertiliser applications, septic tanks and farmyards) has remained unresolved to date. Furthermore, the large number of sampling sites scattered across a large geographical area provided ideal conditions to carry out the large-scale testing of chemical analysis (along with isotopic analysis as discussed in chapter 7) as a tool to determine the origin of groundwater nitrate. At the same time, research was undertaken at Curtin's farm in Moorepark Research Centre as a complementary work to investigations carried out by Bartley (2003). The main interest for Moorepark RC was that of studying groundwater contamination by nitrate in a hydrogeological and land use context that is different from the Barrow Valley area.

According to the sampling programme detailed in section 4.2.2, two hundred and eighty-three groundwater samples were collected between February 2002 and June 2004 from the Barrow Valley, where most of the fifty-one sampling wells intercepted a shallow sand and gravel aquifer overlying Carboniferous limestone. In addition, thirty-three groundwater samples were collected at Curtin's dairy farm in Moorepark RC, where ten boreholes were drilled in a deep karstified limestone aquifer. Details of the local geology and hydrogeology were explained throughout section 3.2 for each study area, while sites description was discussed in section 3.4 in relation to wells' physical characteristics and the presence of N sources.

In contrast to the soil-water samples discussed in Chapter 5, groundwater samples were not only analysed for major anions (nitrate, chloride and sulphate), but also for major cations (sodium, potassium, calcium and magnesium) and other parameters like pH, conductivity and alkalinity. Microbial analyses were also undertaken for total and faecal coliforms. All values for individual samples are tabulated in Appendix 3, whereas mean and median values by site are given in Appendix 5A for nitrate concentration, in Appendix 5B for chloride concentration, in Appendix 5C for potassium concentration, in Appendix 5D for sodium concentration and in Appendix 5E for potassium to sodium ratio.

In a multi-step approach, the primary purpose of this chapter is to test the utility of groundwater chemistry and sites' spatial characteristics for the identification of nitrate sources in Irish groundwaters, which was used as a preliminary step before discussing the use of nitrate isotopic composition in chapter 7. First groundwater chemistry was analysed alone for the Barrow Valley, groundwater sampling sites being classified according to different classes based on the exceedance of some contamination thresholds set for several chemical parameters (section 6.3). Exceedance of these thresholds indicated abnormal concentrations that were related, whenever possible, to either artificial fertiliser applications or organic point source contamination (farmyard and septic tank effluents), which are the two main N sources present in the study areas (section 3.2.7). The second step consisted of examining sites' spatial characteristics, i.e. % tillage within 300 m radius (section 6.4.2) and N source effects within 100 m and 300 m radius (section 6.4.3), in regard of groundwater chemistry. The final step involved comparing in section 6.4.4 the outcome of the chemical classification with the sites' spatial characteristics.
A secondary purpose of this chapter was to evaluate groundwater quality and the extent of the nitrate problem at Curtin's farm (in Moorepark RC), but mostly in the Barrow Valley study areas where an attempt was made to identify the origin of the contamination, which has been largely unresolved to date.

6.2 Overview of hydrochemistry and water quality parameters in the study areas

6.2.1 Physico-chemical and microbial results

- Barrow Valley

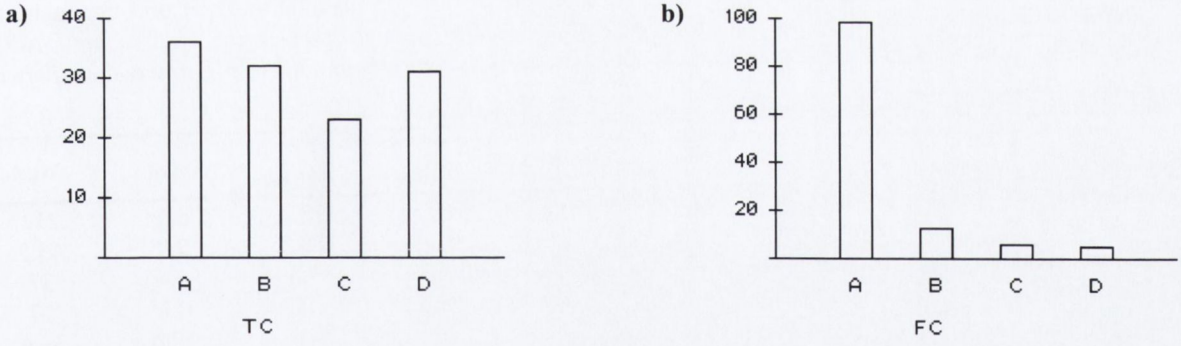
Most groundwater samples were analysed for ten major chemical and two microbial parameters. Table 6.1 presents summary statistics of individual samples for anion concentrations (nitrate, chloride and sulphate), cation concentrations (sodium, potassium, magnesium and calcium), alkalinity, pH and conductivity, while figure 6.1 shows how total and faecal coliform concentrations were distributed (see all values in Appendix 3). Although two hundred and eighty-three groundwater samples were collected, a few samples were not analysed for every physico-chemical parameter due to occasional technical problems, which explains the discrepancy in terms of sample number between

variables. As for microbial analyses, they were only carried out between June 2003 and 2004, and only concerned thirty-six sites on four sampling occasions.

Table 6.1: Central values and spread of major anions and cations concentrations, alkalinity, conductivity and pH measured in groundwater samples of the Barrow Valley. *(nitrate concentration is reported in mg/l NO_3^-, sulphate concentration in mg/l SO_4^{2-} and other concentrations in mg/l, alkalinity is in mg/l $CaCO_3$, pH in units of pH, and conductivity in µS/cm)*

Parameter	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
Nitrate	283	48.9	22.8	47.4	32.7	61.8	1.2	134.9
Chloride	280	32.1	12.6	29.6	24	38.9	5.1	84.1
Potassium	282	5.6	10.4	1.9	1	5	0.2	63
Sodium	282	12.8	6.7	10.8	8.9	15	4	46
Sulphate	280	31.8	10.4	30.6	24.2	36.6	8.8	68.8
Magnesium	281	14.4	4	14	12	17	2	28
Calcium	282	122.7	15.1	122	112	134	83.6	190
Alkalinity	266	306.7	37.2	302	284	330	129	526
pH	282	7.3	0.1	7.3	7.2	7.3	6.8	7.9
Conductivity	269	798.9	97.3	780	742.8	850.5	584	1206

Figure 6.1: Overall distribution of **a)** total coliform concentrations (n = 122) and **b)** faecal coliform concentrations (n = 123) in groundwater samples, collected from thirty-six wells of the Barrow Valley, according to the following classes of concentration: A = 0 bacteria per 100 ml, 0 < B ≤ 10, 10 < C ≤ 50 and D > 50. *(classes of coliform concentration are reported on the x-axis; the frequency is reported on the y-axis)*



Overall, the nitrate concentration showed a large range of values between a minimum of 1.2 mg/l NO_3^- and a maximum of 135 mg/l NO_3^-, with a coefficient of variation (CV) of 47 %. Very few samples showed low nitrate levels, 88 % of groundwater samples (249 out of 283) displaying concentrations above 25 mg/l NO_3^-, which concerned all but three of the fifty-one sampling sites on at least one occasion. In addition, nitrate contaminations higher than 50 mg/l NO_3^- were observed in 44 % of groundwater samples (125 out of 283), which concerned thirty-two of the fifty-one sites on at least one occasion (more site details given in section 6.5).

Like nitrate, the other physico-chemical parameters also showed some very large variations between very low minimum and very high maximum values, which was reflected by similarly elevated coefficients of variation. Chloride concentration varied between 5.1 to

84.1 mg/l with a CV of 39 %, while potassium concentration was between 0.2 and 63 mg/l with a CV of 185 %, and sodium concentration ranged between 4 and 46 mg/l with a CV of 52 %. In comparison, calcium, pH and alkalinity showed far less variation with coefficients of variation below 12 %, as expected since these are generally conservative and reflect hydrogeological conditions (limestone buffering). From the bacterial prospective, figure 6.1a shows that 70.5 % of groundwater samples contained some coliforms (86 out of 122), whereas 20 % of samples (24 out of 123) showed presence of faecal coliforms (figure 6.1b), which concerned fifteen sites out of thirty-six tested on at least one occasion.

- Moorepark RC

Except for alkalinity, groundwater samples from Moorepark RC were measured for the same physico-chemical parameters as the Barrow Valley samples. No microbial analysis was undertaken. Table 6.2 describes the data for these parameters.

Table 6.2: Central values and spread of major anions and cations concentrations, pH and conductivity measured in groundwater samples of Moorepark RC. *(nitrate concentration is reported in mg/l NO_3^-, sulphate concentration in mg/l SO_4^{2-} and other concentrations in mg/l, pH in units of pH, and conductivity in µS/cm)*

Parameter	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
Nitrate	33	62.7	34.4	60.2	46.3	78.8	5.7	212
Chloride	24	19.5	12.1	17.4	12.5	25.3	3.2	45.2
Potassium	33	7.1	10	2.5	1.1	7.3	0.4	37
Sodium	33	7.9	4.3	8	5.8	10.3	0.8	17
Sulphate	15	29.4	6.5	30.1	23.8	34.6	19.6	39.6
Magnesium	33	14.6	4.6	15.9	11	17	2	23
Calcium	33	150.7	23.6	149	133.1	165.0	88	203.9
pH	33	7	0.1	7	6.9	7	6.7	7.3
Conductivity	25	899.5	162.2	886	785.8	966.5	495.0	1240

Similarly to the Barrow Valley results, the nitrate levels in Moorepark RC groundwater showed a wide range of values between the minimum (5.7 mg/l NO_3^-) and the maximum (212 mg/l NO_3^-), the coefficient of variation being of 55 %. It should be noted that the maximum was extremely elevated in comparison with other values, the second highest value being measured at 95.7 mg/l NO_3^-. Like the Barrow Valley, very few samples show low nitrate levels. In 91 % of groundwater samples (30 out of 33), nitrate concentration was higher than 25 mg/l NO_3^-, which concerned all but one of the ten sites on at least one occasion. As for the 50 mg/l NO_3^- drinking water limit, it was exceeded in 64 % of

groundwater samples (21 out of 33), which concerned all but two of the ten sites on at least one occasions.

The other physico-chemical parameters measured in Moorepark groundwater samples displayed wide ranges of values, though generally not as wide as in the Barrow Valley. Similarly to the Barrow Valley, potassium concentration showed the highest coefficient of variation (CV = 140 %), followed by chloride concentration (CV = 62 %) and sodium concentration (CV = 55 %). In comparison, the coefficients of variation for pH, calcium and conductivity were below 20 %, for the reasons indicated above in the Barrow Valley subsection.

6.2.2 Discussion of physico-chemical and microbial results

Summary statistics displayed in section 6.2.1 gave an overview of the groundwater quality in the Barrow Valley and Moorepark RC study areas, from which several observations can be drawn in relation to groundwater contamination. To better understand the significance of these results, it is important to remember that the study areas were highly managed by humans, as discussed earlier in section 3.2.7. The context in the Barrow Valley is that of intensive agricultural lands with a low density of population (about 30 pers/km^2) where unsewered dwellings and farms are scattered, whereas Curtin's farm in Moorepark RC is an intensive dairy farm. In addition, aquifers from both areas qualify as highly to extremely vulnerable to contamination, as already discussed in section 3.2.5.

Nitrate concentrations measured in the Barrow Valley sampling areas and Moorepark RC were often elevated in regard of the limit set out at 50 mg/l NO_3^- in the Drinking Water Directive (Council of the European Communities, 1998). Results of chemical analyses revealed that in the Barrow Valley, 44 % of the groundwater samples exceeded this limit (64 % of the Moorepark samples), which affected thirty-two of the fifty-one sites (eight sites out of ten in Moorepark RC) on at least one sampling occasion (further-developed in section 6.5). The Drinking Water Directive also stipulates that water intended to human consumption should be free of faecal coliforms. In the Barrow Valley though, a positive count was obtained for this type of coliform in 20 % of tested samples, which concerned fifteen of the thirty-six tested sites on at least one occasion. On the other hand, none of the other measured physico-chemical parameters that are listed under the Drinking Water

Directive (i.e. chloride, sulphate, sodium, pH and conductivity) were in exceedance of their respective drinking water limits catalogued in table 2.2.

Yet, some of these physico-chemical parameters showed values that were far more elevated than natural background levels (NBLs). Under uncontaminated conditions, sand/gravel and Carboniferous limestone aquifers, which are the two main types of aquifer in the study areas (section 3.2.5), have low concentrations of nitrate, chloride, potassium and sodium, as opposed to the levels of calcium and bicarbonate that are naturally high due to the hardness of water. Comparing figures in table 2.7 (i.e. NBL values in section 2.5.4) with median, 75th percentile and maximum values recorded in tables 6.1 (Barrow Valley) and 6.2 (Moorepark RC) suggested several observations discussed below.

The NBL for chloride was reported between 22 and 26 mg/l, which is lower than the median chloride Barrow Valley value measured at 29.6 mg/l. Consequently, this implies that at least 50 % of groundwater samples had chloride concentrations between the NBL and the maximum value measured at 84.1 mg/l (more than three times the NBL). In Moorepark RC, the median value for chloride (17.4 mg/l) was lower than the NBL, but the 75th percentile value (25.3 mg/l) matched it, which suggests that about 25 % of the Moorepark samples had chloride concentration between the NBL and the maximum value measured at 45.2 mg/l (less than twice the NBL).

The NBL for potassium was reported between 0.6 and 3 mg/l, which encompassed the median Barrow Valley value of 1.9 mg/l, but was lower than the 75th percentile value of 5 mg/l. This means that more than 25 % of the Barrow Valley groundwater samples had potassium concentrations between the NBL and the maximum of 63 mg/l (twenty times the upper NBL range). In Moorepark RC, the NBL for potassium was matched by the median value (2.5 mg/l), but was much lower than the 75th percentile (7.3 mg/l), which suggests that 25 % of Moorepark groundwater samples at the very least had potassium concentrations between the NBL and the maximum value of 37 mg/l.

The NBL for sodium was reported between 8.8 and 12 mg/l. The sodium median concentration in the Barrow Valley (10.8 mg/l) was within the NBL range, unlike the 75th percentile, which was higher (15 mg/l). This means that at least 25 % of the Barrow Valley groundwater samples had sodium concentrations between the NBL and the maximum value of 46 mg/l (three times the upper NBL range value). The situation was different in Moorepark RC because the median and the 75th percentile values for sodium were within the range displayed by the NBL, which was only exceeded by the maximum value (17 mg/l).

The examination of N sources present in the vicinity of groundwater sampling wells provide some clues about the possible causes for abnormal levels of nitrate, chloride, potassium and sodium in groundwater samples. In the Barrow Valley, the main N sources present within 100 m and 300 m radius around each sampling well (see section 3.4.2) were identified as diffuse applications of artificial fertilisers and organic point sources (farmyard and septic tanks from unsewered houses). In Moorepark RC, N sources around the monitoring boreholes were linked with the presence of a farmyard and septic tank, but also with the diffuse application of artificial fertilisers and animal organic wastes like slurry and dairy wastewater (section 3.4.3).

The artificial fertilisers used by farmers in the Barrow Valley were principally calcium ammonium nitrate (CAN), urea, NPK compounds like 10-10-20 and 18-6-12 (table 3.7 in section 3.4.2), along with sugar beet compound No.1 and potash (KCl). In Moorepark RC, the artificial fertiliser used was CAN (see section 3.4.3). Table 2.5 (section 2.3.2) reveals that apart from nitrogen and nitrate, these artificial fertilisers contain large quantities of potassium and/or chloride (potash contains both) and sometimes sodium (sugar beet compound No.1). On the other hand, animal and human organic wastes, which also have large quantities of nitrogen, are particularly enriched in potassium and sodium, which was discussed earlier in sections 2.3.3 (see table 2.6) and 2.3.4. From the bacterial perspective, faecal coliforms are related to organic wastes only.

In the context of freely-draining soils, two factors should be taken into account to understand groundwater contamination: the ion's mobility in soil, and the type of source (i.e. diffuse or point). Chloride, like nitrate, is a very mobile anion that is not adsorbed by negatively charged soil particles, and consequently, it can move easily through the unsaturated zone, which explains why the diffuse application of KCl or the discharge of organic wastes can result in high chloride levels in groundwater (section 2.5.4). Distinctively, cations like potassium and sodium are strongly held by soil's negatively charged exchange sites, which explains why they tend to be retained by soils (section 2.5.4). It should be added that potassium is generally much more readily adsorbed than sodium at equal concentrations (Levy and Torrento, 1995). But if leaked from a point source, the cation exchange capacity (CEC) of the soil may then be locally exceeded under the point of discharge, and the cations may break through the unsaturated zone to reach groundwater. In contrast, general wisdom suggests that the diffuse applications of artificial fertilisers and organic wastes do not cause such high leaching of cations because soil's CEC is less likely to be overcome (section 2.5.4).

6.3 Classification of the Barrow Valley sites according to hydrochemistry

6.3.1 Estimation of contamination thresholds for chloride, potassium and sodium

Levels of chloride, potassium and sodium were used as indicators of contamination to detect any impact on groundwater chemistry from diffuse sources of artificial fertiliser and from point sources of organic wastes, which are the main N sources of the study areas. As explained in section 6.2.2, these three ions have low NBLs in sand/gravel and Carboniferous limestone aquifers (see table 2.7), whereas they are major constituents of artificial fertilisers and/or organic effluents discharged by farmyards and septic tanks (see sections 2.3.2 to 2.3.4). Because the primary aim of this chapter is to classify groundwater sampling sites according to their chemistry, and to associate them with a type of N source whenever possible, preliminary work consisted of determining limits (or contamination thresholds) of chloride, potassium and sodium concentrations above which contamination can be suspected.

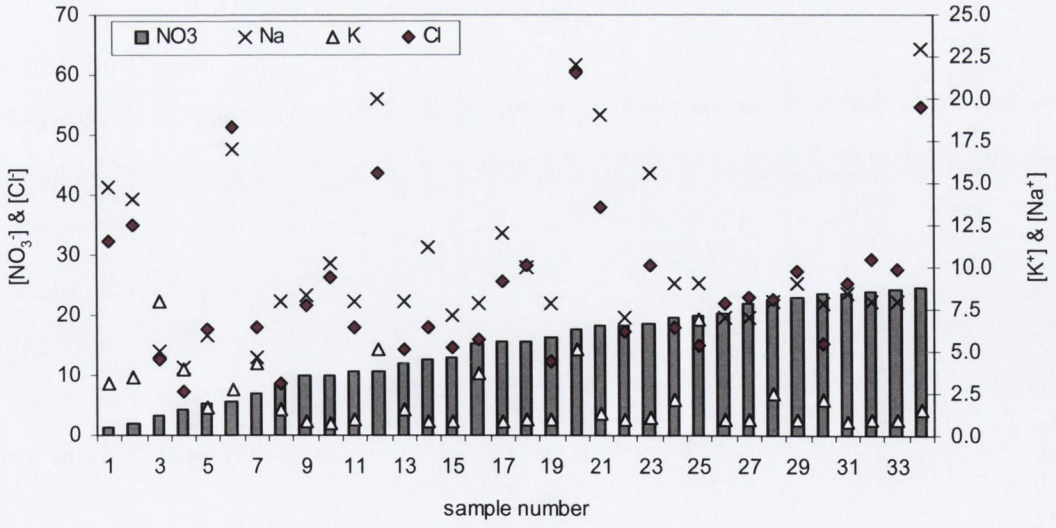
All groundwater sampling sites in the study areas were within a close distance of unsewered houses, farmyards, or tillage land. Therefore, no site was considered as non-impacted by human activities. Because natural background levels have been determined under uncontaminated conditions (EPA, 2003; Baker *et al.*, 2006), i.e. for sites non or little impacted by human activities, it was assumed that NBLs were probably too low to discriminate between different levels of contamination. Therefore, a different approach was adopted in this thesis to determine some background values specific to the study area, which would take into account the fact that all sites are contaminated to some extent. Strictly speaking, these contamination thresholds are not natural background levels.

Attention was given to individual groundwater samples from the Barrow Valley that showed low levels of nitrate contamination. In this thesis, low levels of nitrate contamination are defined as any concentration below 25 mg/l NO_3^-, which was used as a guide line value in the 1980 Drinking Water Directive (see section 2.1.4) and as a contamination trigger value by GSI (see section 2.5.4). The use of low nitrate groundwater samples can be justified by the fact that, despite being possibly caused in some instances by severe denitrification or dilution, low nitrate levels in the context of freely-draining soils were assumed to be mostly the result of low contamination. Therefore relatively uncontaminated samples were thought to give a good estimation of background levels for

the study Barrow Valley area. In the event of denitrification, conservative ions such as chloride are not expected to be attenuated and should still be measured at high concentrations that reflect the original level of contamination. Based on the assumption that most of the low nitrate samples belong to the first category (i.e. genuine low contamination), it was arbitrarily decided to use the 75th percentile values calculated from the low nitrate samples to define contamination thresholds, which should exclude some outliers that one could expect from denitrification (e.g. low nitrate concentration but high chloride level).

Figure 6.2 shows how potassium, sodium and chloride were distributed for each low nitrate groundwater sample (i.e. $[NO_3^-] < 25$ mg/l NO_3^-) from the Barrow Valley. Despite some samples giving rise to some occasional high levels of chloride, sodium, and also potassium to a lesser extent, most low nitrate groundwater samples showed low concentrations for the above species.

Figure 6.2: Distribution of sodium, potassium and chloride concentrations in the thirty-four groundwater samples of the Barrow Valley where nitrate levels were measured below 25 mg/l NO_3^-. *(individual groundwater samples with $[NO_3^-] < 25$ mg/l sorted in ascending order are reported on the x-axis, corresponding nitrate concentration is reported in mg/l NO_3^- and chloride in mg/l on the left y-axis; corresponding potassium and sodium are reported on the right y-axis in mg/l)*



Ranges of values and 75th percentiles are summarised in table 6.3. For comparison, median (50th percentile), 70th and 80th percentiles are also reported. The 75th percentiles used to delineate the upper limit of the background values were low, with values for chloride, potassium and sodium concentration respectively calculated at 28.4 mg/l, 3.1 mg/l and 12 mg/l. The validity of these values is discussed in section 6.3.4.

Table 6.3: Range, median, 70th, 75th and 80th percentile values of chloride, sodium and potassium concentrations measured in the Barrow Valley groundwater samples where nitrate concentration was below 25 mg/l NO_3^-. *(concentrations are reported in mg/l)*

Parameter	n	Median	70th %tile	75th %tile	80th %tile	Min	Max
Chloride	34	22.3	27.8	28.4	31.4	7.5	60.3
Potassium	34	1.4	2.6	3.1	3.6	0.8	8
Sodium	34	8.2	10.5	12	14.6	4.0	23

Setting the thresholds values as 70th or 80th percentiles resulted in limited changes for chloride and potassium contamination thresholds. In comparison with the 75th percentile, the 70th percentile values for chloride were lower by only 0.6 mg/, while the potassium value was lower by 0.5 mg/l and the value for sodium was lower by 1.5 mg/l. Bigger differences were observed with the 80th percentile, values for chloride, potassium and sodium being respectively higher by 3 mg/l, 0.5 mg/l and 2.6 mg/l.

6.3.2 Evidence on N sources provided by hydrochemistry and water quality

- Assumptions about the exceedance of the chloride, potassium and sodium contamination thresholds

Contamination thresholds defined in section 6.3.1 for chloride, potassium and sodium concentrations were used to group groundwater sampling sites with similar water chemistry, based on their exceedance or non-exceedance of the threshold cited earlier. Each category was then associated with either artificial diffuse (i.e. artificial fertilisers) or organic point N source (septic tanks or farmyards) contamination in accordance with several assumptions summarised in table 6.4. Organic diffuse sources (i.e. applications of manure, slurry, and dairy wastewater) were not taken into account because most of the diffuse applications in the Barrow Valley sampling areas were related to artificial fertilisers (see section 3.4.2).

Chloride is a very mobile anion not susceptible to soil adsorption (unlike cations), and contained in large quantities in human and animal wastes. Therefore, groundwater contaminated by organic point N sources (farmyard and septic tanks) is expected to be associated at the very least with high Cl^- levels (categories P_c in Group 2 classification, or P_{c1} and P_{c2} in Group 6 classification of table 6.4).

Table 6.4: Definition of groups and categories relating groundwater chemistry, i.e. exceedance (√) or non-exceedance (×) of contamination thresholds, to artificial diffuse (D_c) or organic point source (P_c) contamination. *(thresholds were defined as the 75th percentile values of chloride, potassium and sodium concentrations when [NO_3^-] < 25 mg/l)*

Group 2	Group 6	[Cl^-] ≥ 28.4 mg/l	[K^+] ≥ 3.1 mg/l	[Na^+] ≥ 12 mg/l
D_c (Artificial diffuse source)	D_{c1}	×	×	×
	D_{c2}	✓	×	×
	D_{c3}	✓	✓	×
	D_{c4}	×	✓	×
P_c (Organic point source)	P_{c1}	✓	✓	✓
	P_{c2}	✓	×	✓

NB: suffix "c" placed after category names (e.g. D_c and P_c) was used to distinguish classification based on chemistry from classification based on spatial characteristics (for which suffix "s" will be used)..

A complication in distinguishing organic point sources from diffuse sources comes from the fact that chloride is also a major component of potash (KCl), commonly used by farmers of the study areas (see section 3.4.2), which may result in high Cl^- levels in groundwater (categories D_{c2} and D_{c3} in Group 6 classification of table 6.4).

Potassium is another major component of organic wastes. Due to its very high affinity for soil's negatively charged exchange sites, it is generally extensively adsorbed and may not necessarily leach in quantities that would reflect the original input. Because organic point sources provide a large loading over a small area, which can exceed soil's cation exchange capacity, potassium may yet break through without all being adsorbed or exchanged, which would result in high concentration in groundwater (category P_{c1} in Group 6 classification of table 6.4).

A further complication in discriminating organic point from artificial diffuse sources is due to the fact that NPK fertilisers or potash also contain large quantities of potassium (section 2.3.2). The general wisdom would suggest that unlike organic point sources, artificial diffuse sources do not leach large quantities of non-nitrogenous compounds. But studies showed that background levels of potassium can sometimes be largely exceeded in groundwater after large amounts of NPK fertilisers had been applied (categories D_{c3} and D_{c4} in Group 6 classification of table 6.4), as discussed in section 2.5.4.

The use of sodium to differentiate point source from diffuse source contamination is simpler because except for sugar beet compound No.1 (see table 2.5 in section 2.3.2), Na^+ is rarely present in artificial fertilisers. Therefore, the diffuse application of artificial fertilisers is not expected to generate high sodium leaching (category D_c of Group 2 classification, or categories D_{c1}, D_{c2}, D_{c3} and D_{c4} in Group 6 classification of table 6.4).

This assumption was backed up by results from the Oak Park monitoring area, where no site showed either mean or median sodium concentration above the 12 mg/l threshold value (see appendix 5D). It is reminded that these sites, which are away from organic point N sources, are located in a tillage area where the diffuse application of artificial fertiliser was identified as the main N input to soils (section 3.4.3).

In addition, sodium is a major component of animal and human wastes discharged by organic point sources (sections 2.3.3 and 2.3.4). Like any cation, it can be retained in soils, but as explained for potassium, point sources often provide the conditions necessary to overcome soil's CEC, allowing sodium leaching to break through (categories P_c in Group 2 classification, or P_{c1} and P_{c2} in Group 6 classification of table 6.4). Nonetheless, high leaching of sodium might not always be accompanied by high leaching of potassium (category P_{c2} in Group 6 classification of table 6.4), depending on the geology. Indeed, the affinity of soils for potassium is far greater than for sodium (Levy and Torrento, 1995), which means that potassium concentrations below the contamination threshold should be envisaged in case of organic point source contamination.

- Assumptions about the exceedance of the potassium to sodium ratio and faecal coliform thresholds

Because faecal coliform analyses were performed on only thirty-six sites out of fifty-one in the Barrow Valley, this parameter was not used for groundwater classification. Nevertheless, results could be used to check the validity of some of the above assumptions. Indeed, faecal coliforms are present in animal and human organic wastes in very large numbers, but they are not related to artificial diffuse sources. Therefore, groundwater samples classified in categories D_c (Group 2 of table 6.4) or D_{c1} to D_{c4} (Group 6 of table 6.4) are not expected to be tested positive. For instance, a low chloride concentration is not compatible with the presence of faecal coliforms, if it is assumed that coliforms do not migrate further than chloride, which is likely considering the short life-expectancy of these bacteria. On the other hand, the absence of faecal coliforms does not inform on anything since their absence may just be attributed to the fact they died before reaching the sampling well. Hence, faecal coliforms may not be detected where contamination is due to organic point sources.

A final parameter to be taken into account was the potassium to sodium ratio. This is a qualitative parameter that can be used to distinguish farmyard from septic tank

contamination, on the basis that human wastes have much lower potassium to sodium ratio than animal wastes due to our diet. A trigger value was set by the GSI at 0.3 (Daly, 2000; EPA, 2003), above which the source of contamination is probably farmyard rather than septic tank effluents (see section 2.5.4 for further details).

6.3.3 Classification of groundwater sampling sites according to hydrochemistry

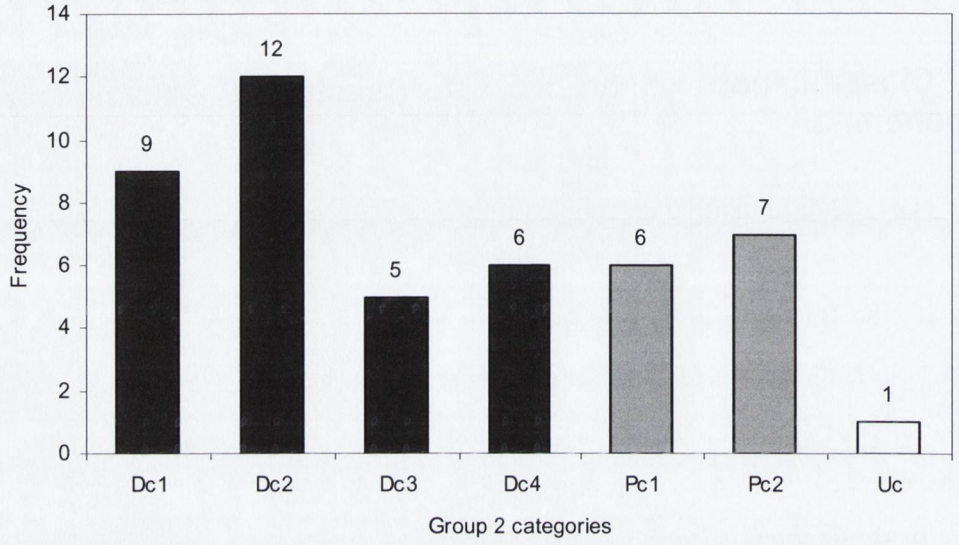
- Site classification using mean concentrations of nitrate, chloride, potassium and sodium

To classify the Barrow Valley sampling sites according to the criteria defined in table 6.4 (section 6.3.2), it was decided to the use mean values of nitrate (Appendix 5A), chloride (Appendix 5B), potassium (Appendix 5C) and sodium (Appendix 5D), calculated for each well. The choice of using the means rather than the medians was dictated by the fact that for most of these chemical parameters, the difference between mean and median values at each site was often so small (indicating normally distributed data) that it was not expected to influence the outcome of the classification.

Five sites (C.9, C.11, O.6, O.10 and BHO.3B) with low mean nitrate concentrations (i.e. mean $[NO_3^-] < 25$ mg/l) were excluded from this classification, which is further discussed in section 6.3.5. It should be noted that three of these sites (C.9, O.6 and O.10) had mean chloride, potassium and sodium concentrations well below the contamination thresholds, whereas the two other sites showed either excessive potassium concentration (mean $[K^+]$ = 4.5 mg/l at BHO.3B), or excessive chloride and sodium concentrations (mean $[Cl^-]$ = 47.5 mg/l and mean $[Na^+]$ = 19.7 mg/l at site C.11).

The first step consisted of classifying sites according to the Group 6 categories from table 6.4 (section 6.3.2), which distinguished different types of hydrochemistry relevant to contamination by either artificial diffuse N sources or organic point N sources. Figure 6.3 shows how many sites belonged to each category according to mean chloride, potassium and sodium concentrations. According to the assumptions made in the previous section, some combinations of exceedance could not be explained: for instance, the potassium and sodium thresholds are not expected to be exceeded if the chloride threshold is not. Sites falling in such category were labelled as undetermined source of contamination (U_c).

Figure 6.3: Frequency distribution of forty-six groundwater sampling sites from the Barrow Valley, with high mean nitrate concentration (i.e. $[NO_3^-] \geq 25$ mg/l) and classified according to the following categories of hydrochemistry: $\mathbf{D_{c1}}$ (mean $[Cl^-] < 28.4$ mg/l, $[K^+] < 3.1$ mg/l, $[Na^+] < 12$ mg/l), $\mathbf{D_{c2}}$ (mean $[Cl^-] \geq 28.4$ mg/l, $[K^+] < 3.1$ mg/l, $[Na^+] < 12$ mg/l), $\mathbf{D_{c3}}$ (mean $[Cl^-] \geq 28.4$ mg/l, $[K^+] \geq 3.1$ mg/l, $[Na^+] < 12$ mg/l), $\mathbf{D_{c4}}$ (mean $[Cl^-] < 28.4$ mg/l, $[K^+] \geq 3.1$ mg/l, $[Na^+] < 12$ mg/l), $\mathbf{P_{c1}}$ (mean $[Cl^-] \geq 28.4$ mg/l, $[K^+] \geq 3.1$ mg/l, $[Na^+] \geq 12$ mg/l), $\mathbf{P_{c2}}$ (mean $[Cl^-] \geq 28.4$ mg/l, $[K^+] < 3.1$ mg/l, $[Na^+] \geq 12$ mg/l), $\mathbf{U_c}$ (mean $[Cl^-] < 28.4$ mg/l, $[K^+] \geq 3.1$ mg/l, $[Na^+] \geq 12$ mg/l). *(D_{c1} to D_{c4} are relevant to artificial diffuse source contamination, P_{c1} and P_{c2} are relevant to organic point source contamination, and U_c is undertermined)*

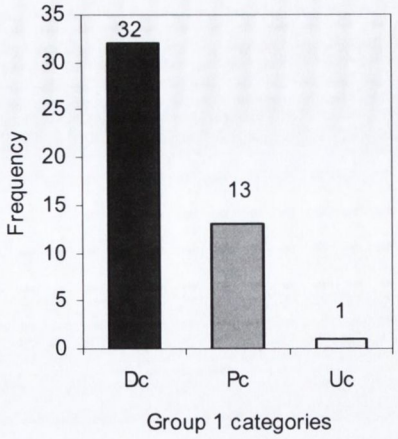


Due to mean concentrations of chloride, potassium and sodium below the contamination threshold values, nine sites were classified in the category D_{c1}, whereas twelve sites fell into category D_{c2} due to only the mean chloride concentration exceeding the chloride threshold. Five sites with mean chloride and potassium concentrations exceeding their respective thresholds were then categorised as D_{c3}, and finally, six sites with only the mean potassium concentration exceeding the potassium threshold belonged to category D_{c4}.

On the other hand, six sites with mean concentrations of chloride, potassium and sodium in exceedance of the contamination thresholds values were classified as P_{c1}, whereas seven sites with mean potassium concentrations below the potassium threshold qualified for category P_{c2}. Finally, one site that showed a mean chloride level below the threshold value while mean potassium and sodium concentrations were in exceedance did not fit in categories related to either artificial diffuse or point source contamination, and was consequently put in the undetermined category U_c.

Categories D_{c1} to D_{c4} were then grouped into a single category D_c (see Group 2 classification in table 6.4), which is indicative of artificial diffuse source contamination, while categories P_{c1} and P_{c2} that are relevant to organic point source contamination were put into category P_c. Figure 6.4 shows the frequency distributed for each category.

Figure 6.4: Frequency distribution of forty-six groundwater sampling sites from the Barrow Valley, with high mean nitrate concentration (i.e. $[NO_3^-] \geq 25$ mg/l) and classified according to the following categories of hydrochemistry: $\mathbf{D_c}$ (artificial diffuse N sources contamination), $\mathbf{P_c}$ (organic point N source contamination), and $\mathbf{U_c}$ (undetermined source).



According to this classification, thirty-two sites out of the forty-six showing high mean nitrate levels (i.e. $[NO_3^-] \geq 25$ mg/l) displayed hydrochemical characteristics relevant to contamination by artificial diffuse sources (category D_c), whereas thirteen sites showed signs allegedly related to organic point source contamination (category P_c). It should be noted that using the 80th percentile values in table 6.3 resulted in a slightly different count, with three sites shifting from the P_c to D_c category.

Table 6.5 identifies the Barrow Valley sites (with mean $[NO_3^-] \geq 25$ mg/l) that belong to each category of the Group 2 and Group 6 classification displayed by figures 6.3 and 6.4.

Table 6.5: Identification of high nitrate sites (i.e. mean $[NO_3^-] \geq 25$ mg/l) across the hydrochemical categories of Group 2 and Group 6 classification detailed in table 6.4.

Group 2	Group 6	Site identification
D_c (Artificial diffuse source)	D_{c1}	B.4, B.6, B.8, C.12, O.1, O.2, O.5, O.8, BHO.6
	D_{c2}	B.3, B.7, B.10, C.4, C.7, C.14, C.17*, C.18, C.20, O.9, O.12, BHO.7
	D_{c3}	B.1, B.5, C.3, BHO.4A, BHO.5
	D_{c4}	C.6*, C.16*, O.13, BHO.1, BHO.4, BHO.8
P_c (Organic point source)	P_{c1}	B.9, C.2, C.5, C.10, C.13, O.11
	P_{c2}	B.2, C.8, C.15, C.19, O.3, O.4*, O.7
U_c (Undetermined source)	U_c	C.1

* had at least one sample with $[NO_3^-] < 25$ mg/l

- Examination of sites at the sample level

Because nitrate, chloride, potassium and sodium concentrations varied from one sampling occasion to another, it was decided to scrutinise each site listed in table 6.5 at the sample level, in order to see whether the classification using mean values gave a description that

was consistent through sampling time. This comparison was made on high nitrate sites (i.e. mean $[NO_3^-] \geq 25$ mg/l) that had been sampled more than once, which excluded five sites (i.e. B.10, C.14, C.18 to C.20) that had been sampled only once. Therefore, forty-one sites sampled between two and seven times remained for this study.

The examination of the results in appendix 3 showed that among these forty-one high nitrate sites sampled more than once, 41 % (17 out of 41) had samples that were consistently within the same Group 6 categories: six sites had all samples in the D_{c1} category (B.8, C.12, O.1, O.2, O.5, BHO.6), one site had all samples in the D_{c3} category (B.1), one site had all samples in the D_{c4} category (BHO.1), three sites had all samples in the P_{c1} category (C.2, C.5, C.13), five sites had all samples in the P_{c2} category (B.2, C.8, C.15, O.4, O.7), and one site had all samples in the U_c category (C.1).
Despite the fact that the remaining 59 % of sites (24 out of 41) had samples that did not belong consistently to the same Group 6 categories (i.e. D_{c1}, D_{c2}, D_{c3}, D_{c4}, P_{c1}, P_{c2} or U_c), half of these sites (12 out of 24) had samples that could yet be classified consistently within the categories of Group 2 classification that relate to artificial diffuse (D_c) or organic point source contamination (P_c). At site B.4 for instance, five samples were classified as D_{c1} ($[Cl^-] < 28.4$ mg/l, $[K^+] < 3.1$ mg/l, $[Na^+] < 12$ mg/l) and two as D_{c2} ($[Cl^-] \geq 28.4$ mg/l, $[K^+] < 3.1$ mg/l, $[Na^+] < 12$ mg/l), but overall, all these seven samples belonged to the same D_c category (artificial diffuse source contamination). Therefore, if looking at the Group 2 classification only, 70 % (29 out of 41) of high nitrate sites visited more than once had samples that consistently belonged to either categories D_c, P_c or U_c. The identification of these sites is displayed in table 6.6.

Table 6.6: Identification of high nitrate sites (i.e. mean $[NO_3^-] \geq 25$ mg/l) that showed through sampling time consistent hydrochemistry indicative of artificial diffuse N sources contamination (category D_c of Group 2 classification - see table 6.4), organic point N source contamination (category P_c of Group 2 classification), or undetermined (category U_c of Group 2 classification).

Group 2	Site identification
D_c (Artificial diffuse source)	B.1, B.3, B.4, B.6, B.7, B.8, C.12, O.1, O.2, O.5, O.8, O.9, O.13, BHO.1, BHO.4, BHO.4A, BHO.5, BHO.6, BHO.8
P_c (Organic point source)	B.2, B.9, C.2, C.5, C.8, C.13, C.15, O.4, O.7,
U_c (Undetermined source)	C.1

Distinctively, 30 % of the high nitrate sites sampled more than once (12 sites out of 41), which were classified in either the D_c or P_c categories in regard of their mean chloride,

potassium and sodium concentrations, had samples that did not belong consistently to one of the Group 2 categories. Instead, samples collected from these sites (identified as B.5, C.3, C.4, C.6, C.7, C.10, C.16, C.17, O.3, O.11, O.12, BHO.7) were a mixture of D_c, P_c and sometimes U_c categorised samples.

Nonetheless, four of these sites that were sampled seven times were very close to consistency (C.3, C.4, C.7 and C.10), with only one sample out of seven classified in a different Group 2 category because of sodium concentration that was recorded on one occasion on a different side of the 12 mg/l threshold value.

- Faecal coliform concentration by site

As mentioned in section 6.2.1, one hundred and twenty-three groundwater samples were collected from thirty-six sites. Thirty-one of these sites were among the high nitrate sampling wells listed in table 6.5 (eleven were classified as P_c, and twenty as D_c), and the remaining five were the low nitrate wells excluded from the classification. The twenty-four groundwater samples that tested positive were distributed between fifteen sites as follows: fifteen samples came from seven sites classified in the P_c category (namely B.2, B.9, C.2, C.8, C.10, C.13 and C.15), six samples came from five sites of the D_c category (namely B.4, B.8, C.3, C.6, C.17), one sample was from the only U_c site (namely C.1), and two more samples originated from two low nitrate sites excluded from the classification (namely C.9 and C.11).

The fifteen samples showing the presence of faecal coliform and collected from P_c sites had all chloride, potassium and sodium concentrations indicative of organic point source contamination. Most of these samples showed high to extreme faecal coliform concentrations, with counts often higher than 10 or 50 FC /100 ml (appendix 3).

On the other hand, only four of the six samples testing positive and collected from the D_c sites (namely B.4, B.8 and C.3) had the characteristics of artificial diffuse point source contamination. These samples all showed counts below 10 FC /100 ml. The two remaining positive samples collected from the D_c sites (C.6 and C.17) had the hydrochemistry indicative of point source contamination.

6.3.4 Discussion of the estimation of chloride, potassium and sodium background levels

By choosing to set out in section 6.3.1 the contamination thresholds for chloride, potassium and sodium concentrations as the 75th percentile values of the low nitrate samples dataset (i.e. $[NO_3^-] < 25$ mg/l), the objective was to eliminate outliers associated with samples that had been highly contaminated by either artificial diffuse or organic point source but that underwent severe denitrification. Hydrochemistry in this type of sample is not representative of a low contamination level since only nitrate is removed, leaving other conservative ions in high concentrations. This possibility was confirmed by the fact that some samples with low nitrate levels showed excessive chloride, potassium or sodium concentrations (see figure 6.2). In table 6.3, maximum values for these three ions were recorded at 60.3 mg/l Cl^-, 8 mg/l K^+ and 23 mg/l Na^+, which are considered as high in regard of NBLs given in table 2.7 for (limestone based) sand/gravel and Carboniferous limestone aquifers.

Because the low nitrate dataset relates to thirty-four samples, setting the contamination threshold for chloride, potassium and sodium concentrations as the 75th percentile meant that nine values were in exceedance for each parameter. Information on which low nitrate samples were affected by exceedance is given here.

Figure 6.2 reveals that chloride and sodium concentrations were simultaneously and widely in exceedance of the 75th percentiles in eight samples (No.1, 2, 6, 12, 20, 21, 23, 34 in figure 6.2). Five of them originated from site C.11, which happened to show some of the lowest nitrate concentrations recorded during this project. This may indicate that the low nitrate levels at this site were rather the result of denitrification (conjugated with organic point source contamination) than uncontaminated groundwater. In four of these eight high chloride and high sodium samples, potassium was also in exceedance of the 75th percentile. Evidence of denitrification was also seen at borehole BHO.3B, where nitrate concentrations were very low in three samples, despite potassium concentrations higher than the 75th percentile value and up to 8 mg/l. In addition, this site was located in the Oak Park monitoring area, where several monitoring boreholes located within a few hundred metres showed nitrate concentrations consistently above the drinking water limit.

Therefore, it can be seen that the 75th percentile limit applied to chloride, potassium and sodium concentrations in the low nitrate dataset excluded samples that showed signs of possible denitrification. Distinctively, nineteen of the thirty-four low nitrate samples

showed concentrations of chloride, potassium and sodium that were simultaneously below the 75th percentile limits. Thirteen of these samples originated from three sites (namely C.9, O.6 and O.10), which were part of the five sites excluded from the classification in section 6.3.3 because of low mean nitrate levels.

The validity of this approach was supported by the fact that the 75th percentile values matched closely the upper ranges of the natural background levels reported by the EPA (2003) for uncontaminated sand/gravel and Carboniferous limestone aquifers, and displayed in table 2.7. Firstly, the chloride NBL was given between 22 and 26 mg/l, while threshold value in this research project was calculated at 28.4 mg/l. Then, the potassium NBL ranged between 0.6 and 3 mg/l, whereas it was calculated at 3.1 mg/l in table 6.3. Finally, the sodium NBL ranged between 8.8 and 12 mg/l according to the EPA (2003), whereas it was calculated at 12 mg/l for the Barrow Valley study areas. It should be noted that chloride contamination threshold in the present study agreed with the value given by Daly (2000), who set it out at 25-30 mg/l (see section 2.5.4). His threshold values for potassium were nonetheless higher, in the range of 4 to 5 mg/l, whereas no threshold value was estimated for sodium.

In comparison with the 75th percentiles, the 70th and 80th percentiles (see table 6.3) yielded values that were less in agreement with the NBLs. The 70th percentile values for potassium and sodium seemed especially low, while the 80th percentiles seemed too high for potassium, with a threshold value of 4.6 mg/l that was yet in good agreement with the range given by Daly (2000).

6.3.5 Discussion of the classification of groundwater sampling sites according to hydrochemistry

Based on their mean nitrate, chloride, potassium and sodium concentrations tabulated in Appendices 5A to 5D, the groundwater sampling sites of the Barrow Valley were classified in section 6.3.3, according to some assumptions formulated in section 6.3.2 and summarised in table 6.4. The aim was to associate sampling sites with either artificial diffuse or organic point N sources. Five sites were excluded from this classification because they did not show signs of serious nitrate contamination (i.e. mean $[NO_3^-] < 25$ mg/l). These sites were nonetheless very useful because they accounted for twenty-four of the thirty-four samples used to determine background levels in section 6.3.1.

Out of forty-six sites that showed nitrate contamination problems (i.e. mean $[NO_3^-] \geq 25$ mg/l), only one could not be classified appropriately: this site had a mean chloride concentration below the chloride threshold, whereas mean potassium and sodium concentrations were largely above their respective contamination thresholds. The fact that only one site out of forty-six could not be classified according to the assumptions made in section 6.3.2 may in fact indicate that the origin of the contamination was different from artificial diffuse or organic point (farmyard or septic tank), which are the N sources on which the assumptions made in section 6.3.2 were based. Field observation confirmed that there was a possible other source of contamination at this location, as a scrap yard is located less than 100 m away from the well.

As illustrated in figure 6.4, thirty-two sites were related to artificial diffuse N source contamination, whereas thirteen were associated with organic point N source contamination. Nonetheless, some limitations to this approach appeared, as all samples from each sites could not always be classified consistently within the same categories. Indeed, the examination of sites at the sample level revealed some discrepancies: some sites that were related to artificial diffuse N source contamination (based on mean values) had occasionally some samples that were yet associated with organic point source contamination, and *vice versa*. Therefore, the site classification based on mean concentrations of chloride, potassium and sodium did not allow categorising every site in a consistent way that was not affected by sampling time.

Several comments can be made. Firstly, question marks remain on how correctly contamination thresholds can be used to describe background levels in the Barrow Valley context. A prime example of the limitations met was illustrated by site C.10, which was sampled seven times and had six samples classified in the P_{c2} category (i.e. $[Cl^-] \geq 28.4$ mg/l, $[K^+] < 3.1$ mg/l, $[Na^+] \geq 12$ mg/l). But sodium concentration was measured once at 8.8 mg/l, i.e. below the 12 mg/l threshold value, this sample falling then into the D_{c3} category ($[Cl^-] \geq 28.4$ mg/l, $[K^+] \geq 3.1$ mg/l, $[Na^+] < 12$ mg/l) and being associated with artificial diffuse source contamination. As seen in section 3.2, the study areas are subjected to large spatial variations in terms of soil, subsoil and bedrock, which could not be taken into account for the data analysis. Therefore, values set out for the contamination thresholds in section 6.3.1 may not be suitable for the whole study area (some values may be too high or too low for some sites) due to local hydrogeological heterogeneity. There is also the possibility that due to seasonal variations in the water-table depth, the groundwater direction flow may have locally changed from one sampling event to another. For instance,

a sampling site that intercepts a plume of contamination from a farmyard or septic tank when the water-table is high may not necessarily intercept the contaminants when the water-table is low if the groundwater flow path has been affected. Therefore, seasonal variation may affect water chemistry locally, which could result in some of the discrepancy observed.

The use of chemical parameters to classify groundwater sampling sites and help determine the source of groundwater nitrate has another limitation, which is directly related to the fact that the above indicators of contamination are far less mobile than nitrate and can only travel shorter distances within plumes of contamination. Therefore, the non-detection of potassium, sodium or chloride concentrations above contamination threshold values may be misleading as some sites can be mistakenly classified in the D_c category when nitrate is mostly of organic origin.

When studying the classification from the faecal coliform perspective, groundwater analysis gave some contradictory results at first sight. As expected, seven out of eleven tested sites related to organic point N source contamination (P_c sites) showed presence of faecal coliform. On the other hand, five out of twenty tested sites associated with artificial diffuse N source contamination (D_c sites) also showed presence of faecal coliforms.

This can raise more question marks about the validity of the site classification since presence of faecal coliforms is not expected in groundwater contaminated by artificial fertilisers. Nevertheless, some important differences could yet be witnessed between contaminated P_c and D_c sites. In fact, the extent of the faecal contamination was far greater at the P_c sites than at the D_c sites. This may suggest that these sites associated with artificial diffuse N source contamination intercepted the edge of some contamination plumes caused by nearby point N sources.

6.4 Effect of sites' spatial characteristics on hydrochemistry in the Barrow Valley

6.4.1 Introduction to sites' spatial characteristics

Based on the number of unsewered houses and farms within 100 m and 300 m radius, and taking into account the fact that all land of the sampling areas not occupied by private properties and roads was used for agriculture as tillage or grassland, four categories of sites were identified in table 3.8 (see section 3.4.2) and associated with a type of N source.

- No farmyard and no house = artificial diffuse N source category (applications of organic animal wastes like manure or slurry were not deemed to be a major organic diffuse source of N in section 3.4.2).
- No farmyard and more than one unsewered house = septic tank N source category.
- One farmyard and its unsewered farm = farmyard N source category (despite the possibility that the farm's septic tank contributes to the overall contamination).
- One or more farmyards and more than one unsewered house = undetermined point source category.

Table 6.7: Identification of groundwater sampling sites from the Barrow Valley across the following N source categories within two radii (100 m and 300 m): D_s = only tillage and grassland (i.e. no farmyard and no unsewered house), PS_s = unsewered houses but no farmyard, PF_s = one farmyard and the unsewered farm house, PFS_s = one or more farmyards and more than one unsewered house.

N source spatial group		Radius	n	Site identification
Artificial diffuse (D_s)		100m	9	B.10, BHO.1, BHO.3B*, BHO.4, BHO.4A, BHO.5, BHO.6, BHO.7, BHO.8
		300m	8	BHO.1, BHO.3B*, BHO.4, BHO.4A, BHO.5, BHO.6, BHO.7, BHO.8
Organic point (P_s)	**Septic tank (PS_s)**	100m	17	B.4, B.6, C.1, C.4, C.6, C.7, C.8, C.12, C.15, C.18, C.19, C.20, O.11, O.4, O.5, O.6*, O.7
		300m	11	B.10, B.6, C.1, C.4, C.6, C.7, C.8, C.12, C.15, C.20, O.6*
	Farmyard (PF_s)	100m	18	B.1, B.2, B.3, B.5, B.7, B.8, B.9, C.2, C.9*, C.10, C.11*, C.13, C.14, O.3, O.8, O.9, O.10*, O.12
		300m	10	B.2, B.3, B.7, B.8, C.11*, C.14, O.8, O.9, O.10*, O.12
	Undetermined point (PFS_s)	100m	7	C.3, C.5, C.16, C.17, O.1, O.2, O.13
		300m	22	B.1, B.4, B.5, B.9, C.2, C.3, C.5, C.9*, C.10, C.13, C.16, C.17, C.18, C.19, O.1, O.2, O.3, O.4, O.5, O.7, O.11, O.13

* Low nitrate sites (i.e. mean $[NO_3^-] < 25$ mg/l)

Table 6.7 above identifies groundwater sampling sites belonging to the different N source categories (within 100 m radius and 300 m radius), and for which the following notations were adopted and used throughout chapters 6 and 7: the first capital letter designates the type of N source (i.e. D for diffuse and P for point), the second capital letter designates the type of point N source (i.e. F for farmyard, S for septic tank, and FS if both are present), and the suffix "s" was used to distinguish site classification based on spatial characteristics from classification based on hydrochemistry, for which suffix "c" was employed (see table 6.4).

Additionally to N sources, four categories of groundwater sampling sites were defined in relation to the percentage of tillage within a 300 metres radius around each groundwater

sampling site, which was originally introduced in table 3.6 (section 3.4.2). The site identification by category is summarised in table 6.8.

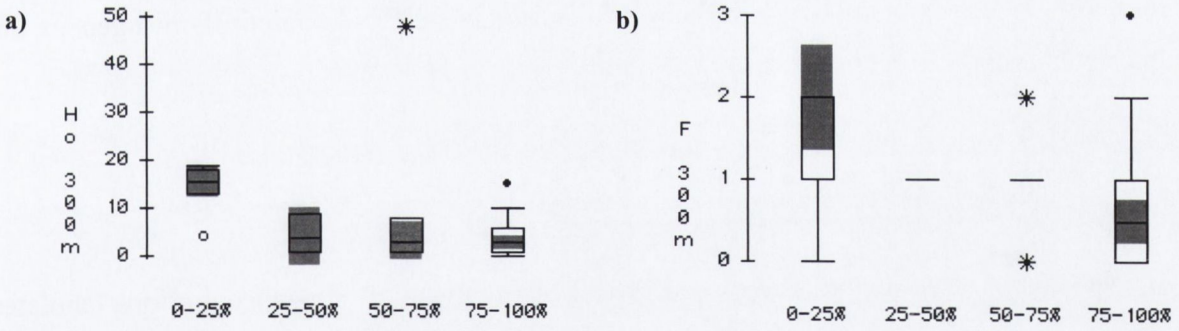
Table 6.8: Identification of groundwater sampling sites from the Barrow Valley according to percentage tillage within 300 m radius.

% tillage within 300 m	n	Site identification
0 % < T ≤ 25 %	6	B.5, O.1, O.4, O.6*, O.7, O.13
25 % < T ≤ 50 %	4	O.3, O.5, O.10*, O.11
50 % < T ≤ 75 %	7	B.1, B.4, B.6, B.9, C.11*, O.12, O.9
75 % < T ≤ 100 %	34	B.2, B.3, B.7, B.8, B.10, C.1, C.2, C.3, C.4, C.5, C.6, C.7, C.8, C.9*, C.10, C.12, C.13, C.14, C.15, C.16, C.17, C.18, C.19, C.20, O.2, O.8, BHO.1, BHO.3B*, BHO.4, BHO.4A, BHO.5, BHO.6, BHO.7, BHO.8

* Low nitrate sites (i.e. mean [NO_3^-] < 25 mg/l)

Figures 6.5a and 6.5b combine information contained in tables 3.6 and 3.8 (within 300 m radius) by displaying the distribution of the number of unsewered houses and farmyards that were counted around sampling wells for each % tillage category.

Figure 6.5: Distribution of the number of unsewered **a)** houses and **b)** farm houses / farm buildings (with farmyard) present within 300 m radius around groundwater sampling sites of the Barrow Valley across the following % tillage categories: 0 % < T ≤ 25 % (n = 6), 25 % < T ≤ 50 % (n = 4), 50 % < T ≤ 75 % (n = 7), 75 % < T ≤ 100 % (n = 34)



Because of one extreme outlier in the 50-75 % tillage category in figure 6.5a (48 houses counted within 300 m around site B.6), attention was given to the median number of unsewered houses located within 300 m around groundwater sampling sites rather than the mean.

In figure 6.5a, it can be see that more unsewered houses were generally counted around wells surrounded by 0-25 % tillage, in comparison with other categories. The examination of the median values reveals that fifteen houses were located in average within 300 m of sites that had 0-25 % tillage, whereas a median number of three to four houses were counted around sampling wells from each of the other three categories. In figure 6.5b, the mean number of farmyards was also slightly higher in the 0-25 % tillage category (two

farmyards) than in the 25-50 % and 50-75 % (one farmyards), or in the 75-100 % tillage category (0.5 farmyards). It should also be noted that the outlier in figure 6.5a was identified as site B.6, where most unsewered houses are served by two large communal septic tanks (see table 3.8).

In fact, it was discussed in section 3.2.7 that nine of the ten sites falling into the 0-25 % and 25-50 % tillage categories were located in the same neighbourhood of the Oak Park outer area where a higher percentage of grassland was found. Therefore, the decrease in % tillage in the vicinity of sampling wells did not seem to be directly related to an increase in the number of private properties and unsewered houses, but it was rather associated with an increase in % grassland.

6.4.2 Contamination indicator values in relation to % tillage

In this section, nitrate, chloride and potassium concentrations are examined in relation to the four classes of % tillage within 300 m radius. Attention is given to these three chemical parameters because these ions are linked with the diffuse applications of artificial fertilisers to tillage land from the Barrow Valley study areas (see section 6.3.2). It is reminded that animal wastes were not regarded as a major organic diffuse source of nitrogen in this particular area (see section 3.4.2).

- Nitrate concentration

Table 6.9 relates to central values and spread of site mean nitrate concentrations tabulated in Appendix 5A.

Table 6.9: Central values and spread of mean nitrate concentration at the groundwater sampling sites of the Barrow Valley across the following % tillage categories: 0 % < T ≤ 25 %, 25 % < T ≤ 50 %, 50 % < T ≤ 75 % and 75 % < T ≤ 100 %. *(nitrate concentration is reported in mg/l NO_3^-)*

Group	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
0 % < T ≤ 25 %	6	35.4	13.8	32.2	29.3	45.3	16.8	56.3
25 % < T ≤ 50 %	4	27.9	10.3	31.8	22.0	33.8	12.7	35.2
50 % < T ≤ 75 %	7	49.8	18.3	48.4	48.0	60.9	12.9	70.3
75 % < T ≤ 100 %	34	53.5	21.3	49.2	38.8	68.3	5.0	97.7

It can be seen that the 75-100 % and the 50-75 % tillage categories had the highest mean nitrate concentrations, which came very close to the 50 mg/l NO_3^- drinking water limit. Distinctively, the lowest mean was observed in the 25-50 % tillage category (27.9 mg/l

NO_3^-), whereas the 0-25 % tillage category showed an intermediate value (35.4 mg/l NO_3^-). An ANOVA test, which was carried out on the untransformed nitrate concentration as the dependent variable and the % tillage group as the independent variable (4:1 ratio of the largest to smallest variance), revealed that there was a significant % tillage effect on nitrate concentrations at the 0.05 level ($F_{3,47} = 3.09$, $p = 0.0359$). In fact, the LSD *Post-Hoc* tests showed that the differences were significant at the 0.05 level only between the 75-100 % and the 25-50 % categories ($p = 0.018$), and also between the 75-100 % and the 0-25 % categories ($p = 0.042$).

As an alternative approach, results were also analysed after merging i) categories 0-25 % and 25-50 % into a 0-50 % category, and ii) categories 50-75 % and 75-100 % into a 50-100 % category. This improved the distribution of sites between categories (4.1:1 ratio of the number of sites between categories 50-100 % and 0-50 %), and more importantly the homogeneity of variance between groups on the NO_3^- variable (2.8:1 ratio of the largest to smallest variance between categories 50-100 % and 0-50 %). The mean of the 0-50 % category (32.4 mg/l NO_3^-) was then found to be almost 20 mg/l NO_3^- lower than that of the 50-100 % category (52.9 mg/l NO_3^-). An ANOVA test, which was carried out on the untransformed nitrate concentration as the dependent variable and the % tillage group as the independent variable, revealed that the difference between both % tillage categories was highly significant at the 0.005 level ($F_{1,49} = 8.98$, $p = 0.0043$).

Except for the 25-50 % tillage category, all other categories showed a wide range of nitrate concentrations, with minimum values below 25 mg/l NO_3^- and maximum values above the 50 mg/l NO_3^- drinking water limit. In fact, the range of the 75-100 % tillage category encompassed ranges of all other category, having the lowest minimum value (5 mg/l NO_3^-) and the highest maximum value (97.7 mg/l NO_3^-).

- Chloride concentration

Table 6.10 relates to central values and spread of site mean chloride concentrations tabulated in Appendix 5B.

The results show no clear pattern in mean chloride concentrations between the % tillage categories: the 0-25 % category had a slightly higher mean value (32.7 mg/l) than the 75-100 % category (31.9 mg/l), whereas the lowest mean was observed in the 25-50 % category (26.7 mg/l) and the maximum mean was recorded in the 50-75 % category. An

ANOVA test, carried out with the log-transformed chloride concentration as the dependent variable and the % tillage group as an independent variable (8.3:1 ratio of the largest to smallest variance, which may limit the reliability of the test as explained in section 6.4.5), showed that none of these differences in chloride concentrations between % tillage groups were significant to the 0.05 level.

Table 6.10: Central values and spread of mean chloride concentration at the groundwater sampling sites of the Barrow Valley across the following % tillage categories: 0 % < T ≤ 25 %, 25 % < T ≤ 50 %, 50 % < T ≤ 75 % and 75 % < T ≤ 100 %. *(chloride concentration is reported in mg/l)*

Group	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
0 % < T ≤ 25 %	6	32.7	15.1	27.0	21.2	50.9	17.8	52.3
25 % < T ≤ 50 %	4	26.7	4.2	26.7	23.1	30.3	22.9	30.6
50 % < T ≤ 75 %	7	36.4	8.1	37.2	28.7	42.8	26.0	47.5
75 % < T ≤ 100 %	34	31.9	10.3	30.1	24.4	38.0	14.0	64.2

The merging of four % tillage categories into two groups (0-50 % and 50-100 % groups) improved greatly the homogeneity of variance between both groups on the log-transformed variable (1.3:1 ratio of the largest to smallest variance). The mean of the 0-50 % tillage group (30.3 mg/l) was very similar to that of the 50-100 % category (32.7 mg/l), and this difference was not found to be significant at the 0.05 level when the log-transformed variable was tested with an ANOVA.

Except for the 25-50 % category, large ranges of chloride concentrations were observed in each category, with the lowest concentrations witnessed below 20 mg/l in the 0-25 % and 75-100 % categories, and the maximum seen in the 75-100 % category at 64.2 mg/l.

- Potassium concentration

Table 6.11 relates to central values and spread of site mean potassium concentrations tabulated in Appendix 5C.

Table 6.11: Central values and spread of mean potassium concentration at the groundwater sampling sites of the Barrow Valley across the following % tillage categories: 0 % < T ≤ 25 %, 25 % < T ≤ 50 %, 50 % < T ≤ 75 % and 75 % < T ≤ 100 %. *(potassium concentration is reported in mg/l)*

Group	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
0 % < T ≤ 25 %	6	2.1	1.2	2.1	0.9	3.2	0.7	3.6
25 % < T ≤ 50 %	4	2.9	2.5	2.2	1.1	4.7	0.8	6.4
50 % < T ≤ 75 %	7	8.5	15.9	2.5	1.5	4.2	1.0	44.5
75 % < T ≤ 100 %	34	5.1	7.7	2.2	1.2	5.8	0.2	37.2

Due to some extremely skewed distributions, the comparison of potassium concentrations between % tillage categories was done using median values rather than means. All median values of each category were low and within similar ranges: the highest median was 2.5 mg/l in the 50-75 % tillage category while the lowest median was 2.1 in the 0-25 % category. An ANOVA test, carried out with the log-transformed potassium concentration as the dependent variable and the % tillage group as an independent variable (3.5:1 ratio of the largest to smallest variance), confirmed that there was no significant % tillage effect on potassium concentrations at the 0.05 level.

Similarly to what was observed with chloride, the merging of the four % tillage categories into two groups (0-50 % and 50-100 % groups) improved the homogeneity of variance between groups on the log-transformed variable (2.8:1 ratio of the largest to smallest variance). The medians of both categories were very similar (2.05 mg/l for the 0-50 % category, 2.2 mg/l for the 50-100 % category), and no significant difference was observed at the 0.05 level when comparison was carried out on the log-transformed variable with an ANOVA test.

The ranges of potassium concentrations were extremely uneven between categories. Whereas all categories showed low minimum values (the highest minimum was 1.0 mg/l in the 50-75 % category), only the 0-25 % category showed a low maximum value (3.6 mg/l). In comparison, both the 50-75 % and 75-100 % categories displayed extremely high maximum potassium concentrations (as high as 44.5 mg/l).

6.4.3 Contamination indicator values in relation to N sources

In this section, the concentrations of nitrate, chloride, potassium and sodium are examined in relation to the presence (and the absence) of organic point N sources within 100 m and 300 m radius around groundwater sampling sites. These latter three ions were discussed in section 6.3.2 as indicators of organic point source contamination.

The results were also analysed for the 75-100 % tillage category within 300 m radius, which contains thirty four of the fifty-one groundwater sampling wells (see table 6.8). This was decided in order to hold constant any potential tillage effect. N source effect within other % tillage classes could not be analysed because not all N source categories were represented (e.g. 0-25 % tillage class contains one PS_s and five PFS_s sites within 300 m radius).

It should be added that faecal coliform data could not be used for comparison between D_s and P_s categories, because no groundwater samples from D_s sites (i.e. the eight monitoring boreholes of the Oak Park monitoring area and site B.10 from the Ballyroe area) were analysed for faecal bacteria.

- Nitrate concentration

Table 6.12 displays the central values and spread of the site mean nitrate concentrations (see Appendix 5A) within the following N source categories and organic point source subcategories within 100 m radius and 300 m radius: artificial fertiliser diffuse N source (labelled D_s), organic point N source (labelled P_s), which is broken down into septic tank N source (labelled PS_s), farmyard N source (labelled PF_s) and undetermined point N source, i.e. septic tank and farmyard N source (labelled PFS_s).

Table 6.12: Central values and spread of mean nitrate concentration at the groundwater sampling sites of the Barrow Valley across the following N source categories within two radii (100 m and 300 m): D_s = artificial diffuse, P_s = organic point, PS_s = septic tank, PF_s = farmyard, PFS_s = undetermined point. *(nitrate concentration is reported in mg/l NO_3^-)*

Group	Radius	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
D_s	100 m	9	62.0	27.2	68.2	51.1	83.3	5.0	87.7
	300 m	8	65.5	26.7	72.0	60.1	83.7	5.0	87.7
P_s	100 m	42	46.1	18.6	43.4	32.3	59.5	12.7	97.7
	300 m	43	45.8	18.4	43.4	32.7	58.7	12.7	97.7
PS_s	100 m	17	46.3	18.5	43.2	36.4	50.1	16.8	97.7
	300 m	11	48.6	21.8	42.6	38.1	58.8	16.8	97.7
PF_s	100 m	18	48.4	20.2	47.8	36.0	62.8	12.7	84.7
	300 m	10	47.1	23.3	45.3	36.0	63.1	12.7	84.7
PFS_s	100 m	7	39.4	14.8	32.1	30.4	46.9	29.1	68.3
	300 m	22	43.8	14.6	44.4	31.3	56.2	19.2	72.2

The results show that the mean nitrate concentration of the D_s category (artificial diffuse N source) was higher than that of the P_s category (organic point N source). Within 100 m radius, the mean nitrate concentration in the D_s category (62 mg/l NO_3^-) was higher than in the P_s category (46.1 mg/l NO_3^-) by 16 mg/l NO_3^- (median higher by 25 mg/l NO_3^-). An ANOVA test, which was performed on the nitrate untransformed dependent variable and the N source group with two categories (i.e. D_s and P_s) as the independent variable within 100 m radius (2.1:1 ratio of the largest to smallest variance), showed that the difference between the D_s and P_s categories was significant at the 0.05 level ($F_{1,49} = 4.6$, $p = 0.0368$). Within 300 m radius, the difference between both categories was slightly larger, the mean nitrate concentration of the D_s category (65.5 mg/l NO_3^-) being higher than that of the P_s

category (45.8 mg/l NO_3^-) by almost 20 mg/l NO_3^- (median higher by almost 30 mg/l NO_3^-). Again, this difference was found to be significant at the 0.05 level ($F_{1,49} = 6.7$, $p = 0.0127$, and 2.1:1 ratio of the largest to smallest variance). When the independent variable used for the ANOVA test was the N source group with four categories (i.e. D_s, PS_s, PF_s and PFS_s), no significant difference was observed at the 0.05 level (3.4:1 ratio of the largest to smallest variance within 100 m and 300 m radius), despite the fact that categories PS_s, PF_s, and PFS_s displayed mean values that were between 39.4 and 48.6 mg/l NO_3^- within 100 m and 300 m radius, i.e. lower than the D_s mean by 15 to 20 mg/l NO_3^-.

It should be noted that nitrate values varied greatly within each category, causing ranges to overlap extensively from one group to another. Except for the PFS_s category within 100 m radius, each category had a minimum value below 25 mg/l NO_3^- and a maximum value that largely exceeded the 50 mg/l NO_3^- drinking water limit.

Figure 6.6: Distribution within the 75-100 % tillage category (i.e. 300 m radius) of mean nitrate concentration at the groundwater sampling sites of the Barrow Valley across the following N source categories: **a)** D_s (n = 8) and P_s (n = 26), and **b)** D_s (n = 8), PS_s (n = 9), PF_s (n = 6) and PFS_s (n = 11). *(nitrate concentration is reported in mg/l NO_3^-)*

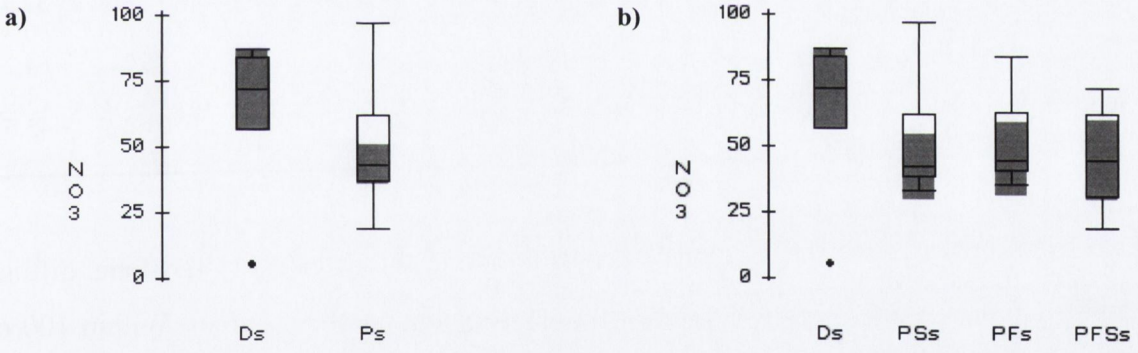


Figure 6.6a above shows how nitrate concentrations were distributed within 300 m radius within categories D_s (artificial diffuse N source) and P_s (organic point N source) at sites surrounded by 75 % to 100 % tillage. In figure 6.6b, the distinction is made between organic point N source subcategories, i.e. PS_s (septic tank source), PF_s (farmyard source) and PFS_s (septic tank and farmyard sources). It should be noted that the D_s category was not affected by restricting the study to the 75-100 % tillage group since all its eight sites were already within this % tillage category.

Restricting the study to high tillage sites changed very little to the values displayed in table 6.12, as means and medians within the P_s category and its subcategories increased by less than 4 mg/l NO_3^- (within 300 m radius). In fact, the only important shift towards higher values concerned the minimum nitrate concentrations in the PS_s (33.8 mg/l NO_3^-) and PF_s

categories (36 mg/l NO_3^-). As for the difference between the D_s and P_s category, it was no longer significant at the 0.05 level (2.1:1 ratio of the largest to smallest variance).

- Chloride concentration

Table 6.12 reports the central values and spread of site mean chloride concentrations (see Appendix 5B) within the different N source categories and organic point source subcategories from table 6.7 within 100 m radius and 300 m radius.

Table 6.13: Central values and spread of mean chloride concentration at the groundwater sampling sites of the Barrow Valley, across the following N source categories within two radii (100 m and 300 m): D_s = artificial diffuse, P_s = organic point, PS_s = septic tank, PF_s = farmyard, PFS_s = undetermined point. *(chloride concentration is reported in mg/l)*

Group	Radius	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
D_s	100 m	9	27.9	9.6	27.5	21.2	32.9	14.0	43.5
	300 m	8	26.4	9.0	27.2	19.9	29.8	14.0	43.5
P_s	100 m	42	33.1	10.4	30.6	25.4	38.2	16.2	64.2
	300 m	43	33.3	10.3	30.6	25.6	39.8	16.2	64.2
PS_s	100 m	17	32.2	9.8	30.5	23.6	38.1	17.8	52.3
	300 m	11	29.9	7.6	30.5	23.4	37.7	17.8	40.3
PF_s	100 m	18	35.3	11.5	32.1	28.5	42.1	16.2	64.2
	300 m	10	33.3	9.5	30.3	26.9	37.2	23.3	51.6
PFS_s	100 m	7	29.7	8.2	27.4	24.4	33.3	21.2	45.6
	300 m	22	35.0	11.7	32.6	26.0	42.1	16.2	64.2

The results show that the mean chloride concentration of the D_s category (artificial diffuse N source) was lower than that of the P_s category (organic point N source). Within 100 m radius, the difference was almost 5 mg/l, the mean chloride concentration of the D_s category being slightly below 28 mg/l while that of the P_s category was slightly above 33 mg/l. An ANOVA test, which carried out on the chloride log-transformed dependent variable and the N source group with two categories (i.e. D_s and P_s) as the independent variable within 100 m radius (1.4:1 ratio of the largest to smallest variance), showed that the difference between the D_s and P_s categories was not significant at the 0.05 level. Within 300 m radius, the slightly larger difference of 7 mg/l became significant at the 0.05 level ($F_{1, 49} = 4.07$, $p = 0.0491$, and 1.4:1 ratio of the largest to smallest variance). When the independent variable used for the ANOVA test was the N source group with four categories (i.e. D_s, PS_s, PF_s and PFS_s), no significant N source effect was observed at the 0.05 level (2.1:1 ratio of the largest to smallest variance within 100 m radius, and 1.8:1 ratio of the largest to smallest variance within 300 m radius). This occurred despite the fact that within 100 m and 300 m radius, the mean chloride concentrations of categories PS_s

(septic tank source), PF_s (farmyard source) and PFS_s (septic tank and farmyard source) ranged from 29.9 to 35 mg/l, which was up to 8.6 mg/l higher than for the D_s category.

Like nitrate, chloride values varied considerably, which resulted in very large overlaps between the D_s and the point N source categories (i.e. P_s, PS_s, PF_s and PFS_s). The minimum chloride value was 14 mg/l in the D_s category and 16.2 mg/ in the P_s category within 100 m and 300 m radius, whereas the maximum was 43.5 mg/l in the D_s category and 64.2 mg/ in the P_s category.

Figure 6.7: Distribution within the 75-100 % tillage category (i.e. 300 m radius) of mean chloride concentration at the groundwater sampling sites of the Barrow Valley across the following N source categories: **a)** D_s (n = 8) and P_s (n = 26), and **b)** D_s (n = 8), PS_s (n = 9), PF_s (n = 6) and PFS_s (n = 11). *(chloride concentration is reported in mg/l)*

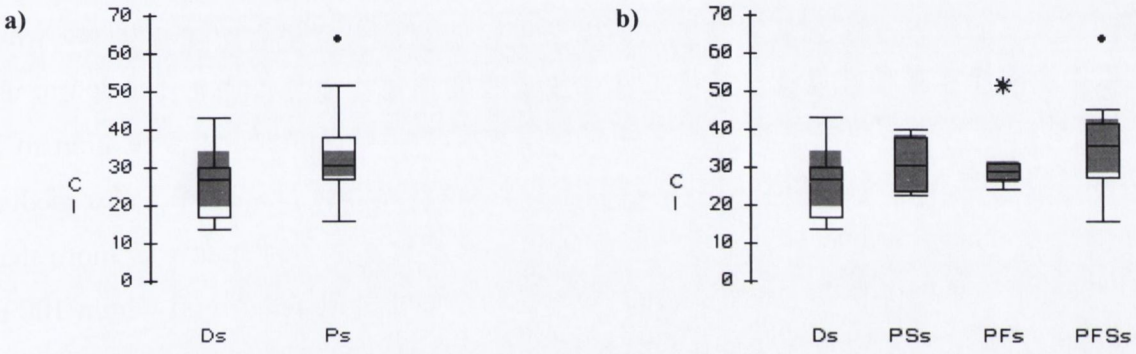


Figure 6.7a shows how chloride concentrations were distributed within categories D_s (artificial diffuse N source) and P_s (organic point N source) at sites surrounded by 75 % to 100 % tillage (within 300 m radius). In figure 6.7b, the distinction is made between organic point source subcategories, i.e. PS_s (septic tank source), PF_s (farmyard source) and PFS_s (septic tank and farmyard sources).

Means and medians of the P_s category and its subcategories were within 3 mg/l of values described in table 6.13 within 300 m radius. Minimum and maximum values remained unchanged. As for the difference between the D_s and P_s category (mean $[Cl^-]$ in P_s higher than in D_s), it edged towards significance at the 0.05 level (p = 0.0507, 1.4:1 ratio of the largest to smallest variance).

- Potassium concentration

Table 6.14 shows the central values and spread of site mean potassium concentrations (see Appendix 5C) within the different N source categories and organic point source subcategories from table 6.7 within 100 m radius and 300 m radius.

Table 6.14: Central values and spread of mean potassium concentration at the groundwater sampling sites of the Barrow Valley across the following N source categories within two radii (100 m and 300 m): D_s = artificial diffuse, P_s = organic point, PS_s = septic tank, PF_s = farmyard, PFS_s = undetermined point. *(potassium concentration is reported in mg/l)*

Group	Radius	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
D_s	100 m	9	4.7	3.9	4.5	1.7	6.8	0.2	13.0
	300 m	8	5.0	4.1	4.5	2.1	7.0	0.2	13.0
P_s	100 m	42	5.1	9.3	2.0	1.2	3.9	0.3	44.5
	300 m	43	5.0	9.2	2.1	1.2	3.8	0.3	44.5
PS_s	100 m	17	2.3	1.9	1.6	1.1	2.3	0.7	6.4
	300 m	11	2.2	1.9	1.6	1.0	2.2	0.7	6.0
PF_s	100 m	18	7.9	13.3	2.5	1.2	4.3	0.3	44.5
	300 m	10	1.5	1.2	1.3	0.7	2.2	0.3	4.3
PFS_s	100 m	7	4.6	5.6	3.2	1.3	5.2	0.7	16.8
	300 m	22	8.0	12.1	3.1	1.6	6.4	0.7	44.5

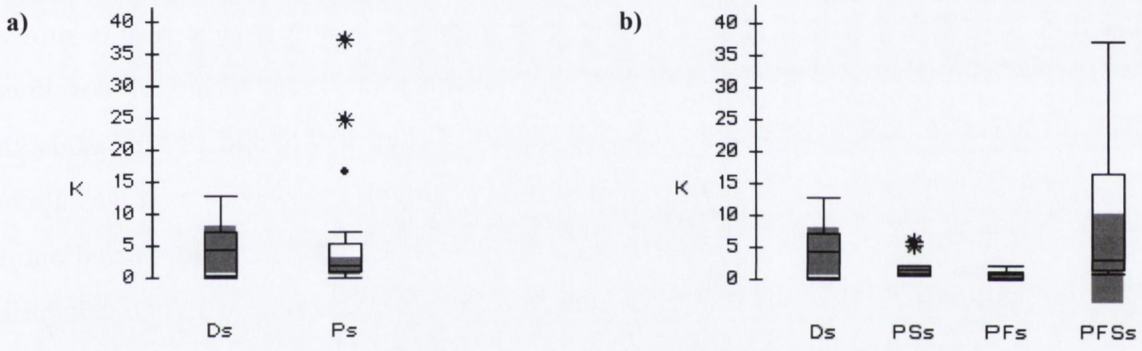
Owing to seriously skewed distributions in some categories, which were detected when large differences were observed between mean and median values, it was decided to use the medians rather than the means to analyse potassium concentrations in relation to N sources. The results show that the D_s category (artificial diffuse N source) had a median potassium concentration (4.5 mg/l within 100 m and 300 m radius) that was more than twice as high as that of the organic point source category P_s (around 2 mg/l within 100 m and 300 m radius). An ANOVA test, which was carried out within 100 m and 300 m radius on the potassium log-transformed dependent variable and the N source group with two categories (i.e. D_s and P_s) as the independent variable, revealed that differences between D_s and P_s categories were not significant ($p > 0.05$; 1.4:1 ratio of the largest to smallest variance within 100 m radius, 1.6:1 ratio of the largest to smallest variance within 300 m radius). When the independent variable was the N source group with four categories (i.e. D_s, PS_s, PF_s and PFS_s), no significant N source effect was observed within 100 m and 300 m radius (4.3:1 ratio of the largest to smallest variance within 100 m radius, 3.7:1 ratio of the largest to smallest variance within 300 m radius). This happened despite the fact that the median potassium concentrations in the organic point source subcategories ranged between 1.3 and 3.2 mg/l, which was lower by up to 3.2 mg/l than the median of the D_s category.

Very large overlapping ranges of values were observed within the artificial diffuse D_s and the organic point N source P_s categories. In the D_s category, the lowest concentration was 0.2 mg/l, whereas the maximum rose to 13 mg/l. In comparison, the minimum potassium value in the P_s category was equally low (0.3 mg/), whereas the maximum reached 44.5 mg/l. In fact, most of these extremely high values were accounted for by the PF_s category

within 100 m radius, and by the PFS_s category within 300 m radius, while the PS_s category showed lower maximum values around 6 mg/l.

Figure 6.8a shows how potassium concentrations were distributed within categories D_s (artificial diffuse N source) and P_s (organic point N source) at sites surrounded by 75 % to 100 % tillage (within 300 m radius). In figure 6.8b, the distinction is made between organic point source subcategories, i.e. PS_s (septic tank source), PF_s (farmyard source) and PFS_s (septic tank and farmyard sources).

Figure 6.8: Distribution within the 75-100 % tillage category (i.e. 300 m radius) of mean potassium concentration at the groundwater sampling sites of the Barrow Valley across the following N source categories: **a)** D_s (n = 8) and P_s (n = 26), and **b)** D_s (n = 8), PS_s (n = 9), PF_s (n = 6) and PFS_s (n = 11). *(potassium concentration is reported in mg/l)*



Potassium concentrations in the P_s category and its subcategories were hardly affected by restricting the study to the 75-100 % tillage category, potassium median concentrations being within 0.4 mg/l of the values reported in table 6.14 within 300 m radius. Minimum and maximum values were almost unchanged. In addition, there was not significant N source effect between the D_s and P_s categories at the 0.05 level (1.4:1 ratio of the largest to smallest variance).

- Sodium concentration

Table 6.15 shows the central values and spread of site mean sodium concentrations (Appendix 5D) within the different N source categories and organic point source subcategories from table 6.7 within 100 m radius and 300 m radius.

Table 6.15: Central values and spread of mean sodium concentration at the groundwater sampling sites of the Barrow Valley across the following N source categories within two radii (100 m and 300 m): D_s = artificial diffuse, P_s = organic point, PS_s = septic tank, PF_s = farmyard, PFS_s = undetermined point. *(sodium concentration is reported in mg/l)*

Group	Radius	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
D_s	100 m	9	7.9	2.4	7.6	5.9	9.6	4.9	11.9
	300 m	8	7.5	2.2	7.5	5.8	8.4	4.9	11.9
P_s	100 m	42	13.4	6.0	11.1	9.7	16.3	6.9	34.2
	300 m	43	13.4	6.0	11.1	9.8	15.9	6.9	34.2
PS_s	100 m	17	15.0	7.9	11.1	10.2	19.2	7.3	34.2
	300 m	11	14.1	7.7	10.9	10.1	17.3	7.3	34.2
PF_s	100 m	18	13.0	4.7	11.3	9.4	16.7	6.9	22.5
	300 m	10	11.6	4.5	10.4	9.3	11.3	6.9	19.7
PFS_s	100 m	7	10.6	2.0	10.8	9.2	11.2	8.2	14.4
	300 m	22	13.8	5.7	11.6	10.2	16.3	8.0	29.6

Owing to skewness in some categories, it was decided to scrutinise the medians rather than the means to analyse sodium concentrations in relation to N sources. The results showed that the sodium median concentration of the D_s category (artificial fertiliser) was lower than that of the P_s category (organic point N source). Within 100 m and 300 m radius, the sodium median value in the D_s category was slightly below 8 mg/l, whereas it was almost 3.5 mg/l higher in the P_s category at 11.1 mg/l. An ANOVA test, which was carried out on the sodium log-transformed dependent variable and the N source group with two categories (i.e. D_s and P_s), showed that the difference between both categories was highly significant at the 0.001 level within the 100 m radius ($F_{1, 49} = 13.5$, $p = 0.0006$, 1.6:1 ratio of the largest to smallest variance) and within the 300 m radius ($F_{1, 49} = 14.8$, $p = 0.0003$, 1.7:1 ratio of the largest to smallest variance). Median values showed some remarkable consistency between organic point source subcategories (i.e. PS_s, PF_s and PFS_s), being all recorded between 10.4 and 11.6 mg/l within 100 m and 300 m radius. In fact, the N source effect was still highly significant at the 0.005 level ($F_{3, 47} = 5.4$ and $p = 0.0028$ within 100 m and 300 m radius) when the independent variable was the N source group with four categories (6.1:1 ratio of the largest to smallest variance within 100 m radius, and 2.3:1 ratio within 300 m radius). The LSD *Post-Hoc* tests revealed then that differences were significant between categories D_s and PS_s category ($p = 0.0003$ within 100 m radius, $p = 0.0016$ within 300 m radius), between categories D_s and PF_s ($p = 0.0022$ within 100 m radius, $p = 0.0211$ within 300 m radius), and also between D_s and PFS_s within 300 m radius ($p = 0.0003$).

Similarly to other chemical variables, all categories showed a large range of overlapping sodium concentrations. In the D_s category, sodium levels ranged from 4.9 mg/l to 11.9

mg/l, whereas this range was much wider in the P_s category, with maximum values as high as 34.2 mg/l.

Figure 6.9: Distribution within the 75-100 % tillage category (i.e. 300 m radius) of mean sodium concentration at the groundwater sampling sites of the Barrow Valley across the following N source categories: **a)** D_s (n = 8) and P_s (n = 26), and **b)** D_s (n = 8), PS_s (n = 9), PF_s (n = 6) and PFS_s (n = 11). *(sodium concentration is reported in mg/l)*

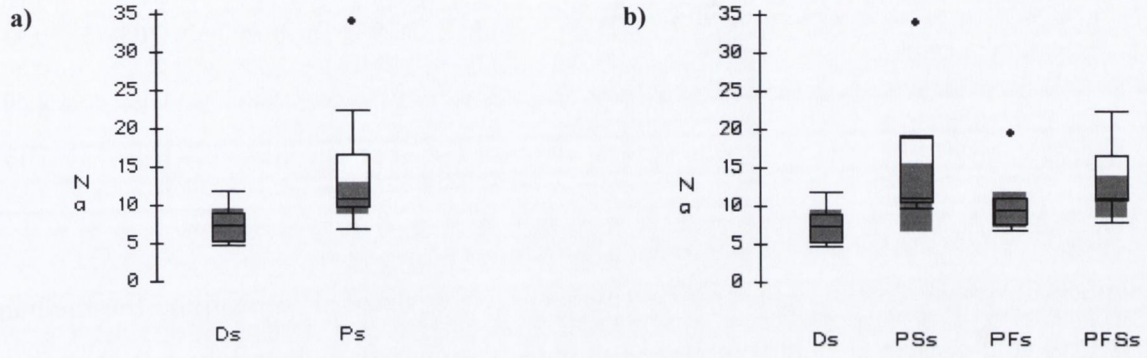


Figure 6.9a shows how sodium concentrations were distributed within categories D_s (artificial diffuse N source) and P_s (organic point N source) when sites were surrounded by 75 % to 100 % tillage (within 300 m radius). In figure 6.9b, the distinction is made between organic point source subcategories, i.e. PS_s (septic tank source), PF_s (farmyard source) and PFS_s (septic tank and farmyard sources).

Like other ions, sodium concentrations was little affected by this restriction to the 75-100 % tillage category, all medians of the P_s category and its subcategories being within 1 mg/l of values given in table 6.15 (within 300 m radius). In addition, minimum and maximum concentrations were almost unchanged. It should be noted that sodium concentration in the P_s category was significantly higher than in the D_s category at the 0.001 level ($F_{1, 32}$ = 14.55, p = 0.0006, 1.7:1 ratio of the largest to smallest variance). When comparing the four categories, the N source effect was still highly significant at the 0.005 level ($F_{3, 30}$ = 6.07, p = 0.0023, 2.2:1 ratio of the largest to smallest variance), LSD *Post-Hoc* tests showing that values in the D_s category were significantly lower than in the PS_s category (p = 0.00054) and the PFS_s category (p = 0.0013, 2.2:1 ratio of the largest to smallest variance).

- Potassium to sodium ratio

Table 6.16 displays the central values and spread of site mean potassium to sodium ratios (see Appendix 5E) within each N source category and organic point source subcategory from table 6.7 within 100 m radius and 300 m radius.

Table 6.16: Central values and spread of mean potassium to sodium ratio at the groundwater sampling sites of the Barrow Valley across the following N source categories within two radii (100 m and 300 m): D_s = artificial diffuse, P_s = organic point, PS_s = septic tank, PF_s = farmyard, PFS_s = undetermined point. *(potassium and sodium concentrations are originally in mg/l)*

Group	Radius	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
D_s	100 m	9	0.72	0.72	0.54	0.17	0.94	0.02	2.39
	300 m	8	0.79	0.74	0.71	0.31	0.94	0.02	2.39
P_s	100 m	42	0.34	0.53	0.16	0.09	0.33	0.02	2.80
	300 m	43	0.34	0.52	0.16	0.09	0.33	0.02	2.80
PS_s	100 m	17	0.17	0.15	0.13	0.07	0.16	0.05	0.53
	300 m	11	0.17	0.14	0.13	0.07	0.19	0.05	0.50
PF_s	100 m	18	0.49	0.74	0.22	0.12	0.36	0.02	2.80
	300 m	10	0.13	0.07	0.13	0.08	0.20	0.02	0.23
PFS_s	100 m	7	0.37	0.38	0.24	0.13	0.48	0.08	1.17
	300 m	22	0.52	0.68	0.27	0.14	0.52	0.07	2.80

Owing to skewed distributions in each category, it was decided to examine the medians rather than the means to analyse potassium to sodium ratios in relation to N source categories. The results showed that among the artificial diffuse N source category (i.e. D_s) and the three organic point N source subcategories (i.e. PS_s, PF_s and PFS_s), the D_s category (artificial fertiliser) had the highest median value (0.54 within 100 m radius and 0.71 within 300 m radius). In contrast, the PS_s category had the lowest median value (0.13 within 100 m and 300 m radius), followed by the PF_s category (0.22 within 100 m radius, 0.13 within 300 m radius), and then the PFS_s category (0.24 within 100 m radius, 0.27 within 300 m radius).

Both D_s and organic point N source subcategories showed very large and overlapping ranges of values. Each category had a minimum value below 0.1, whereas maximum value reached 2.39 in the D_s category, which was only overcome by the PF_s category within 100 m radius and the PFS_s category within 300 m radius (ratio 2.80). In comparison, the maximum in the PS_s category was slightly equal to or above 0.5 within 100 m and 300 m radius.

Figure 6.10 shows how the potassium to sodium ratios were distributed within category D_s (artificial diffuse N source) and the three organic point N source categories (i.e. PS_s, PF_s and PFS_s) at sites surrounded by 75 % to 100 % tillage (within 300 m radius).

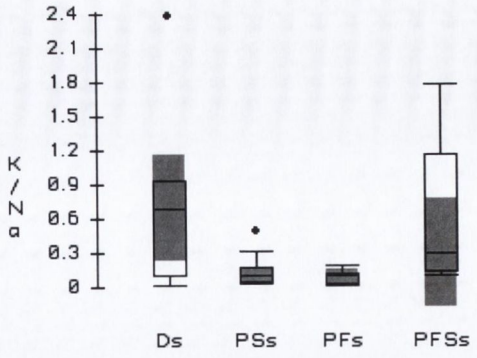


Figure 6.10: Distribution within the 75-100 % tillage category (i.e. 300 m radius) of mean potassium to sodium ratio at the groundwater sampling sites of the Barrow Valley across the following N source categories: D_s (n = 8), PS_s (n = 9), PF_s (n = 6) and PFS_s (n = 11). *(potassium and sodium concentrations are originally in mg/l)*

The median potassium to sodium ratios were within 0.03 unit of the values reported in table 6.16 for the P_s category and its subcategories within 300 m radius. Minimum values were almost unchanged whereas the only change affecting the maximum values concerned the PFS_s category, for which the highest ratio dropped to 1.79 (which is still extremely elevated).

6.4.4 Comparison between site classifications based on hydrochemistry and on sites' spatial characteristics

This section aims to compare the outcome of the site classifications based on i) hydrochemistry in table 6.5 (section 6.3.3) and ii) spatial characteristics in table 6.7 (section 6.4.3). Table 6.17 displays the number of groundwater sampling sites with high mean nitrate concentration (i.e. mean $[NO_3^-] \geq 25$ mg/l) that belonged to the different N source categories based on hydrochemistry (see Group 2 categories in table 6.5) for each N source category of table 6.7 based on spatial characteristics, within 100 m radius and 300 m radius.

Table 6.17: Number of high nitrate groundwater sampling sites (i.e. mean $[NO_3^-] \geq 25$ mg/l) within Group 2 categories (D_c, P_c and U_c) across each spatial N source category (D_s, Ps, PS_s, PF_s and PFS_s) within 100 m radius and 300 m radius.

N source spatial group	Radius	n	N source hydrochemical group		
			Artificial diffuse D_c	Organic point P_c	Undetermined U_c
Artificial diffuse (D_s)	100 m	8	8	0	0
	300 m	7	7	0	0
Organic point (P_s)	100 m	38	24	13	1
	300 m	39	25	13	1
Septic tank (PS_s)	100 m	16	9	6	1
	300 m	10	7	2	1
Farmyards (PF_s)	100 m	15	9	6	0
	300 m	8	7	1	0
Undetermined point (PFS_s)	100 m	7	6	1	0
	300 m	21	11	10	0

The comparison of site classification based on hydrochemistry and spatial characteristics gave some contrasting results. Firstly, all the sites classified in the D_s category (i.e. sites with only agricultural land and no organic point N source in their vicinity) showed groundwater chemistry that was indicative of diffuse contamination by artificial fertilisers, according to assumptions made in table 6.4. In fact, eight sites out of eight were classified in both D_s and D_c categories within 100 m radius (seven out of seven within 300 m radius), none of them showing signs of organic point n source contamination.

On the other hand, the situation was radically different in the P_s category (i.e. sites with organic point N sources in their vicinity), where the hydrochemistry of most sites disagreed with sites' spatial characteristics as it showed signs of artificial diffuse N source contamination: twenty-four sites out of thirty-eight were classified in the P_s and D_c categories within 100 m radius (twenty-five out of thirty-nine within 300 m radius), whereas only thirteen sites were classified in the P_s and P_c categories within 100 m and 300 m radius. It should be noted that these thirteen sites (belonging to category P_{cs} in table 6.18) were the same thirteen sites of the P_c category listed in table 6.5.

Table 6.18: Identification of high nitrate groundwater sampling sites from the Barrow Valley where both hydrochemistry and spatial characteristics within 100 m radius and 300 m radius agreed across the following N source categories: D_{cs} = artificial diffuse N source contamination, PS_{cs} = septic tank N source contamination, PF_{cs} = farmyard N source contamination, PFS_{cs} = undetermined point N source contamination (i.e. farmyard and/or septic tanks).

N source group		Radius	n	Site identification
Artificial diffuse (D_{cs})		100m	8	B.10, BHO.1, BHO.4, BHO.4A, BHO.5, BHO.6, BHO.7, BHO.8
		300m	7	BHO.1, BHO.4, BHO.4A, BHO.5, BHO.6, BHO.7, BHO.8
Organic point (P_{cs})	**Septic tank (PS_{cs})**	100m	6	C.8, C.15, C.19, O.4, O.7, O.11
		300m	2	C.8, C.15
	Farmyard (PF_{cs})	100m	6	B.2, B.9, C.2, C.10, C.13, O.3
		300m	1	B.2
	Undetermined point (PFS_{cs})	100m	1	C.5
		300m	10	B.9, C.2, C.5, C.10, C.13, C.19, O.3, O.4, O.7, O.11

Table 6.18 identifies the sites where both hydrochemistry and spatial characteristics agreed: at the intersections of the D_s row with D_c column, and also at the intersection of the P_s rows (also PS_s, PF_s and PFS_s rows) with the P_c column in table 6.17. The following

symbols are then used in the table above: the first capital letter designate the type of N source (i.e. D for diffuse and P for point), the second capital letter designates the type of point N source (i.e. F for farmyard, S for septic tank, and FS if both are present), and the suffix "cs" indicates that both hydrochemistry and spatial characteristics agreed.

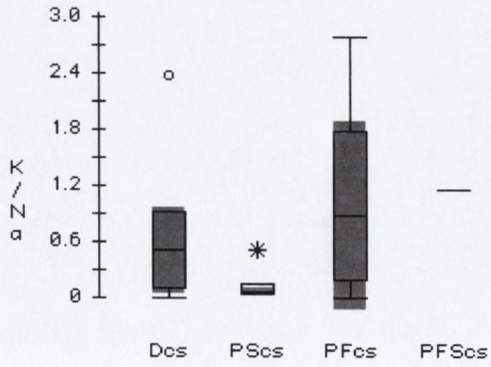
In contrast, table 6.19 identifies sites where hydrochemistry disagreed with sites' spatial characteristics.

Table 6.19: Identification of high nitrate groundwater sampling sites from the Barrow Valley where both hydrochemistry and spatial characteristics within 100 m radius and 300 m radius disagreed across the following N source categories: D_c/PS_s, D_c/PS_{cs}, D_c/PF_{cs} and D_c/PFS_{cs}.

N source group	Radius	n	Site identification
D_c / PS_s	100 m	9	B.4, B.6, C.4, C.6, C.7, C.12, C.18, C.20, O.5
	300 m	7	B.6, B.10, C.4, C.6, C.7, C.12, C.20
D_c / PF_s	100 m	9	B.1, B.3, B.5, B.7, B.8, C.14, O.8, O.9, O.12
	300 m	7	B.3, B.7, B.8, C.14, O.8, O.9, O.12
D_c / PFS_s	100 m	6	C.3, C.16, C.17, O.1, O.2, O.13
	300 m	11	B.1, B.4, B.5, C.3, C.16, C.17, C.18, O.1, O.2, O.5, O.13
U_c / PS_s	100 m	1	C.1
	300 m	1	C.1

Figure 6.11 displays potassium to sodium ratios for sites where both hydrochemistry and spatial characteristics within 100 m radius agreed. Except for one outlier, this ratio was generally much lower at sites associated with septic tank contamination (below 0.15) than at sites associated with farmyard contamination (up to 2.8).

Figure 6.11: Distribution of mean potassium to sodium ratio at the groundwater sampling sites of the Barrow Valley where hydrochemistry and spatial characteristics within 100 m radius agreed across the following N source categories: D_{cs} (n = 8), PS_{cs} (n = 6), PF_{cs} (n = 6) and PFS_{cs} (n = 1). *(potassium and sodium concentrations are originally in mg/l)*



6.4.5 Discussion of contamination indicators values in relation to % tillage

The first aim of section 6.4 was to examine the effects of % tillage within 300 m radius on site mean concentrations of nitrate, chloride and potassium, which are all three major ions

of artificial fertilisers (see table 2.5) that were introduced in section 6.3.1 as contamination indicators. An obvious limitation to this study came from the fact that most of the lowland in Barrow Valley study areas, chosen because of the high nitrate levels (see section 4.1.1), was mainly dedicated to tillage, as seen in figures 3.7 and 3.8. Consequently, most sites (34/51) belonged to the same 75-100 % tillage category. In order to lessen this potential problem, it was also decided to analyse results after merging the low and high % tillage categories into two 0-50 % and 50-100 % tillage groups, which improved the distribution of sites between categories.

Prior to discussing the results, a few preliminary remarks should be made about the use of ANOVA tests when investigating % tillage effects on concentrations of nitrate, chloride and potassium. According to Quinn and Keough (2003 / p.193), the most important assumption to be met (even more important than normality) for the reliability of the test is the homogeneity of variance between groups of the independent variable. Despite not giving any limit to the ratio of the largest to smallest variance, their conclusions suggest that only ratios many folds higher than 1:1 violate the assumption of homogeneity. Therefore, ratios as those observed in section 6.4.2 were deemed low enough to ensure the reliability of the hypothesis testing: exception made of the 8.3:1 ratio of the largest to smallest variance when comparing chloride values between the four % tillage categories, all other ratios were below 4:1. Furthermore, the merging of % tillage categories into two groups always improved the homogeneity of variance, the highest ratio of the largest to smallest variance being then recorded at 2.8:1.

- <u>% tillage effect on nitrate concentration</u>

In section 6.4.2, the site mean concentrations of nitrate were examined in order to detect any shift associated with an increase or a decrease in % tillage within a 300 m radius around sampling wells. The results suggest that there was a significant % tillage effect ($p \leq 0.05$) affecting nitrate concentrations, values in the 75-100 % tillage category (53.5 mg/l NO_3^- as mean) being significantly higher than in the 0-25 % (35.4 mg/l NO_3^- as mean) and 25-50 % tillage categories (27.9 mg/l NO_3^- as mean). The merging of the four % tillage categories into two larger groups greatly increased the significance of N source effect. When comparing the 0-50 % and 50-100 % tillage categories, values in the high % tillage group (52.9 mg/l NO_3^- as mean) were found to be significantly higher than in the low % tillage group (32.4 mg/l NO_3^- as mean) at the 0.005 level.

The results showing higher nitrate concentrations at sites surrounded by higher % tillage were expected for several reasons. Firstly, tillage crops are known for not being efficient at absorbing nutrients like nitrate (section 2.4.2) because i) they leave soil bare between crop rows and after harvesting, and ii) their rooting system is not well-developed. In the Barrow Valley, most of the tillage areas are used for the cultivation of cereals like wheat and barley (table 3.1), approximately half of it as winter crops and the other half as spring crops (Hugh McCreevy, Teagasc Crop Advisor Officer, personal communication). Although cereals are generally not considered to leave as much unused nitrogen in soils as root crops like potatoes (MAFF, 1999), experiments carried out at Knockbeg on spring and winter crops showed that they can yet cause very high nitrate leaching. With spring crops, the soil is often bare throughout the winter between harvesting and planting so they have higher leaching than winter crops. In section 5.2.1, nitrate concentration was measured in soil-water from some spring barley plots up to 152.2 mg/l NO_3^- (section 5.2.1), which confirmed similar findings from earlier investigations by Hooker (2005). In addition to the build up of unused nitrogen originating from fertiliser applications prior to the beginning of the drainage in autumn (see figure 3.6), ploughing stimulates the gross rates of mineralisation and nitrification of soil organic matter (section 2.4.1), as well as causing the incorporation of crop residues that undergo nitrification. Therefore, it becomes evident that the larger the area tilled, the larger the diffuse N source and the larger the amount of nitrate available for leaching. Although his work concerned surface-water bodies, Neill (1989) highlighted the importance of the % tillage to the understanding of contamination by nitrate as he observed a positive relationship between nitrate concentration in rivers in south-east Ireland and the percentage tillage in the river catchment. In fact, his results are currently incorporated into the groundwater risk assessment methodology related to nitrate (WGG, 2005), which was developed in Ireland by the River Basin District Management Systems (RBDMS) under the Water Framework Directive. In this risk assessment, a high pressure magnitude tillage threshold of 33 % tillage was set as limit above which a groundwater body is deemed at risk of being contaminated by nitrate, i.e. that the nitrate concentration is at risk of exceeding the 50 mg/l NO_3^- drinking water limit.

The second reason for expecting high nitrate levels around sites with high % tillage is related to the ease with which nitrate can leach in the Barrow Valley study areas. Overall, soils and subsoil allow a good drainage (sections 3.2.3 and 3.2.4), despite some considerable lateral and vertical variation that sees frequent clays or tills above and below the individual sand and gravel units. In addition, a thin unconfining unsaturated zone (with the water-table typically less than 5 metres bgl - see figure 3.4) increases greatly the risk of

groundwater contamination since it provides little opportunity for natural attenuation (see section 3.2.5).

Finally, another reason for the difference in groundwater nitrate level between high and low % tillage areas comes from the fact that in the Barrow Valley study areas, most of the land not used for tillage is permanent grassland (see figures 3.7 and 3.8). Due to its very dense rooting system, grass is very efficient at taking up nutrients (section 2.4.2), and it is generally not associated with high nitrate leaching, unless it is intensively managed in systems like dairy farms with high stocking rate (Bartley, 2003). Experiments in Moorepark RC showed that high nitrate concentrations (up to 150 mg/l NO_3^-) could be observed in soil-water beneath permanent grassland after artificial fertiliser or dairy wastewater was applied at rates that were often widely in exceedance of Teagasc recommendations, which was further commented in section 5.2.4. In the Barrow Valley study areas though, no intensive dairy farm was present around sampling sites.

An obvious complication to the study of the % tillage effect on groundwater contamination by nitrate was related to the presence of organic point sources such as septic tanks and farmyards, which discharge some of the chemical species found in artificial fertilisers (i.e. nitrogen, chloride and potassium). Therefore, it was decided to check whether there was a relationship between the % tillage and the number of unsewered houses (section 6.4.1). The assumption to be confirmed was that the decrease in % tillage within a 300 m radius was not caused by an increase in the number of houses within this radius, which would otherwise seriously alter the reliability of the % tillage effect analysis. From figures 6.5a and 6.5b, it can be seen that there was no obvious relationship between the number of point N sources (i.e. unsewered houses and farmyards) and % tillage, despite a higher number of point sources in the 0-25 % tillage category, which was area-related as most of these sites (5/6) were located in the same neighbourhood of north Carlow town where there is a high % grassland.

- <u>% tillage effect on potassium and chloride concentrations</u>

The results in section 6.4.2 did not show any % tillage effect on site mean concentrations of potassium (analysed as log-transformed values) as the median levels in the difference % tillage categories were very consistent (slightly above 2 mg/l). The lack of relationship between potassium concentration and % tillage may be attributed to the low mobility of this cation once in soils. Unlike nitrate, it has a high affinity for negatively charged soil

particles, which is why the leaching of large amounts from artificial diffuse sources (NPK fertilisers) is rarely contemplated according to Böhlke (2002), although some suggested differently (Gallardo and Tase, 2006). Therefore, % tillage did not appear to be an important factor influencing site mean concentrations of potassium.

No significant relationship was observed between % tillage and chloride (analysed as log-transformed values), whether merging the different % tillage categories into two groups or not (all means around 30 mg/l). Like nitrate, chloride is a very mobile anion, but it is mainly found in potash (KCl), which is commonly used in the Barrow Valley study area (section 3.4.2). The lack of a strong relationship may just suggest that applications of chloride are considerably lower than those of nitrogen. Although mean application rates of KCl were unknown for the whole Barrow Valley study area, data for Oak Park RC (see table 3.9) suggests that overall, the amount of nitrogen exceeds greatly the amount of chloride applied every year.

6.4.6 Discussion of contamination indicators values in relation to sites' spatial characteristics

The second aim of section 6.4 was to examine the N sources effect (within 100 m and 300 m radius) on site mean concentrations of nitrate, chloride, potassium and sodium, along with the potassium to sodium ratio. In the context of the Barrow Valley where intensively managed tillage and grassland are present in the vicinity of all sampling wells, several groups of sites were compared:

- No organic point N source present within 100 m and 300 m radius, i.e. artificial diffuse source group D_s.
- Presence within 100 m and 300 m radius of organic point N sources (group P_s) such as unsewered houses (group PS_s), farmyards (group PF_s) or unsewered houses and farmyards (group PFS_s).

Because not every N source group was represented in each % tillage category, interactions between % tillage and N source could not be studied. As an alternative, the study of the N source effect was additionally conducted within the 75-100 % tillage category (within 300 m radius), which held most sites, in order to hold the % tillage as constant as possible while varying the point N sources.

Similarly to what was observed during the % tillage effect analysis, the distribution of sites was not even between N source categories. However, this was not thought to be a problem for the reliability of ANOVA tests as for most of them, the variance was fairly homogeneous between groups, ratios of the largest to smallest variance being often close to or lower than 2.1:1 (and never higher than 6.1:1, which was observed only once in the analysis of chloride concentrations with four N source categories within 100 m radius).

- N source effect on nitrate concentration

The results in section 6.4.3 showed that, whether the N source(s) identified within 100 m or 300 m radius was artificial diffuse or organic point, site mean nitrate concentrations were within a wide range of values, i.e. the minimum was below 25 mg/l NO_3^- (except PFS_s category within 100 m radius) and the maximum was largely above the 50 mg/l NO_3^- drinking water limit. Differences were observed between the different categories as nitrate concentrations were significantly higher in the D_s than in the P_s group (within 100 m and 300 m radius). However, the significance of this difference disappeared once the study was restricted to sites that belonged to the 75-100 % tillage category. In addition no significant N source effect on nitrate concentration was observed when the comparison was made between the D_s category and the three organic point N source subcategories (i.e. PS_s, PF_s and PFS_s).

At first sight, these results may seem surprising as one could expect nitrate concentrations to be higher in the vicinity of organic point sources than underneath fields where artificial fertiliser was applied. Such expectations are based on the following reasons. First, animal/human organic wastes are extremely enriched in nitrogen, which could potentially lead to extremely high levels of nitrate within a three-dimensional contamination plume if all this nitrogen was nitrified in soil. In table 2.6, the lowest TN value among animal wastes was reported for dairy wastewater at 300 mg/l N, which could theoretically lead to nitrate concentrations as high as 1300 mg/l NO_3^- (i.e. 300 × 4.43). In human wastes (section 2.3.4), Wakida and Lerner (2005) reported that TN concentrations in septic tank effluents typically range from 25 to 60 mg/l N, which could cause nitrate concentrations to range from 110 to 265 mg/l NO_3^-. As organic point N sources discharge their highly contaminated effluents over a small area, processes like dilution and denitrification may have a limited impact on the natural attenuation of nitrate levels. In contrast, artificial fertilisers (i.e. diffuse N sources) are applied to large areas, which should in theory

maximise natural attenuation (denitrification and dilution) and plant uptake, hence leading to less nitrate leaching provided the plant biological requirements are not exceeded.

The fact that the results showed significantly higher nitrate concentration in the D_s category than in the P_s group could be attributed to several factors. Firstly, application rates of artificial fertilisers in the Barrow Valley were reported to be often higher than Teagasc recommendations (see section 3.4.2), which should put the sand and gravel aquifer at great risk considering the high vulnerability of the study areas (section 3.2.5). Therefore, artificial diffuse N sources were likely to cause some substantial nitrate contamination to groundwater. The importance of the artificial diffuse N source in comparison with organic point N sources was illustrated by the non-significance of the N source effect observed when studying sites surrounded by 75 % to 100 % tillage. This may indicate that where sites are surrounded by high % tillage, the diffuse N source becomes the dominant source of nitrogen, regardless of the presence of organic point N sources within 300 m radius.

A second reason for the significantly lower nitrate concentrations in the P_s than in the D_s category may also be attributed to oversimplification when classifying sites according to the presence of organic point N sources. Unsewered houses and farmyards generate three-dimensional plumes of contamination, which can only be intercepted (hence sampled) by sampling wells under certain conditions, the first one being that a sampling site be down hydraulic gradient of the point of release. Despite the fact that groundwater is known to flow towards the River Barrow at a regional scale, the relatively flat topography (section 3.2.1) did not help determine without doubts the groundwater flowpath at a local scale, which can prove quite different from the overall flowpath. Furthermore, the vast majority of sites are water supply wells, and pumping of these will create a cone of depression with flow towards the borehole, but in the case of domestic wells this cone of depression may be quite small, so there is no certainty that it would draw the contaminant plume towards the borehole.

In the case of a sampling well downgradient of an organic point N source, the distance from the point of discharge may also be an important parameter, as mentioned in section 2.5.2. Although some studies showed that contamination plumes of septic tank origin can stretch over more than 100 m in sand and gravel aquifers with nitrate levels still higher than the drinking water limit (Robertson *et al.*, 1991), almost complete nitrate attenuation can be observed within a few metres downgradient of the point of discharge due to denitrification (Gerritse *et al.*, 1995). Even though most of the Barrow Valley sampling sites were located in freely-draining soils and subsoils (see sections 3.2.3 and 3.2.4), large

horizontal and vertical variation was nonetheless observed at a local scale. As witnessed in the Oak Park monitoring areas (see borehole logs in Appendix 1), the Quaternary deposits consist of interbedded sands and gravels, sands and clays, with frequent clays or tills above and below the individual sand and gravel units. Therefore, the potential for local denitrification of nitrate of organic point source origin should be contemplated as a serious option for nitrate attenuation, which would be favoured by the high DOC content of organic effluents. This means that a well being down hydraulic gradient of a point source may not necessarily be a sufficient condition to sample nitrate derived from animal/human wastes.

Another possible explanation for nitrate levels lower than expected in the vicinity of organic point sources is related to the hydrogeological context of the Barrow Valley, i.e. high effective rainfall (see section 3.2.6) combined with freely-draining conditions and a shallow water-table. Under these conditions, a substantial fraction of TN may have leached faster than bacteria could nitrify, resulting in some untransformed ammonia/ammonium reaching the aquifer instead.

One should also consider the possibility that close to the point of discharge, the nitrogen may still be largely held in the sediment in the form of organic N and ammonium, and the peak of nitrate concentration may be reached at greater distance, and then gradually decreasing again due to dilution with cleaner water. Although nitrification is usually expected to take place in the topsoil where aerobic conditions prevail (see section 2.4.1), Robertson *et al.* (1991) suggested that it could also take place within the a plume of contamination caused by a septic tank.

A final possible reason explaining why nitrate concentrations were significantly lower in the P_s category and its subcategories than in the D_s group may be related to differences in groundwater abstraction rates between piezometers and private wells. Distinctively from most sites of the D_s category (i.e. all eight sites within 300 m radius were piezometers from the Oak Park monitoring area), all wells from the P_s category were used as drinking water supplies. This implies higher abstraction rates and larger cones of depression that may draw contaminated water from contamination plumes along with cleaner water, which can result in diluting contaminants.

- N source effect on chloride, potassium and sodium concentrations

The results in section 6.4.3 showed that site mean concentrations of chloride and potassium were within a large range of values, for which the maximum widely exceeded natural

background levels (NBLs) reported in table 2.7 regardless of the N source category (i.e. D_s or P_s). Nonetheless, maximum values in the P_s category (64.2 mg/l Cl^- and 44.5 mg/l K^+) were found to be much higher than in the D_s category (43.5 mg/l Cl^- and 13 mg/l K^+). The most important difference between the D_s and P_s categories was in fact observed when examining site mean sodium concentrations, as the highest value in the D_s category (11.9 mg/l Na^+) did not exceed the NBLs reported in table 2.7, quite distinctively from the P_s category where the maximum reached 34.2 mg/l Na^+.

Comparing chloride, potassium and sodium values between the D_s and the P_s categories, or between the D_s category and the organic point source subcategories (i.e. PS_s, PF_s and PFS_s), showed very contrasting results. First of all, no significant N source effect on site mean potassium concentrations (in fact the log-transformed variable) was detected at the 0.05 level. Second, site mean chloride concentrations (i.e. log-transformed values) were found to be significantly lower ($p \leq 0.05$) in the D_s category than in the P_s category within 300 m radius. If studying only sites from the 75-100 % tillage category, the N source effect within 300 m radius edged towards significance at the 0.05 level ($p = 0.0507$). Third, site mean sodium concentrations (i.e. log-transformed values) were found to be significantly lower ($p \leq 0.001$) in the D_s category than in the P_s category within 100 m and 300 m radius. This significance remained ($p \leq 0.001$) when the study was restricted to sites surrounded by 75 % to 100 % tillage (within 300 m radius). Furthermore, a highly significant N source effect (at the 0.005 level) was also detected when comparing log-transformed sodium values between the D_s category and the organic point source subcategories (i.e. PS_s, PF_s and PFS_s): site mean sodium concentrations (i.e. log-transformed values) were significantly lower than in the PS_s, PF_s and PFS_s categories within 100 m and 300 m radius. In fact, only one pairwise comparison involving the D_s category was not found to be significant (comparison between D_s and PFS_s within 100 m radius). When restricting the study to sites from the 75-100 % tillage category (within 300 m radius), the N source effect on the log-transformed site mean sodium concentrations remained highly significant ($p \leq 0.005$), and values in the D_s category were still significantly lower than in the PS_s or PFS_s category (no significant difference at the 0.05 level between the D_s and PF_s category).

At first sight, the absence of significant N source effect ($p > 0.05$) on site mean potassium concentration, in conjugation with the fact that the D_s category had a higher median potassium value (4.5 mg/l within 100 m or 300 m radius) than the P_s category (about 2 mg/l within 100 m or 300 m radius), may suggest that organic point sources (i.e.

unsewered houses and farmyards) were not the main contributors to the contamination observed at most sites of the P_s category. In general, it is expected that because they discharge highly concentrated effluents (see sections 2.3.3 and 2.3.4) over a small area, organic point N sources can cause soil's CEC to be overcome, which can eventually result in the leaching of large quantities of potassium, despite its strong affinity for positively charged soil particles. Therefore, elevated potassium levels can be expected in groundwater collected from sampling wells that intercept contamination plumes (see section 2.5.4). However, the highest potassium levels in the groundwater should really be observed closest to the point of entry to the saturated zone, and concentrations at a borehole up to 100 or 300 metres away may be far lower. Distinctively from organic point sources, high potassium leaching subsequent to the diffuse application of NPK fertilisers and potash (KCl) is rarely reported in the literature (Böhlke (2002), which was contradicted by the high median value of the D_s category (4.5 mg/l).

The hypothesis that organic point N sources may not contribute to the contamination of sites from the P_s category was slightly weakened by the observation of site mean chloride concentrations significantly higher ($p \leq 0.05$) in the P_s category (33.3 mg/l as mean value) than in the D_s group (26.4 mg/l as mean value) within 300 m radius. Such results would be expected in the event of organic point source contamination (see section 2.5.4) because chloride, a very mobile anion once in soils, is a major constituent of animal/human wastes (see sections 2.3.3 and 2.3.4). However, chloride is also present in potash (KCl), which is commonly used across the Barrow Valley study areas (section 3.4.2) and can also generate high chloride leaching according to Böhlke (2002).

Finally, the observation within 100 m and 300 m radius of highly significant N source effects associated with sodium (at 0.001 or 0.005 level), which were attributed to site mean sodium concentrations significantly lower in the D_s category than in the P_s category and any organic point source subcategories (i.e. PS_s, PF_s and PFS_s), can only mean that organic point sources located within 100 m or 300 m radius had an impact on groundwater quality at most sites of the P_s category (hence at most sites of the organic point source subcategories). This assumption is based on the fact that sodium is a major contaminant present in animal/human wastes (see sections 2.3.3 and 2.3.4), but generally absent from artificial fertilisers (except for sugar beet compounds). Supporting evidence also lies in the fact that NBLs were only exceeded at sites from the P_s categories and the organic point sources subcategories, i.e. where septic tanks and farmyards were present.

- N source effect on potassium to sodium ratio

In table 6.16, most N source categories displayed a large range of site mean potassium to sodium ratios, with minimum values reported below 0.1 in every category while maximum values much higher than 1.0 were observed in the D_s (within 100 m and 300 m radius), PF_s (within 100 m radius only) and PFS_s categories (within 100 m and 300 m radius). Also, the D_s category had the highest median value within 100 m and 300 m radius (0.54 and 0.71 respectively), followed by the PFS_s category (0.24 and 0.27), then the PF_s category (0.22 and 0.13) and finally the PS_s category (0.13).

The high values reported in the D_s category were surprising at first. Under uncontaminated conditions, groundwater displays low potassium to sodium ratios, NBLs reported in table 2.7 suggesting that it is about 0.34 in Carboniferous limestone aquifers (i.e. 3.0 mg/l ÷ 8.8 mg/l), and 0.05 in sand/gravel (i.e. 0.6 mg/l ÷ 12 mg/l). Since artificial diffuse N sources are rarely reported to leach potassium (due to soil's CEC) and sodium (because not contained in most fertilisers), applications of artificial fertiliser would not normally be expected to influence the ratio originally observed for uncontaminated groundwater. However, the results from this study contradicted this as elevated potassium to sodium ratios were observed at sites from the D_s category, which is consistent with the high potassium and the low sodium levels recorded in tables 6.14 and 6.15.

In the literature, animal wastes are reported to contain a higher proportion of potassium in relation to sodium (5:1 ratio based on figures from table 2.6), compared with human waste (0.3:1 ratio based on figures from Robertson *et al.* (1991)), as discussed in section 2.5.4. Therefore, it may seem surprising that values in the PF_s category (i.e. sites close to farmyards) were not much higher than in the PS_s category (i.e. sites close to unsewered houses). However, a condition to the observation of distinctively high potassium to sodium ratios in case of proven contamination by farmyards requires that a large fraction of all the potassium contained in animal wastes breaks through soil and subsoil, so that the original high ratio is not masked. This condition was obviously not met at many sites from the PF_s category, by judging from the low median potassium values in this category (see table 6.14) within 100 m (2.5 mg/l) and 300 m radius (1.3 mg/l). In addition, there is also the possibility that contamination at sites from the PF_s category may have originated from farms' own septic tank system, which would contribute to low ratios.

Simultaneously to low potassium levels, sodium concentrations remained high in all organic point source subcategories (i.e. PS_s, PF_s and PFS_s), which contributed to keeping

potassium to sodium ratio relatively low around most sites located nearby organic point sources, including farmyards.

6.4.7 Discussion of the comparison between site classifications based on hydrochemistry and on sites' spatial characteristics

The third objective of section 6.4 was the comparison of site classifications based on hydrochemistry (see table 6.5 for high nitrate sites, i.e. mean $[NO_3^-] \geq 25$ mg/l) and on spatial characteristics (see table 6.7). The outcome introduced in table 6.17 (see section 6.4.4) was as follows:

- 100 % of high nitrate sites classified in the D_s category (8/8 within 100 m radius, 7/7 within 300 m radius) showed groundwater chemistry indicative of contamination by artificial diffuse sources (i.e. artificial fertilisers) = category labelled D_{cs} (list of sites in table 6.18).
- About 34 % of high nitrate sites classified in the P_s category (13/38 within 100 m radius, 13/39 within 300 m radius) showed groundwater chemistry indicative of contamination by organic point N source such as septic tank or farmyard effluents = category labelled P_{cs} (list of sites in table 6.18), which can be subcategorised into PS_{cs} (septic tank contamination), PF_{cs} (farmyard contamination) and PFS_{cs} categories (septic and/or farmyard contamination).
- About 64 % of high nitrate sites from the P_s category (24/38 within 100 m radius and 25/38 within 300 m radius) had groundwater chemistry indicative of contamination by artificial diffuse sources = category labelled D_c/P_s (list of sites in table 6.19), which can be subcategorised into D_c/PS_s, D_c/PF_s and D_c/PFS_s.
- About 2 % of high nitrate sites classified in the P_s category (1/38 within 100 m radius, 1/39 within 300 m radius) showed hydrochemistry that could not be related to any type of N source = U_c/P_s category (see table 6.19).

In addition, potassium to sodium ratios were compared in figure 6.11 between categories where both spatial characteristics and hydrochemistry agreed within 100 m radius (i.e. categories D_{cs}, PS_{cs}, PF_{cs} and PFS_{cs}). It can be seen that those ratios were generally higher at sites from the PF_{cs} category (4/6 sites with ratio higher than 0.46) than sites from the PS_{cs} category (5/6 sites with ratio below 0.15).

Overall, classifications based on hydrochemistry and on spatial characteristics agreed for those sites for which the source of contamination could be identified beyond reasonable doubts as either artificial fertiliser (D_{cs} category), septic tanks (PS_{cs} category), farmyards (PF_{cs} category), or else septic tank and/or farmyards (PFS_{cs} category). A part of this conclusion was supported by the observation of potassium to sodium ratios far more elevated in the PF_{cs} category than in the PS_{cs} group, which is consistent with the literature (see section 2.5.4).

On the other hand, the groundwater chemistry contradicted the spatial characteristics at most sites of the P_s category as it was generally associated with artificial diffuse contamination. For these sites, the main question is then to know which classification is the most reliable for the source identification of groundwater contamination by nitrate, both approaches showing advantages amid inherent limitations.

Firstly, the classification of sampling sites based on spatial characteristics seemed to find some justification as sodium levels were significantly higher when organic point sources were present within 100 m or 300 m radius (i.e. higher in P_s than in D_s), which means that groundwater quality was systematically impacted in the vicinity of unsewered houses and farmyards. Nevertheless, it also emerged from discussions in section 6.4.6 that the conditions for a sampling well to intercept a plume of contamination are complex, which makes the site classification based on spatial characteristics alone maybe too uncertain for a reliable determination of nitrate sources. This could also be the main reason why groundwater chemistry and spatial characteristics disagreed around organic point sources only.

As for site classification based on hydrochemistry, it presents the advantage of being based on direct measurements of chemical parameters, but as previously discussed in section 6.3.5, the use of contamination indicators less mobile than nitrate may lead one to mistakenly conclude the presence of artificial diffuse contamination rather than organic point source contamination.

To conclude, the need for additional tools appears evident if the source of groundwater nitrate is to be more reliably identified. This topic is addressed in chapter 7.

6.5 Case studies: use of hydrochemistry and correlations to identify NO_3^- sources in the study areas

6.5.1 The Barrow Valley

- Extent of the nitrate problem

Table 6.20 displays the number of groundwater samples that exceeded the 25 mg/l NO_3^- guide level value and the 50 mg/l NO_3^- drinking water limit across the different sampling areas of the Barrow Valley (introduced in section 6.2.1). For both thresholds, the table additionally reveals the number of sites that were in exceedance i) on at least one sampling occasion, or ii) on each sampling occasion. It should be noted that except for five sites located in the Castlemitchell and Ballyroe areas, all the other forty-six sampling sites were sampled more than once. Between February 2002 and June 2004, one site was sampled twice, two sites were sampled three times, one site was sampled four times, seven sites were sampled five times, fourteen sites were sampled six times, and twenty-one sites were sampled seven times.

Table 6.20: Number of groundwater samples in exceedance of the 25 mg/l NO_3^- guide level value and the 50 mg/l NO_3^- drinking water limit across each Barrow Valley sampling area, and number sites in exceedance i) on at least one sampling occasion or ii) all sampling occasions (BAL for Ballyroe, CAS for Castlemitchell, OAK RC for Oak Park monitoring area, and OAK for the outer Oak Park area).

Area	Threshold	% samples (by area) in exceedance	Number of sites with exceedance	Number of sites always exceeding
BAL (10 sites)	25 mg/l NO_3^- (GL value)	100	10	10
CAS (20 sites)		84	20	15
OAK (13 sites)		84	11	10
OAK RC (8 sites)		89	7	7
TOTAL (51 sites)		**88**	**48**	**42**
BAL (10 sites)	50 mg/l NO_3^- (drinking water limit)	52	9	1
CAS (20 sites)		45	13	6
OAK (13 sites)		18	3	2
OAK RC (8 sites)		81	7	5
TOTAL (51 sites)		**44**	**32**	**14**

It can be seen that groundwater contamination by nitrate was widespread across the Barrow Valley study areas, with forty-two sites out of fifty-one sampled consistently above the 25 mg/l NO_3^- guide level value. However, some differences emerged between the different areas in terms of exceedance of the 50 mg/l NO_3^- drinking water limit. The outer Oak Park area had 33 % of sites (three out of thirteen) in exceedance at least once, which was lower than in the Castlemitchell (65 %), Ballyroe (90 %) or Oak Park (62 %)

monitoring areas. Overall, fourteen sites were always in exceedance of the drinking water limit, most of them being located in the Castlemitchell area or within Oak Park RC.

- Examination of hydrochemistry

In section 6.3.3, high nitrate sites (i.e. mean $[NO_3^-] \geq 25$ mg/l) were classified according to their hydrochemistry in regard of the exceedance (or non-exceedance) of contamination thresholds (based on assumptions made in section 6.3.2). The conclusions were that thirty-two high nitrate sites out of forty-six exhibited groundwater chemistry characteristic of artificial diffuse contamination, whereas only thirteen of these high nitrate sites exhibited hydrochemistry indicative of organic point source contamination (see figure 6.4). Additionally, nitrate concentrations were found to be significantly higher ($p = 0.0043$) at the forty-one sampling sites (out of fifty-one) that were surrounded with more than 50 % tillage within 300 m, compared with sites with less than 50 % tillage (section 6.4.2). On the other hand, sodium levels in section 6.4.3 were found to be significantly higher ($p \leq 0.001$) at forty-two sites out of fifty-one that were located within 100 m radius from unsewered houses and/or farmyards (forty-three sites within 300 m radius; $p \leq 0.0005$), compared with sites located away from any organic point sources.

- Correlations between nitrate and other physico-chemical parameters

Table 6.21 displays Spearman's rank correlation coefficients between nitrate concentrations and physico-chemical parameters calculated for seven sampling events carried out in the Barrow Valley between February 2002 and June 2004.

Table 6.21: Spearman's rank r_s values between nitrate concentrations and chemical variables (concentration of chloride, potassium, sodium, sulphate, magnesium and calcium, alkalinity, pH and conductivity) for each sampling event carried out in the Barrow Valley ($p \leq 0.05$ in bold, $p \leq 0.01$ in bold and single-underlined, $p \leq 0.001$ in bold and double-underlined).

$[NO_3^-]$	$[Cl^-]$	$[K^+]$	$[Na^+]$	$[SO_4^{2-}]$	$[Mg^{2+}]$	$[Ca^{2+}]$	Alkalinity	pH	Conductivity
February 2002	**0.492**	0.239	0.047	0.301	-0.106	**0.646**	0.207	0.025	**0.569**
September 2002	**0.53**	0.128	**0.418**	**0.418**	-0.089	**0.513**	-0.036	-0.183	**0.62**
February 2003	**0.434**	0.091	0.121	0.092	-0.25	**0.476**	-0.2	-0.115	**0.451**
June 2003	**0.407**	0.119	0.043	**0.354**	**-0.351**	**0.455**	-0.255	0.045	**0.374**
September 2003	**0.397**	0.071	-0.035	**0.435**	-0.212	**0.375**	-0.244	-0.001	**0.446**
February 2004	0.24	0.117	0.104	0.255	**-0.411**	**0.433**	-0.11	0.088	**0.354**
June 2004	0.229	0.187	0.02	0.277	**-0.499**	**0.572**	-0.166	-0.088	**0.544**

The results show that nitrate was most strongly correlated with chloride, calcium and conductivity. In samples from 2002 and 2003, nitrate concentrations were significantly (and positively) correlated at the 0.01 level with chloride concentrations. Significant positive relationships were also observed with calcium concentration and conductivity on each sampling occasion.

- Assumptions about the origin of the nitrate contamination in the Barrow Valley

Early clues about the origin of the nitrate contamination were found in section 3.4.2, where the main N sources present in the Barrow Valley study areas were identified as i) diffuse applications of artificial fertiliser, and ii) organic point sources (septic tanks and farmyards).

The analysis of hydrochemistry in regard to contamination thresholds suggested that most sites were contaminated by artificial diffuse sources of agricultural origin, which was supported by the fact that nitrate concentrations were significantly higher at high % tillage sites than low % tillage sites. At first sight, this is consistent with the context of the Barrow Valley, where freely-draining soils overlie a largely unconfined shallow aquifer are primarily used for tillage (see figures 3.7 and 3.8). Therefore, one would expect diffuse applications of artificial fertiliser to be an important contributor to groundwater contamination by nitrate. However, the examination of hydrochemistry, in particular sodium levels, with respect to the presence/absence of organic point sources (within 100 m and 300 m radius) suggests that organic point sources such as unsewered houses or farmyard have some influence on groundwater quality. This was further supported by the presence of faecal coliforms at fifteen sites out of thirty-six tested (section 6.2.1). Therefore, organic point sources also appear to contribute to the nitrate problem, although the extent of their contribution is uncertain. Finally, the uncertainty as to which type of N source contributed most to the nitrate contamination was highlighted in section 6.4.4. As both site classifications based on hydrochemistry and spatial characteristics were compared, it emerged that only a small number of sites showed hydrochemistry in agreement with spatial characteristics (i.e. presence/absence of organic point sources within 100 m and 300 m radius).

The examination of correlations between nitrate and other physico-chemical parameters produced some ambiguous results that did not help clarify the contradictory results referred

to above. Significant (positive) correlations were observed between nitrate and chloride. However, as already mentioned in section 6.3.2, chloride is found in both organic wastes and potash, which is commonly used in the Barrow Valley as fertiliser. In addition, the fact that nitrate does not show significant relationships with other indictors of organic contamination (i.e. potassium and sodium) might be because in some instances, adsorption on soil's negatively charged particles has removed these other indictors. As for the significant relationship between nitrate and calcium, it might be taken to imply that the nitrate is associated with calcium from a fertiliser like calcium ammonium nitrate, but this ignores the effect of ion exchange. Although divalent cations should be more strongly adsorbed, calcium is a dominant ion in the calcareous deposits of the Barrow Valley that may be displaced by other cations like potassium or sodium.

6.5.2 Moorepark RC

- Extent of the nitrate problem

Groundwater chemistry analysis, which was introduced earlier in section 6.2.1, indicated high nitrate levels beneath Curtin's farm. Out of ten boreholes drilled in Waulsortian limestone, and sampled a maximum of four times between February 2002 and September 2003, seven produced samples that were always in exceedance of the 25 mg/l NO_3^- guide level value, whereas four boreholes produced samples that contained nitrate concentrations always higher than the 50 mg/l NO_3^- drinking water limit (see Appendix 3).

- Examination of hydrochemistry

As no contamination thresholds were defined for the Moorepark area and its surroundings, hydrochemistry was analysed for each site on a sample basis, which was facilitated by the small number of groundwater samples collected. Overall, concentrations of chloride, sodium and potassium concentrations (tabulated in Appendix 3), which were used as contamination indicators for the Barrow Valley investigation, showed wide variations (see CV values in section 6.2.1). However, important differences were observed between sites. In regard of NBLs reported for Carboniferous limestone in table 2.7, elevated concentrations of sodium and especially potassium were observed at sites BHM.3 ($[Na^+]$ as high as 13.2 mg/l, $[K^+]$ as high as 22 mg/l) and BHM.4 ($[Na^+]$ as high as 17 mg/l, $[K^+]$ as

high as 37 mg/l), which was occasionally accompanied by high chloride concentrations ($[Cl^-]$ as high as 43.8 mg/l at BHM.4).

- Correlations between nitrate and other physico-chemical parameters

Table 6.22 displays Spearman's rank correlation coefficients between nitrate concentrations and physico-chemical parameters calculated for four sampling events carried out in Moorepark RC between February 2002 and September 2003.

Table 6.22: Spearman's rank r_s values between nitrate concentrations and chemical variables (concentration of chloride, potassium, sodium, sulphate, magnesium and calcium, pH and conductivity) for each sampling event carried out in Moorepark RC (no correlation with $p \leq 0.05$).

	$[NO_3^-]$	$[Cl^-]$	$[K^+]$	$[Na^+]$	$[SO_4^{2-}]$	$[Mg^{2+}]$	$[Ca^{2+}]$	pH	Conductivity
Feb-02			0.143	0.42		0.574	0.552	-0.485	0.603
Dec-02	0.238		0.381	-0.084	0.024	0.667	0.19	-0.317	
Jun-03	0.51		-0.326	0.522		0.075	0.377	-0.363	0.3
Sep-03	-0.393		-0.643	-0.393	0.714	-0.382	-0.357	0.12	-0.393

In contrast to Barrow Valley data, no significant correlations were observed between nitrate and other physico-chemical parameters.

- Assumptions about the origin of the nitrate contamination at Moorepark RC

As discussed earlier in section 3.4.3, there were several types of N sources potentially responsible for nitrate leaching at Curtin's farm. Table 3.10 displays estimates of total N inputs to this permanent grassland area for the following N sources: diffuse applications of artificial fertiliser, diffuse applications of dairy wastewater or slurry, excreta from grazing cattle. Work carried out by Bartley (2003) suggests that animal wastes were likely contributors to the nitrate problem. Her findings showed that groundwater nitrate concentrations were highest in the areas of highest organic nitrogen loading. Furthermore, she found that there was a strong relationship between grazing intensity and the following year's average groundwater nitrate concentration. The important result for the present project was the observation of elevated sodium and potassium concentrations (and occasionally chloride) at sites BHM.3 and BHM.4, which are both located about 50 m downgradient of the farmyard (see figure 3.13). This suggests that the farmyard is responsible for nitrate contamination at both sites.

6.6 Conclusions

In the Barrow Valley study areas, chloride, potassium and sodium were used as indicators of contamination to detect any impact on groundwater chemistry from diffuse applications of artificial fertiliser and from point sources of organic wastes. Contamination thresholds defined for these three ions were used to group groundwater sampling sites with similar water chemistry. Each category was then associated with either artificial diffuse (i.e. artificial fertilisers) or organic point N source (septic tanks or farmyards) contamination. On the other hand, groundwater sampling sites were classified according to spatial characteristics. Based on the presence/absence of unsewered houses and farmyards within 100 m and 300 m radius, sites were either associated with diffuse N (no house or farmyard) or organic point source contamination.

Despite the fact that most sites were located in the vicinity of unsewered houses, hydrochemistry at a majority of wells could still be associated with artificial diffuse contamination. The comparison of both site classifications resulted in the following outcome:

- 100 % of high nitrate sites with no organic point source within 100 m and 300 m radius showed groundwater chemistry indicative of contamination by artificial diffuse sources (i.e. artificial fertilisers).
- About 34 % of high nitrate sites with organic point sources (i.e. unsewered houses and/or farmyards) within 100 m and 300 m radius showed groundwater chemistry indicative of contamination by organic point N sources, whereas 64 % of sites with organic point sources within 100 m and 300 m radius had groundwater chemistry indicative of contamination by artificial diffuse sources.
- About 2 % of high nitrate sites classified with organic point sources within 100 m and 300 m radius showed hydrochemistry that could not be related to any type of N source.

Several elements supported the validity of site classification based on hydrochemistry. Firstly, the disagreements between both site classifications only occurred at sites located near organic sources, as groundwater chemistry was mainly associated with artificial diffuse contamination. On the other hand, groundwater chemistry was never related to organic point source contamination when organic point sources were not present within 100 m and 300 m radius. In the context of the Barrow Valley where artificial diffuse

sources are ubiquitous given the high percentage of tillage in the study areas, this means hydrochemistry always suggested contamination from sources that were present within 100 m and 300 m radius. A second supporting evidence came from the fact that nitrate concentrations were significantly higher at sites with high % tillage (> 50 %) within 300 m radius than at sites with low % tillage (< 50 %). Considering that most sites were surrounded by more than 50 % tillage, artificial diffuse sources are likely to be important contributors to nitrate contamination, which agrees with conclusions drawn from site classification based on hydrochemistry.

Oppositely, there was also supporting evidence for site classification based on spatial characteristics. Firstly, hydrochemistry analysis revealed that sodium concentrations were significantly higher at sites located nearby unsewered houses and/or farmyards. This does not necessarily contradict site classification based on hydrochemistry, but it implies that organic point sources had some impact on groundwater quality. The risk that hydrochemistry could lead to some erroneous conclusions is nonetheless evident if one considers that its conclusions are based on contamination indicators that are less mobile than nitrate. Second, the presence of faecal coliforms in 20 % of samples suggests that septic tanks and farmyards contribute to groundwater contamination.

CHAPTER 7: SATURATED ZONE INVESTIGATION: ISOTOPE RESULTS AND DISCUSSION

7.1 Introduction

As noted in chapter 6, a total of two hundred and eighty-three groundwater samples were collected between February 2002 and June 2004 in the Barrow Valley, which was the main study area investigated during this project. Following the procedure described in section 4.4, nitrate was extracted from two hundred and thirty-eight of these groundwater samples (originating from forty-six sampling sites), and subsequently converted into silver nitrate. In addition, the nitrate extraction and conversion process was also applied to twenty-four out of the thirty-three groundwater samples originating from nine boreholes at Curtin's farm in Moorepark RC.

Isotopic analysis was then carried out by CF-IRMS on each solid $AgNO_3$ sample, which involved the measurement of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$. The isotopic composition of groundwater ($\delta^{18}O\text{-}H_2O$ and $\delta^{2}H\text{-}H_2O$) was also investigated for samples collected between September 2002 and September 2003 in both the Barrow Valley and Moorepark RC. All these isotopic measurements are tabulated for individual samples in Appendix 4, whereas mean and median $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values are given for each site in Appendices 6A and 6B respectively.

The primary aim of this chapter was to test the worth of $\delta^{15}N$ and $\delta^{18}O$ analyses in nitrate as a tool to determine the origin of groundwater contamination and discriminate between the two main N sources identified in the Barrow Valley test areas: i) artificial N fertilisers (agricultural diffuse N sources), and ii) septic and/or farmyard effluents (organic point N sources). As a follow up to chapter 6, where groundwater sampling sites were classified according to the exceedance of contamination thresholds used to characterise artificial diffuse from organic point contamination, groundwater nitrate isotopic composition was analysed in relation to groundwater chemistry. Thereafter, the approach adopted was similar to that taken in chapter 5, where soil-water nitrate was analysed in relation to different types of treatment that involved artificial fertiliser and animal waste applications. In this chapter, groundwater nitrate isotopic values were analysed first in relation to the presence of artificial diffuse and organic point N sources within 100 m radius and 300 m radius of sampling wells, site spatial characteristics being earlier discussed in section 3.4.2.

Finally, the isotopic composition of groundwater nitrate was scrutinised where the origin of the contamination was well established, i.e. where spatial characteristics and hydrochemistry converged, as an ultimate step to test the usefulness of the stable isotope tool in this complex context of mixed diffuse and point N sources. In addition, the effect of % tillage within 300 m on groundwater nitrate isotopic composition was also examined.

Secondary objectives addressed in this chapter involved the use of $\delta^{18}O\text{-}H_2O$ values to make a prediction on the ^{18}O content of nitrate generated by nitrification in soils. Combined with $\delta^{2}H\text{-}H_2O$, $\delta^{18}O\text{-}H_2O$ was also used to determine the origin of the aquifer recharge, which was first discussed in section 3.2.6. Correlations between isotopic and chemical variables were also examined, which proved potentially valuable in the soil-water experiments (see section 5.3.3) or for the identification of denitrification (see section 2.6.4). The last objective of this chapter was to use stable isotope analyses in an attempt to bring further evidence that could help identify the cause of the nitrate problem in the Barrow Valley aquifers and at Moorepark RC.

7.2 Overview of nitrate and groundwater stable isotope composition in samples

7.2.1 $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in groundwater nitrate samples

- Barrow Valley

Table 7.1 below summarises the isotopic data for two hundred and thirty-eight nitrate samples that were prepared from groundwater collected in the Barrow Valley (see Appendix 4). The difference between the total number of groundwater samples collected and the number of silver nitrate samples prepared and analysed for isotopes was caused by the failure of the nitrate extraction procedure for fifty-five samples, which involved the loss of all the fifty-two samples collected in February 2002 plus three other samples from later sampling events (C.11 from September 2002, O.2 and BH.4A from February 2004). Consequently, no isotopic data were available for the five sites that were sampled only once in February 2002 (i.e. B.10, C.14, C.18, C.19 and C.20).

$\delta^{15}N\text{-}NO_3^-$ in groundwater nitrate samples showed an overall range of 16.3 ‰, with values between 2.3 to 18.6 ‰. But this very large range was deceptive as $\delta^{15}N\text{-}NO_3^-$ was measured below 4 ‰ in forty-five samples, whereas it was found above 10 ‰ in only

twelve samples. In addition, the examination of the 25th and 75th percentiles informs that the central half of the values was confined to a narrow range of values between 4.3 ‰ and 7.0 ‰. $\delta^{18}O\text{-}NO_3^-$ showed an overall range of 13.3 ‰, which stretched from -2.4 to 10.9 ‰. However for this parameter, the central half was also restricted to a narrow range, with values between 1.1 ‰ and 3.3 ‰.

Table 7.1: Central values and spread of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ measured by CF-IRMS in groundwater nitrate samples (in $AgNO_3$ form) from the Barrow Valley. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*

Parameter	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
$\delta^{15}N\text{-}NO_3^-$	238	5.9	2.3	5.5	4.3	7.0	2.3	18.6
$\delta^{18}O\text{-}NO_3^-$	238	2.4	1.8	2.2	1.1	3.3	-2.4	10.9

- Moorepark RC

Similarly to the Barrow Valley, nine nitrate samples prepared from groundwater collected in February 2002 could not be analysed for stable isotope composition. Consequently, no isotopic data were available for the site that was sampled only once in February 2002 (i.e. BHM.6). Table 7.2 displays the central values and spread for the remaining twenty-four nitrate samples prepared from later sampling events.

Table 7.2: Central values and spread of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ measured by CF-IRMS in groundwater nitrate samples (in $AgNO_3$ form) from Moorepark RC. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*

Parameter	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
$\delta^{15}N\text{-}NO_3^-$	24	6.6	3.5	6.0	5.5	6.7	-0.5	20.8
$\delta^{18}O\text{-}NO_3^-$	24	3.6	2.6	3.0	1.9	4.5	0.2	12.8

Despite an overall range of 20.3 ‰, with $\delta^{15}N\text{-}NO_3^-$ values between -0.5 and 20.8 ‰, few samples showed extreme values: only one sample had $\delta^{15}N\text{-}NO_3^-$ measured below 4 ‰, and only two samples had values above 10 ‰. In fact, half of the measurements were between 5.5 ‰ and 6.7 ‰ (the 25th and 75th percentiles).

As for $\delta^{18}O\text{-}NO_3^-$, the overall range was 12.6 ‰, with values between 0.2 to 12.8 ‰. Nonetheless, the central half was found between 1.9 ‰ and 4.5 ‰, which represented an interquartile range very similar to that observed for the Barrow Valley in table 7.1.

7.2.2 δ^2H-H_2O and δ^{18}O-H_2O in groundwater: overview and predictions for nitrification

- Overview

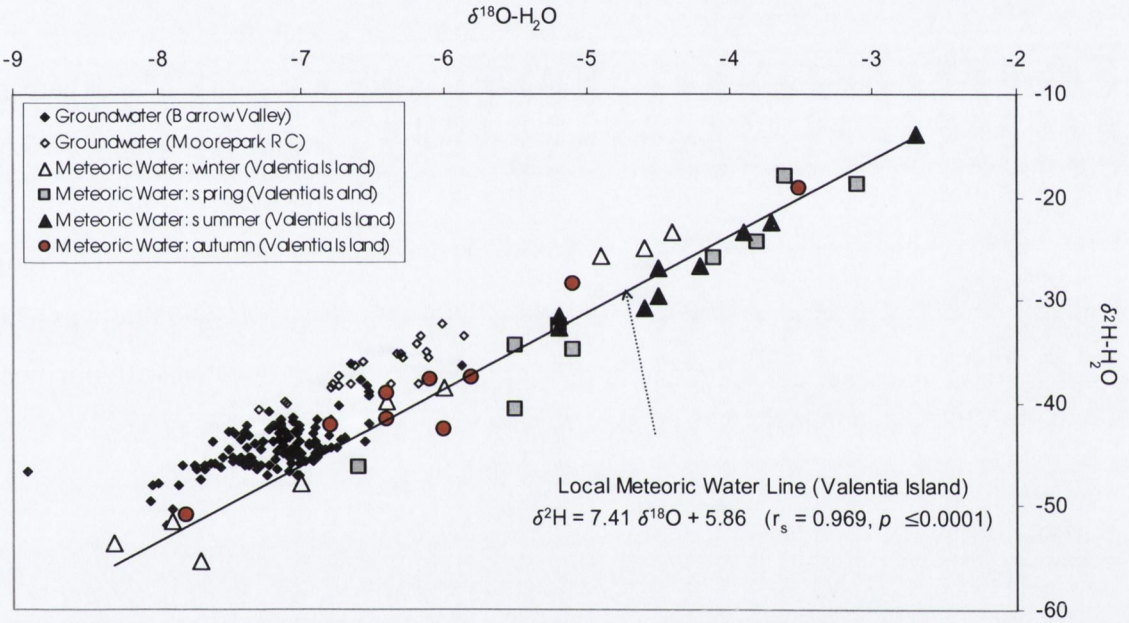
During groundwater sampling carried out in the Barrow Valley in September 2002, February 2003, June 2003 and September 2003, aliquots of one hundred and twenty-two groundwater samples collected from forty-five wells were analysed for δ^2H and δ^{18}O in water. In addition, twenty-two groundwater aliquots from the Moorepark RC sampling undertaken in December 2002, June 2003 and September 2003 were also analysed for these stable isotopes.

Figure 7.1 shows the plotting of measured δ^2H-H_2O and δ^{18}O-H_2O values for the Barrow Valley and Moorepark RC, in addition to the isotopic composition of meteoric water measured by the IAEA on the 15th day of each month between January 2000 and December 2002 at the meteorological station of Valentia Island in Co. Kerry (IAEA, 2004). In figure 7.1, astronomical seasons were defined as follows (based on equinoxes and solstices in the Northern Hemisphere): winter relates to days between 21st December (winter solstice) and 20th March (spring equinox), spring to days between 21st March and 20th June (summer solstice), summer to time between 21st June and 20th September (autumnal equinox), and autumn to time between 21st September and 20th December.
Ideally, meteoric data from the study areas would have been welcome, but isotopic measurement on Irish precipitation was only performed by the IAEA at Valentia Island. In reality, it is likely that meteoric water in the study areas is slightly ^{2}H- and ^{18}O-depleted relative to that at Valentia Island due to a continental effect that depletes rainfall from its heaviest elements during its travel across Ireland from the west (or south-west) to the east (section 2.6.5). But this difference is probably very limited due to the relatively small distance between Valentia Island and the Barrow Valley (170 km) or Moorpark RC study areas (80 km).

δ^{18}O-H_2O and δ^2H-H_2O were strongly correlated in meteoric water at Valentia Island (r_s = 0.969, $p \leq 0.0001$). Along the regression line, which represents the local meteoric water line, winter precipitation showed lower δ^2H-H_2O and δ^{18}O-H_2O values than summer precipitation, despite some overlap caused by three samples from months of February and March: the mean (and median) δ^{18}O-H_2O winter value was reported at -6.4 ‰, whereas the

mean δ^{18}O-H_2O summer value was -4.3 ‰ (-4.5 ‰ as median). A similar trend was also observed with δ^2H-H_2O, the mean (and median) winter values being -40.1 ‰ while the mean summer value was -26.4 ‰ (-26.9 ‰ as median). On the other hand, spring and autumn values were intermediate, although spring values appeared to be closer to summer values and autumn values closer to winter values.

Figure 7.1: Variation of δ^{18}O-H_2O with δ^2H-H_2O in groundwater collected during winter and summer times in the Barrow Valley (n = 122) and Moorepark RC (n = 22) between 2002 and 2004; variation of monthly δ^{18}O-H_2O and δ^2H-H_2O values for meteoric water (n = 36) at Valentia Island in Co. Kerry (IAEA, 2004) measured on the 15th of each month between January 2000 and December 2002 (astronomical seasons based on spring and autumnal equinoxes, winter and summer solstices). *($\delta^{18}O$ and δ^2H are both reported in ‰ against V-SMOW) (the solid regression line represents the meteoric water line for Valentia Island)*



The results showed that the isotopic composition of groundwater collected in the study areas followed closely the Valentia Island meteoric water line. In the Barrow Valley, groundwater δ^{18}O-H_2O values lay within a narrow range along this line, from -8.9 ‰ and -5.9 ‰, which was very similar to the range measured at Moorepark RC (values between -7.6 ‰ and -5.9 ‰). Simultaneously, δ^2H-H_2O varied between -51.8 ‰ and -36.1 ‰ in the Barrow Valley, and between -45.8 ‰ and -32.3 ‰ at Moorepark RC.

A visual observation of figure 7.1 suggests that whatever the sampling time, all groundwater values were within the range displayed by winter precipitation at Valentia Island, whereas there were also overlaps with ranges of spring and autumn precipitations. Distinctively, no groundwater sample showed values within the range of summer precipitation.

- Predictions for $\delta^{18}O\text{-}NO_3^-$ after nitrification

As explained in section 2.4.1, nitrification is the process that causes the oxidation of ammonium into nitrate. In terms of stable isotopes, this microbial reaction is often described as the incorporation of two oxygen atoms from soil-water and one oxygen atom from dissolved atmospheric O_2 (Andersson and Hopper, 1983; Kumar *et al.*, 1983; Hollocher, 1984). Assuming that the above assumptions are valid, an estimate of $\delta^{18}O\text{-}NO_3^-$ value in nitrate generated by nitrification can be predicted from Equation 2.15 (section 2.6.3), which necessitates the knowledge of $\delta^{18}O\text{-}H_2O$ (in groundwater) and $\delta^{18}O\text{-}O_2$ (in atmospheric air).

In the Barrow Valley, the lowest $\delta^{18}O\text{-}H_2O$ value was measured at -8.9 ‰, whereas the highest value was -5.9 ‰. Considering that $\delta^{18}O\text{-}O_2$ is generally close to 23.5 ‰ (Kroopnick and Craig, 1972), applying Equation 2.15 to minimum and maximum $\delta^{18}O\text{-}H_2O$ values suggests that nitrification should produce nitrate with $\delta^{18}O\text{-}NO_3^-$ ranging between 1.9 and 3.9 ‰. In Moorepark RC, where the lowest $\delta^{18}O\text{-}H_2O$ value was -7.6 ‰ and the highest value -5.9 ‰, predictions for $\delta^{18}O\text{-}NO_3^-$ values associated with nitrification led to a similar range that stretched between 2.8 and 3.9 ‰.

7.2.3 Discussion of the overall isotopic results

- $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in groundwater nitrate

Although nitrate isotopic composition in groundwater is discussed in more detail in section 7.3, where the effects of hydrochemistry and sites' spatial characteristics are discussed, several observations could yet be made about the overall ranges of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values measured in individual silver nitrate samples and presented in section 7.2.1.

The $\delta^{15}N\text{-}NO_3^-$ values measured in groundwater nitrate from the Barrow Valley ranged between 2.3 and 18.6 ‰ (table 7.1), which overlapped in 19 % of the observations (45/238) with the upper end of the range reported in the literature (see table 2.8) for nitrate derived from artificial fertilisers (from -4 to 4 ‰). On the other hand, the lower end of the range reported for nitrate derived from animal/human waste (from 10 to 22 ‰) was overlapped by only 5 % of the samples (12/238). Distinctively, more similarities were

found with nitrate derived from soil organic matter, as the range reported in the literature (4 to 9 ‰) was entirely overlapped. It should be noted that all observations showed δ^{15}N-NO_3^- values that were outside the range displayed by the artificial fertilisers used in Oak Park and Moorepark RC (from -2.4 to 2 ‰ – see table 5.4 in section 5.2.2).

Likewise, the δ^{15}N-NO_3^- values measured in groundwater nitrate at Moorepark RC showed a similarly large range of values in table 7.2 (from -0.5 to 20.8 ‰) that mainly overlapped with the range expected for soil organic N-derived nitrate.

The δ^{18}O-NO_3^- values measured in groundwater nitrate from the Barrow Valley ranged between -2.4 and 10.9 ‰, which encompassed widely the 0 to 5 ‰ range often reported in the literature for nitrification (Durka *et al.*, 1994). Values observed were in fact lower by at least 8 ‰ than what would have been expected from fertiliser nitrate, for which the literature reports a 18 ‰ to 22 ‰ range (see table 2.8) that was also measured in fertilisers used by Teagasc (see table 5.4).

Identical comments can be made for the Moorepark RC results, where δ^{18}O-NO_3^- values ranged from 0.2 and 12.8 ‰.

- δ^2H-H_2O and δ^{18}O-H_2O in groundwater

The use of Valentia Island meteoric stable isotope data had two aims. The first one was to gain information on the temporal origin of groundwater (see early comments in section 2.6.5) that was sampled in the Barrow Valley and at Moorepark RC, bearing in mind the limitation of this approached explained in section 7.2.2. The pattern displayed by δ^2H-H_2O and δ^{18}O-H_2O values in precipitation at Valentia Island was comparable to that described in figure 2.6, where rainfall was reported to show higher δ values in summer than during winter. Both isotopic variables were significantly and strongly correlated, which allowed the drawing of the local meteoric water line. As observed in figure 7.1, the isotopic composition of groundwater collected in the Barrow Valley and at Moorepark RC followed closely the Valentia Island local meteoric water line. The results suggested that the groundwater sampled was distinctively different from summer precipitation, and was therefore not of summer origin. This is in agreement with figure 3.6 in section 3.2.6, where the modelling of effective rainfall and soil moisture deficit (Schulte *et al.*, 2005) ruled out summer recharge.

The second purpose of using Valentia Island meteoric stable isotope data was for Equation 2.15 in order to make predictions on δ^{18}O-NO_3^- values after nitrification in Irish soils. This

equation assumes that during nitrification, nitrogen is oxidised by two atoms of oxygen coming from soil-water and one atom of oxygen from atmospheric air without any isotopic fractionation (section 2.6.3). This is obviously very questionable, considering the fact that most microbial processes generate some isotopic fractionation.

Nevertheless, the results of the calculation suggested that $\delta^{18}O\text{-}NO_3^-$ in nitrified nitrate may range between 1.9 and 3.9 ‰ in the Barrow Valley, and between 2.8 and 3.9 ‰ at Moorepark RC. These values are similar to the 0 to 5 ‰ range given by Durka *et al.* (1994), which is widely adopted in the literature to describe microbial nitrification.

7.3 Effects of hydrochemistry and sites' spatial characteristics on site mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values in the Barrow Valley

7.3.1 Introduction to isotopic data analysis

In order to simplify data analysis and to be consistent with the way chemical data were handled in chapter 6, it was decided to analyse mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values calculated for each of the Barrow Valley sampling sites (see Appendices 6A and 6B), rather than values for individual samples tabulated in Appendix 4. Furthermore, means were preferred to medians because the difference between both was often small, which ruled out skewness: only three sites showed a difference between the mean and the median $\delta^{15}N\text{-}NO_3^-$ value that was higher than ±0.5 ‰, whereas the maximum difference between the site mean and median $\delta^{18}O\text{-}NO_3^-$ values was 0.9 ‰.

The approach that consists of using site means rather than values for individual samples was justified by the fact that most sites showed a limited variation in $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ between different sampling occasions. The coefficients of variation (i.e. ratio of standard deviation to the mean) by site remained generally low: CV was lower than 10 % at twenty-six sites, lower than 20 % at thirty-five sites, and lower than 30 % at forty-three sites. In fact, high CVs were observed at only two locations (41 % at C.11 and 100 % at BHO.3B). Therefore, mean isotopic values for each site were thought to be an acceptable way of summarising the dataset.

Before the isotopic data are analysed in the following subsections in relation to several site-related factors, an overview of mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values is given in table 7.3 for the forty-six sites from the Barrow Valley where isotopic analyses were undertaken.

It must be remembered that no isotopic data were available for the five sites that were sampled only once in February 2002 (i.e. B.10, C.14, C.18, C.19 and C.20).

Table 7.3: Central values and spread of mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*

Parameter	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
$\delta^{15}N\text{-}NO_3^-$	46	5.9	1.9	5.7	4.3	7.4	3.0	10.9
$\delta^{18}O\text{-}NO_3^-$	46	2.5	1.5	2.2	1.3	3.2	0.5	7.2

The sites showed mean $\delta^{15}N\text{-}NO_3^-$ values ranging from 3 ‰ to 10.9 ‰. Seven sites showed mean $\delta^{15}N\text{-}NO_3^-$ values that were below 4 ‰, whereas only one site had a mean $\delta^{15}N\text{-}NO_3^-$ slightly higher than 10 ‰. As for $\delta^{18}O\text{-}NO_3^-$, site mean values were likewise within a narrow range (i.e. between 0.5 ‰ and 7.2 ‰), with only four sites above 5 ‰.

7.3.2 Nitrate isotopic composition in relation to hydrochemistry groups

In section 6.3.3, forty-six groundwater sampling sites with high mean nitrate concentration (i.e. mean $[NO_3^-] \geq 25$ mg/l) were classified according to their exceedance (or non-exceedance) of contamination thresholds previously assessed in section 6.3.1 for chloride, potassium and sodium. Based on assumptions made in section 6.3.2, high nitrate sites were linked to either artificial diffuse N source contamination or organic point N source contamination whenever possible. Two types of classification were used (see table 6.4 in section 6.3.2): Group 6 classification defined four categories relevant to artificial diffuse N source contamination (labelled D_{c1}, D_{c2}, D_{c3} and D_{c4}), and two categories relevant to organic point source contamination (labelled P_{c1} and P_{c2}), whereas Group 2 classification merged categories linked to artificial diffuse N source (labelled D_c) and organic point N source contamination (labelled P_c). For both classifications, an additional category was created for sites that did not fit in any of the previous classes (labelled U_c). As a reminder of table 6.4, each Group 6 category was defined according to the following exceedance of contamination threshold values:

- D_{c1} = mean $[Cl^-] < 28.4$ mg/l, $[K^+] < 3.1$ mg/l, and $[Na^+] < 12$ mg/l
- D_{c2} = mean $[Cl^-] \geq 28.4$ mg/l, $[K^+] < 3.1$ mg/l, and $[Na^+] < 12$ mg/l
- D_{c3} = mean $[Cl^-] \geq 28.4$ mg/l, $[K^+] \geq 3.1$ mg/l, and $[Na^+] < 12$ mg/l
- D_{c4} = mean $[Cl^-] < 28.4$ mg/l, $[K^+] \geq 3.1$ mg/l, and $[Na^+] < 12$ mg/l

- P_{c1} = mean $[Cl^-] \geq 28.4$ mg/l, $[K^+] \geq 3.1$ mg/l, and $[Na^+] \geq 12$ mg/l
- P_{c2} = mean $[Cl^-] \geq 28.4$ mg/l, $[K^+] < 3.1$ mg/l, and $[Na^+] \geq 12$ mg/l
- U_c = mean $[Cl^-] < 28.4$ mg/l, $[K^+] \geq 3.1$ mg/l, and $[Na^+] \geq 12$ mg/l

In this section, site mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in groundwater nitrate are examined at forty-one high nitrate sites across Group 6 and Group 2 categories (list of sites in table 6.5, minus B.10, C.14, C.18, C.19 C.20 for which no isotopic data is available). The groundwater nitrate isotopic composition in each category is firstly compared with predicted $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values that were reported from the literature in table 2.8 for nitrate derived from artificial fertilisers (-4 ‰ $\leq \delta^{15}N\text{-}NO_3^- \leq$ 4 ‰, and 18 ‰ $\leq \delta^{18}O\text{-}NO_3^- \leq$ 22 ‰ in fertiliser nitrate) and nitrate derived from animal/human organic wastes (10 ‰ $\leq \delta^{15}N\text{-}NO_3^- \leq$ 22 ‰ and 0 ‰ $\leq \delta^{18}O\text{-}NO_3^- \leq$ 5 ‰). Thereafter, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ are compared between categories in order to detect any significant differences between sites associated with artificial fertiliser diffuse and organic point source contaminations. Finally, nitrate isotopic composition is also studied at the five low nitrate sites (i.e. mean $[NO_3^-] < 25$ mg/l).

- $\delta^{15}N\text{-}NO_3^-$ at high nitrate groundwater sampling sites (i.e. mean $[NO_3^-] \geq 25$ mg/l)

Table 7.4 describes mean $\delta^{15}N\text{-}NO_3^-$ values at high nitrate sites (i.e. mean [NO3-] ≥ 25 mg/l) across the different categories of Group 6 and Group 2 classifications. To facilitate the reading of this table, a dotplot of site mean $\delta^{15}N\text{-}NO_3^-$ values for each category of the Group 6 classification is provided as figure 7.2. The dotplot also helps visualise the distribution of mean values at each site, which cannot be showed by a boxplot.

Table 7.4: Central values and spread of mean $\delta^{15}N\text{-}NO_3^-$ values at the high nitrate groundwater sampling sites of the Barrow Valley (i.e. mean $[NO_3^-] \geq 25$ mg/l), across Group 6 and Group 2 categories as defined in table 6.4. *($\delta^{15}N$ is reported in ‰ against AIR)*

Group	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
Group 6 classification								
D_{c1}	9	5.1	1.2	5.6	4.2	6.0	3.0	6.4
D_{c2}	8	5.4	1.4	5.5	4.6	6.0	3.4	7.8
D_{c3}	5	4.8	0.8	4.3	4.3	5.6	4.2	5.9
D_{c4}	6	4.4	0.8	4.4	4.0	4.8	3.1	5.5
P_{c1}	6	8.0	1.6	8.0	7.2	9.5	5.7	9.9
P_{c2}	6	6.5	2.3	7.0	3.8	8.5	3.6	8.9
U_c	1	8.4		8.4	8.4	8.4	8.4	8.4
Group 2 classification								
D_c	28	5.0	1.1	5.1	4.2	5.8	3.0	7.8
P_c	12	7.2	2.0	7.6	6.1	8.7	3.6	9.9
U_c	1	8.4		8.4	8.4	8.4	8.4	8.4

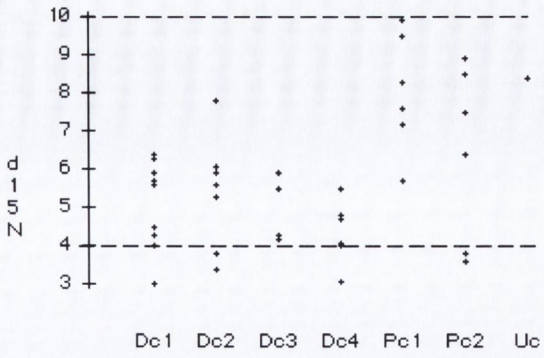


Figure 7.2: Distribution of mean $\delta^{15}N\text{-}NO_3^-$ values at the high nitrate groundwater sampling sites of the Barrow Valley (i.e. mean $[NO_3^-] \geq 25$ mg/l), across Group 6 categories (D_{c1}: n = 9, D_{c2}: n = 8, D_{c3}: n = 5, D_{c4}: n = 6, P_{c1}: n = 6, P_{c2}: n = 6, U_c: n = 1) as defined in table 6.4. *($\delta^{15}N$ is reported in ‰ against AIR) (bottom dashed line represents the upper end of the range expected for artificial fertiliser-derived nitrate, top dashed line represents the lower end of the range expected for organic waste-derived nitrate)*

In categories linked to artificial diffuse N source contamination (i.e. D_{c1}, D_{c2}, D_{c3} and D_{c4}), $\delta^{15}N\text{-}NO_3^-$ ranged between 3.0 ‰ and 7.8 ‰. When making comparisons with values from table 2.8, it can be seen that measured $\delta^{15}N\text{-}NO_3^-$ in these categories overlapped with the upper end of the range expected for artificial fertiliser-derived nitrate (-4 to 4 ‰). But this overlap was attributed to only four sites out of twenty-eight. In fact, all other twenty-two values overlapped with the range expected for soil organic N-derived nitrate (4 to 9 ‰).

In categories associated with organic point N source contamination (i.e. P_{c1} and P_{c2}), $\delta^{15}N\text{-}NO_3^-$ was observed between 3.6 ‰ and 9.9 ‰, which largely overlapped the range expected from the literature for organic soil N-derived nitrate (at ten sites). The range expected for artificial fertiliser-derived nitrate was also overlapped, but only because of two sites from the P_{c2} category with distinctively low $\delta^{15}N\text{-}NO_3^-$. Importantly, no sites showed values matching the range expected for organic waste-derived nitrate (10 to 22 ‰). Finally, the only site belonging to the U_c category showed a relatively high $\delta^{15}N\text{-}NO_3^-$ in comparison with most sites, which was reported at 8.4 ‰.

Observation of figure 7.2 suggests that despite some overlap, sites classified in the D_c subcategories (i.e. D_{c1}, D_{c2}, D_{c3} and D_{c4}) had nitrate consistently ^{15}N-depleted in comparison with sites from the P_c subcategories (i.e. P_{c1} and P_{c2}). In fact, the overlap between D_c and P_c subcategories was caused by only five sites: one site in category D_{c2} with a distinctively high $\delta^{15}N\text{-}NO_3^-$ value (7.8 ‰), and four sites in categories P_{c1} and P_{c2} with values lower or equal to 6.4 ‰.

An examination of table 7.4 confirms this trend as all D_c subcategories (i.e. D_{c1}, D_{c2}, D_{c3} and D_{c4}) had consistently low means ranging between 4.4 ‰ and 5.4 ‰, whereas P_{c1} and P_{c2} categories showed higher means at 8 ‰ and 6.5 ‰ respectively. When looking at Group 2 classification, the mean of the D_c category (5 ‰) was more than 2 ‰ lower than that of the P_c category (7.2 ‰). An ANOVA test, which was performed on the $\delta^{15}N\text{-}NO_3^-$ log-transformed dependent variable and the Group 2 classification as the independent

variable (from which the U_c group-site was excluded), showed that the difference between the D_c and P_c categories was highly significant at the 0.0005 level ($F_{1, 38} = 15.2$, $p = 0.0004$ and 2:1 ratio of the largest to smallest variance)). If the high outlier from the D_{c2} category and two low outliers from the P_{c2} category were excluded from the study, the significance of the difference between D_c and P_c categories strongly improved ($F_{1, 35} = 42.9$, $p \leq 0.0001$ and 1.5: ratio of the largest to smallest variance).

- $\delta^{18}O\text{-}NO_3^-$ at high nitrate groundwater sampling sites (i.e. mean $[NO_3^-] \geq 25$ mg/l)

Table 7.5 describes site mean $\delta^{18}O\text{-}NO_3^-$ data at the high nitrate sites (i.e. mean [NO3-] ≥ 25 mg/l) across the categories of Group 6 and Group 2 classifications. The results are also displayed in figure 7.3 as a dotplot in relation to Group 6 classification, which also gives a better insight of the distribution of mean values at each site.

Table 7.5: Central values and spread of mean $\delta^{18}O\text{-}NO_3^-$ values at the high nitrate groundwater sampling sites of the Barrow Valley (i.e. mean $[NO_3^-] \geq 25$ mg/l), across Group 6 and Group 2 categories as defined in table 6.4. *($\delta^{18}O$ is reported in ‰ against V-SMOW)*

Group	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
Group 6 classification								
D_{c1}	9	2.3	1.0	2.4	1.8	3.1	0.7	3.9
D_{c2}	8	2.1	1.5	1.8	0.9	3.2	0.5	4.4
D_{c3}	5	1.7	0.9	1.6	1.0	2.2	0.8	3.1
D_{c4}	6	1.4	0.4	1.5	1.2	1.7	0.8	1.8
P_{c1}	6	3.2	1.4	2.9	2.5	4.4	1.2	5.2
P_{c2}	6	2.6	1.0	2.6	2.0	3.5	1.1	3.6
U_c	1	2.5		2.5	2.5	2.5	2.5	2.5
Group 2 classification								
D_c	28	1.9	1.1	1.8	1.2	2.5	0.5	4.4
P_c	12	2.9	1.2	2.8	2.1	3.6	1.1	5.2
U_c	1	2.5		2.5	2.5	2.5	2.5	2.5

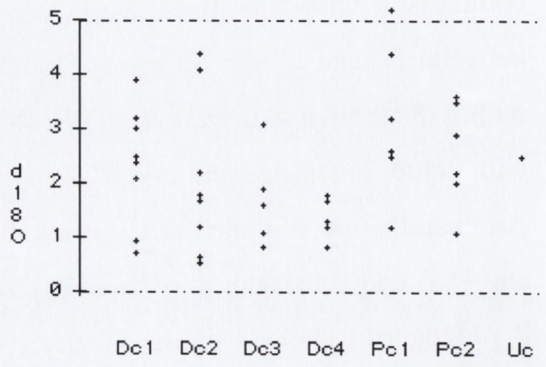


Figure 7.3: Distribution of mean $\delta^{18}O\text{-}NO_3^-$ values at the high nitrate groundwater sampling sites of the Barrow Valley (i.e. mean $[NO_3^-] \geq 25$ mg/l), across Group 6 categories as defined in table 6.4. *($\delta^{18}O$ is reported in ‰ against V-SMOW) (dashed lines represent the upper and the lower limits of the range reported by Durka et al. (1994) for nitrification)*

In D_c subcategories linked with artificial diffuse contamination (i.e. D_{c1}, D_{c2}, D_{c3} and D_{c4}), $\delta^{18}O\text{-}NO_3^-$ ranged between 0.5 ‰ and 4.4 ‰, which was lower by at least 13 ‰ than the 18 to 22 ‰ range given in the literature for synthetic fertiliser nitrate (table 2.8). On the other hand, $\delta^{18}O\text{-}NO_3^-$ values in these D_c subcategories matched remarkably well the 0 to 5 ‰ range expected for nitrate generated by nitrification (Durka *et al.*, 1994).
In the P_c subcategories associated with organic point source contamination (i.e. P_{c1} and P_{c2}), $\delta^{18}O\text{-}NO_3^-$ ranged between 1.1 ‰ and 5.2 ‰, which matched the nitrification range.
As for the only site belonging to the U_c category, $\delta^{18}O\text{-}NO_3^-$ was calculated at 2.5 ‰ in the middle of the nitrification range.

Unlike $\delta^{15}N\text{-}NO_3^-$ values, the observation of the dotplot (figure 7.3) did not highlight any obvious difference between groups of sites for which hydrochemistry was associated with artificial diffuse and organic point source contaminations, as values in the D_c subcategories largely overlapped those of the P_c subcategories. In addition, the examination of table 7.5 shows that the mean $\delta^{18}O\text{-}NO_3^-$ value of the D_c category (1.9 ‰) was lower by 1 ‰ than that of the P_c category (2.9 ‰). This small difference was significant at the 0.05 level when carrying out an ANOVA test on the $\delta^{18}O\text{-}NO_3^-$ log-transformed dependent variable and the Group 2 classification as the independent variable from which the U_c group-site was excluded ($F_{1, 38} = 5.58$, $p = 0.0234$ and 1.5:1 ratio of the largest to smallest variance).

- <u>$\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ at low nitrate groundwater sampling sites (i.e. mean $[NO_3^-] \leq$ 25 mg/l)</u>

As explained in section 6.3.3, five sites showed mean nitrate concentrations below 25 mg/l NO_3^-. If taking into account contamination indicators other than nitrate (i.e. chloride, potassium and sodium concentrations), four of these sites had the hydrochemical characteristics of either D_{c1} (C.9, O.6 and O.10) or D_{c4} category (BHO.3B), whereas one site showed similarities with the P_{c2} category (C.11).

Contrasting results were found for these sites. Firstly, sites C.9 and O.6 showed low $\delta^{15}N\text{-}NO_3^-$ (5.7 ‰ and 3.4 ‰) and $\delta^{18}O\text{-}NO_3^-$ values (2.3 ‰ and 2 ‰) that fell within ranges displayed by category D_{c1} in tables 7.4 and 7.5. Distinctively, sites O.10 and BHO.3B showed higher $\delta^{15}N\text{-}NO_3^-$ (8.1 ‰ and 7.5 ‰) and $\delta^{18}O\text{-}NO_3^-$ values (6.6 ‰ and 7.2 ‰) outside ranges of categories D_{c1} and D_{c4} for both isotopes.

On the other hand, site C.11 showed high $\delta^{15}N\text{-}NO_3^-$ (10.9 ‰) and $\delta^{18}O\text{-}NO_3^-$ values (5.3 ‰) outside the ranges displayed by category P_{c2}.

7.3.3 Nitrate isotopic composition in relation to % tillage groups

In this section, site mean values for $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in groundwater nitrate are examined in relation to the four classes of % tillage, which were originally identified in section 3.4.2 and discussed further in section 6.4.1. It should be noted that table 6.8 showed the classification of sampling sites according to % tillage in the context of chemical analyses, which differed from the context of isotopic analyses as no $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ mean values were available for five sites (i.e. B.10, C.14, C.18, C.19 and C.20).

For each % tillage category, groundwater nitrate isotopic composition is compared with predicted $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values that were reported in table 2.8 (section 2.6.6) for nitrate derived from artificial fertilisers (-4 ‰ $\leq \delta^{15}N\text{-}NO_3^- \leq 4$ ‰, and 18 ‰ $\leq \delta^{18}O\text{-}NO_3^- \leq 22$ ‰ in fertiliser nitrate). This is justified by the fact that in the Barrow Valley study areas, tillage is mainly associated with diffuse applications of synthetic fertilisers rather than slurry and manure (see section 3.4.2). In addition, comparisons are made between categories in order to detect any shift in isotopic values associated with an increase in % tillage.

- $\delta^{15}N\text{-}NO_3^-$ in groundwater nitrate

Table 7.6 shows central values and spread of site mean $\delta^{15}N\text{-}NO_3^-$ values across four classes of % tillage defined within 300 m radius around sampling sites. In addition, the results are also presented in figure 7.4 as a dotplot in order to help the interpretation of the table and visualise the distribution of mean values at each site.

Table 7.6: Central values and spread of mean $\delta^{15}N\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley across categories of % tillage within 300 m radius. *($\delta^{15}N$ is reported in ‰ against AIR)*

Group	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
0 % < T ≤ 25 %	6	6.0	1.9	6.0	4.7	7.5	3.4	8.5
25 % < T ≤ 50 %	4	6.8	1.9	7.3	5.4	8.2	4.3	8.3
50 % < T ≤ 75 %	7	6.7	2.6	5.6	4.7	9.0	4.3	10.9
75 % < T ≤ 100 %	29	5.5	1.8	5.6	4.0	6.5	3.0	9.5

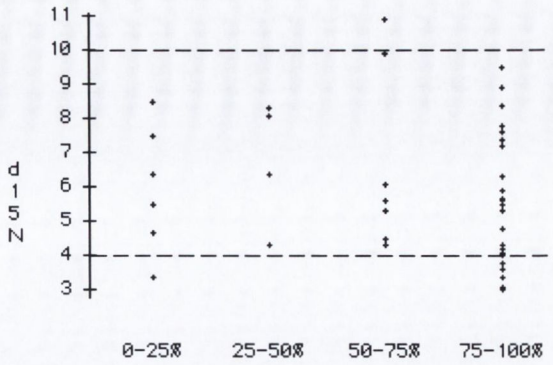


Figure 7.4: Distribution of mean $\delta^{15}N\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley across categories of % tillage within 300 m radius. *($\delta^{15}N$ is reported in ‰ against AIR) (bottom dashed line represents the upper end of the range expected for artificial fertiliser-derived nitrate, top dashed line represents the lower end of the range expected for organic waste-derived nitrate)*

The results showed that in each % tillage category, nearly all $\delta^{15}N\text{-}NO_3^-$ values were above the -4 to 4 ‰ range expected for artificial fertiliser-derived nitrate. Only a few sites had values falling into this range: one site out of six in the 0-25 % tillage category and six sites out of twenty-nine in the 75-100 % tillage category. In fact, most values were within the 4 to 9 ‰ range expected for soil organic N-derived nitrate, whereas only three sites were slightly beyond this range (i.e. values 9.5 ‰, 9.9 ‰ and 10.9 ‰).

The means for each % tillage category lay within a narrow range of values (between 5.5 ‰ and 6.8 ‰), which did not show any clear trend in relation to % tillage. Unsurprisingly, an ANOVA test carried out on the $\delta^{15}N\text{-}NO_3^-$ log-transformed dependent variable with % tillage as the independent variable (1.4:1 ratio of the largest to smallest variance) showed that there was no significant effect of % tillage at the 0.05 level on groundwater nitrate isotopic composition.

If merging the low % tillage categories into a 0-50 % group, and the high % tillage categories into a 50-100 % group (see section 6.4.2), the homogeneity of variance between both groups was improved on the log-transformed variable (1.1:1 ratio of the largest to smallest variance), but no significant difference was detected at the 0.05 level.

- $\delta^{18}O\text{-}NO_3^-$ in groundwater nitrate

Table 7.7 shows central values and spread of site mean $\delta^{18}O\text{-}NO_3^-$ values in the different classes of % tillage. The results are also displayed in figure 7.5 in the form of a dotplot to facilitate the interpretation of the table, but mostly to allow a better picture of the distribution of mean values at each site.

Table 7.7: Central values and spread of $\delta^{18}O\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley across categories of % tillage within 300 m radius. *($\delta^{18}O$ is reported in ‰ against V-SMOW)*

Group	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
0 % < T ≤ 25 %	6	2.8	1.0	2.8	1.9	3.6	1.8	3.9
25 % < T ≤ 50 %	4	4.0	2.2	3.7	2.2	5.9	2.1	6.6
50 % < T ≤ 75 %	7	2.8	1.2	2.5	1.9	3.2	1.7	5.3
75 % < T ≤ 100 %	29	2.1	1.5	1.7	1.1	2.7	0.5	7.2

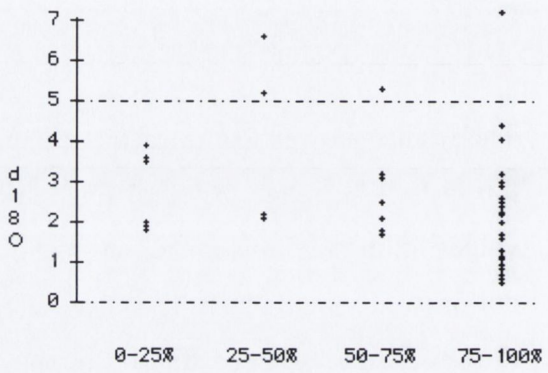


Figure 7.5: Distribution of mean $\delta^{18}O\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley across categories of % tillage within 300 m radius. *($\delta^{18}O$ is reported in ‰ against V-SMOW) (dashed lines represent the upper and the lower limits of the range reported by Durka et al. (1994) for nitrification)*

In each % tillage category, $\delta^{18}O\text{-}NO_3^-$ values were much lower than the 18 ‰ to 22 ‰ range expected for fertiliser nitrate. The highest maximum value was found in the 75-100 % tillage category at 7.2 ‰, i.e. almost 11 ‰ below the lower end of the fertiliser nitrate range. Four sites aside, values for each tillage category were within the 0 to 5 ‰ range expected for nitrification.

The means of all categories, which were between 2.1 ‰ (75-100 % tillage) and 4 ‰ (25-50 % tillage), were within less than 2 ‰ of one another. An ANOVA test carried out on the $\delta^{18}O\text{-}NO_3^-$ log-transformed dependent variable (3.3:1 ratio of the largest to smallest variance) confirmed that there was no significant difference in $\delta^{18}O\text{-}NO_3^-$ values between the different % tillage categories at the 0.05 level.

The merging of the four % tillage categories into two groups (0-50 % and 50-100 % tillage) improved the homogeneity of variance between both groups on the log-transformed variable (1.9:1 ratio of the largest to smallest variance). An ANOVA test carried out on the log-transformed variable showed that values in the 50-100 % tillage group were significantly lower than in the 0-50 % group at the 0.05 level ($F_{1, 44} = 4.46$, $p = 0.0404$).

7.3.4 Nitrate isotopic composition in relation to N source groups

In this section, site mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values measured in groundwater nitrate are examined in relation to the presence (or absence) within 100 m and 300 m radius

around groundwater sampling sites of organic point N sources that were originally identified in section 3.4.2 and discussed further in section 6.4.1. It should be noted that table 6.7 showed the classification of sampling sites according to N sources in the context of chemical analyses, which slightly differed from the context of isotopic analyses as no $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ mean values were available for five sites (i.e. B.10, C.14, C.18, C.19 and C.20).

The following categories and subcategories were identified within 100 m and 300 m radius: artificial fertiliser diffuse N source (labelled D_s), organic point N source (labelled P_s), which was broken down into septic tank N source (labelled PS_s), farmyard N source (labelled PF_s) and undetermined point N source, i.e. septic tank and farmyard N source (labelled PFS_s). A consequence of the absence of isotopic values at five sites was that categories D_s and P_s were identical within 100 m radius and within 300 m radius.

In order to hold constant any potential tillage effect, the results were also analysed within the 75-100 % tillage category (within 300 m radius), which includes twenty-nine of the forty-six groundwater sampling wells analysed for isotopes.

For each N source category, groundwater nitrate isotopic composition is compared with predicted $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values that were reported in table 2.8 (section 2.6.6) for nitrate derived from artificial fertilisers ($-4\text{ ‰} \leq \delta^{15}N\text{-}NO_3^- \leq 4\text{ ‰}$, and $18\text{ ‰} \leq \delta^{18}O\text{-}NO_3^- \leq 22\text{ ‰}$ in fertiliser nitrate) and animal/human organic wastes ($10\text{ ‰} \leq \delta^{15}N\text{-}NO_3^- \leq 22\text{ ‰}$ and $0\text{ ‰} \leq \delta^{18}O\text{-}NO_3^- \leq 5\text{ ‰}$). Additionally, comparisons are made between categories in order to detect any shift in isotopic values associated with the presence of the different types of N sources (i.e. artificial fertiliser, septic tanks and/or farmyards).

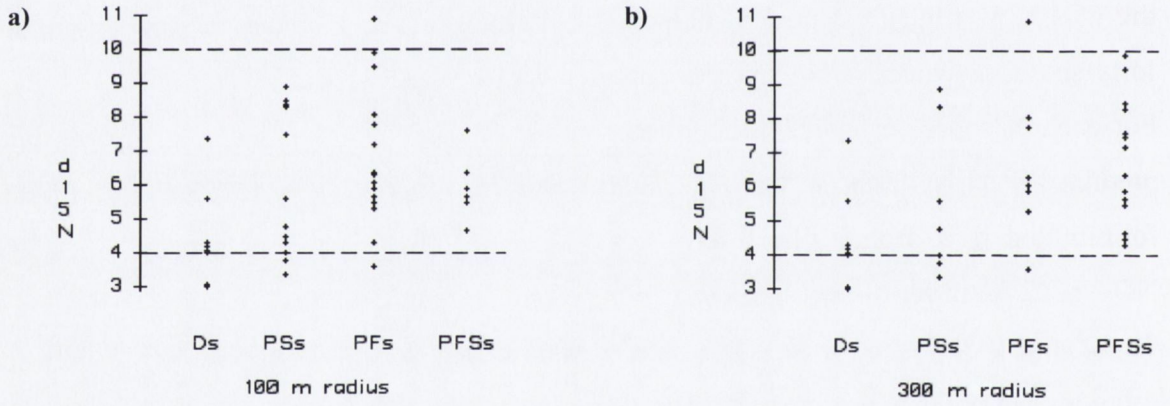
- $\delta^{15}N\text{-}NO_3^-$ in groundwater nitrate

Table 7.8 displays the central values and spread of the site mean $\delta^{15}N\text{-}NO_3^-$ values across the different N source categories and organic point source subcategories within 100 m radius and 300 m radius. The results are also presented in figures 7.6a (100 m radius) and 7.6b (300 m radius) as a dotplot in order to facilitate the interpretation of table 7.8, but mostly to give a better insight of the distribution of mean values at each site.

Table 7.8: Central values and spread of mean $\delta^{15}N\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley across the following N source categories within two radii (100 m and 300 m): D_s = artificial diffuse, P_s = organic point, PS_s = septic tank, PF_s = farmyard, PFS_s = undetermined point. *($\delta^{15}N$ is reported in ‰ against AIR)*

Group	Radius	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
D_s	100 m	8	4.5	1.4	4.2	3.6	5.0	3.0	7.4
	300 m	8	4.5	1.4	4.2	3.6	5.0	3.0	7.4
P_s	100 m	38	6.2	1.9	5.8	4.7	7.6	3.4	10.9
	300 m	38	6.2	1.9	5.8	4.7	7.6	3.4	10.9
PS_s	100 m	14	5.7	2.2	4.7	3.8	8.3	3.4	8.9
	300 m	9	5.1	2.1	4.0	3.7	6.3	3.4	8.9
PF_s	100 m	17	6.7	2.0	6.1	5.5	7.9	3.6	10.9
	300 m	9	6.6	2.1	6.1	5.3	7.9	3.6	10.9
PFS_s	100 m	7	6.0	0.9	5.9	5.6	6.3	4.7	7.6
	300 m	20	6.5	1.7	5.9	5.5	7.6	4.3	9.9

Figure 7.6: Distribution of mean $\delta^{15}N\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley across the artificial diffuse category (D_s) and the organic point N source subcategories (PS_s, PF_s, PFS_s) within **a)** 100 m and **b)** 300 m radius. *($\delta^{15}N$ is reported in ‰ against AIR) (bottom dashed line represents the upper end of the range expected for artificial fertiliser-derived nitrate, top dashed line represents the lower end of the range expected for organic waste-derived nitrate)*



Sites from the D_s category yielded nitrate with $\delta^{15}N\text{-}NO_3^-$ values that ranged between 3 ‰ and 7.4 ‰ within 100 m and 300 m radius, which overlapped with the upper end of the -4 ‰ to 4 ‰ range expected for artificial fertiliser-derived nitrate because of two sites (values 3.0 ‰ and 3.1 ‰). $\delta^{15}N\text{-}NO_3^-$ values from the D_s category overlapped with the 4 ‰ to 9 ‰ range expected for soil organic N-derived nitrate at the six remaining sites.

Sites from the P_s category showed a larger range of $\delta^{15}N\text{-}NO_3^-$ values within 100 m and 300 m radius that stretched from 3.4 ‰ to 10.9 ‰, which overlapped with the upper end of the range expected for artificial fertiliser-derived nitrate because of five sites (3.4 ‰ twice, 3.6 ‰ and 3.8 ‰ twice), with the whole 4 to 9 ‰ range expected for soil organic N-derived nitrate, and also with the lower end of the 10 ‰ to 22 ‰ range expected for animal/human waste-derived nitrate (because of one site).

When looking at the organic point N source subcategories (i.e. PS_s, PF_s and PFS_s), slight differences were observed. The PF_s category (farmyard source) covered almost the same range as the P_s main category within 100 m and 300 m radius (3.6 ‰ to 10.9 ‰), hence overlapped with the artificial fertiliser-derived nitrate range (at one site), with the animal/human waste-derived nitrate range (at one site), but mainly with the soil organic N-derived nitrate range. In the PS_s category (septic tank source), the range of $\delta^{15}N\text{-}NO_3^-$ values was slightly shorter within 100 m and 300 m radius (3.4 ‰ to 8.9 ‰), which meant that only the upper end of the range expected for artificial fertiliser-derived nitrate was overlapped (at four sites) along with the range expected for soil organic N-derived nitrate. In the PFS_s category (septic tank and farmyard sources), $\delta^{15}N\text{-}NO_3^-$ values were slightly above 4 ‰ and below 10 ‰, which meant that the only range overlapped was that of soil organic N-derived nitrate.

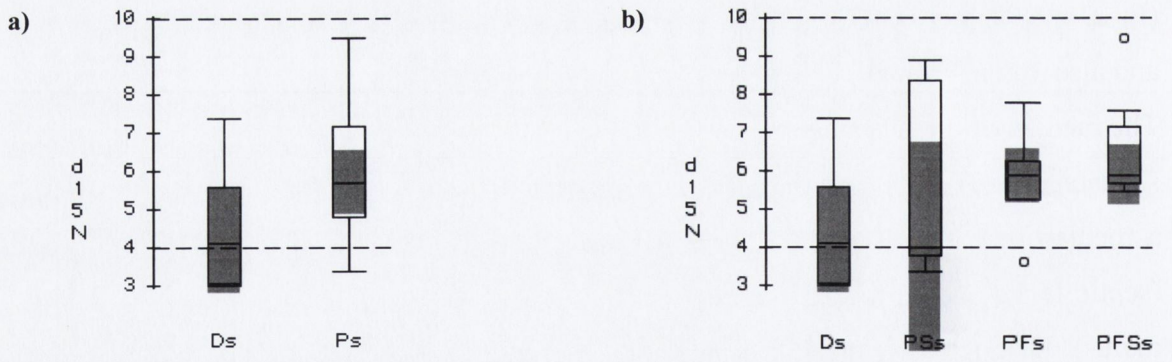
Comparing the medians of each category (rather than the means because of some skewed distribution in the PS_s category) highlighted differences in $\delta^{15}N\text{-}NO_3^-$ values between artificial diffuse and organic point N source groups. With a median of 4.2 ‰, the D_s category had nitrate ^{15}N-depleted relative to the P_s category (5.8 ‰ as median within 100 m and also 300 m radius). An ANOVA test, which was carried out on the $\delta^{15}N\text{-}NO_3^-$ log-transformed dependent variable and the N source group with two categories (i.e. D_s and P_s) as the independent variable, confirmed that this difference was significant at the 0.05 level ($F_{1, 44} = 6.99$, $p = 0.0113$ and 1.1:1 ratio of the largest to smallest variance within 100 m and also 300 m radius).

The median of the D_s category (i.e. 4.2 ‰) was also lower than in any organic point source subcategories (i.e. PS_s, PF_s and PFS_s). Indeed, the PF_s category (farmyard source) exhibited a median of 6.1 ‰ (within 100 m and also 300 m radius), whereas the PFS_s category (septic tanks and farmyard sources) had a median of 5.9 ‰ (within 100 m and 300 m radius). Distinctively, the PS_s category (septic tank source) showed lower median $\delta^{15}N\text{-}NO_3^-$ value (4.7 ‰ within 100 m radius, and 4.0 ‰ within 300 m radius) than the other organic point N sources subcategories. An ANOVA test, which was undertaken on the $\delta^{15}N\text{-}NO_3^-$ log-transformed dependent variable and the N source group with four categories (i.e. D_s, PS_s, PF_s and PFS_s) as the independent variable, revealed that there was a significant N source effect at the 0.05 level within 100 m radius ($F_{2, 42} = 0.0265$, $p = 0.0265$ and 6.5:1 ratio of the largest to smallest variance) and at the 0.01 level within 300 m radius ($F_{3, 42} = 4.411$, $p = 0.0087$ and 2.2:1 ratio of the largest to smallest variance). LSD *Post-Hoc* tests showed that within 100 m radius, there were significant differences in $\delta^{15}N\text{-}NO_3^-$

values between the D_s and PF_s categories (p = 0.0036), and also between the D_s and PFS_s categories (p = 0.049). Within 300 m radius, differences between these categories were also significant (p = 0.0104 for the former, p = 0.0039 for the latter), to which was added a significant difference between the PS_s and PFS_s categories (p = 0.0304).

Figure 7.7a focuses on the 75-100 % tillage category (within 300 m radius) and shows how site mean $\delta^{15}N\text{-}NO_3^-$ values were distributed within categories D_s (artificial diffuse N source) and P_s (organic point N source) at sites belonging to this category. In figure 7.7b, the distinction is made between organic point N source subcategories, i.e. PS_s (septic tank source), PF_s (farmyard source) and PFS_s (septic tank and farmyard sources). As already mentioned for nitrate concentration in section 6.4.3, it should be noted that the D_s category was not affected by restricting the study to the 75-100 % tillage group since all its eight sites were already within this % tillage category. It should be noted that boxplots were used rather than dotplots in order to display median and interquartile values, which facilitates the comparison with table 7.8 and gives a more visual description of the data.

Figure 7.7: Distribution of mean $\delta^{15}N\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley within the 75-100 % tillage category (i.e within 300 m radius) across the following N source categories: **a)** D_s (n = 8) and P_s (n = 21), and **b)** D_s (n = 8), PS_s (n = 7), PF_s (n = 5) and PFS_s (n = 9). *($\delta^{15}N$ is reported in ‰ against AIR) (bottom dashed line represents the upper end of the range expected for artificial fertiliser-derived nitrate, top dashed line represents the lower end of the range expected for organic waste-derived nitrate)*



When restricting the study to the 75-100 % tillage category, the results underwent very little change as the medians of each category within 300 m radius were within 0.3 ‰ of values displayed in table 7.8. An ANOVA test carried out on the $\delta^{15}N\text{-}NO_3^-$ log-transformed dependent variable showed that the difference between the D_s and P_s categories was still significant at the 0.05 level ($F_{1,27}$ = 5.14, p = 0.0316, and 1:1 ratio of the largest to smallest variance).

On the other hand, the ranges of $\delta^{15}N\text{-}NO_3^-$ values were slightly shortened in the PS_s (values between 3.4 ‰ and 9.5 ‰), in the PF_s (values between 3.6 ‰ and 7.8 ‰) and in the PFS_s categories (values between 5.5 ‰ and 9.5 ‰). An ANOVA test undertaken on the log-transformed variable revealed that the N source edged towards significance at the 0.05 level ($p = 0.0574$, and 4.6:1 ratio of the largest to smallest variance).

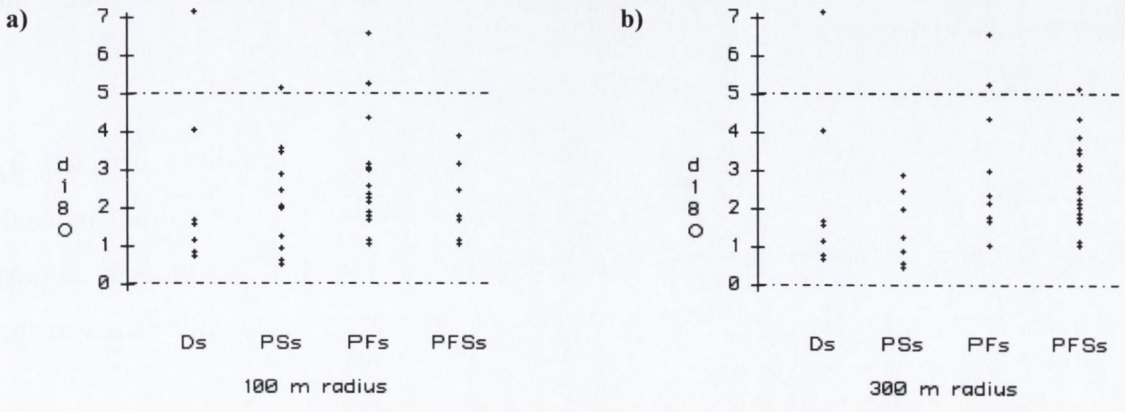
- $\delta^{18}O\text{-}NO_3^-$ in groundwater nitrate

Table 7.9 displays the central values and spread of the site mean $\delta^{18}O\text{-}NO_3^-$ values within each of the N source categories and organic point source subcategories that were reported in table 6.7 within 100 m radius and 300 m radius. The results are also displayed in figure 7.8 in the form of a dotplot to facilitate interpretation and to help view the distribution of mean values at each site.

Table 7.9: Central values and spread of mean $\delta^{18}O\text{-}NO_3^-$ values at the groundwater sampling sites from the Barrow Valley across the following N source categories within two radii (100 m and 300 m): D_s = artificial diffuse, P_s = organic point, PS_s = septic tank, PF_s = farmyard, PFS_s = undetermined point. *($\delta^{18}O$ is reported in ‰ against V-SMOW)*

Group	Radius	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
D_s	100 m	8	2.3	2.3	1.4	0.8	2.9	0.7	7.2
	300 m	8	2.3	2.3	1.4	0.8	2.9	0.7	7.2
P_s	100 m	38	2.5	1.4	2.3	1.7	3.2	0.5	6.6
	300 m	38	2.5	1.4	2.3	1.7	3.2	0.5	6.6
PS_s	100 m	14	2.3	1.3	2.1	1.3	2.9	0.5	5.2
	300 m	9	1.7	0.9	2.0	0.8	2.5	0.5	2.9
PF_s	100 m	17	2.9	1.5	2.4	1.9	3.5	1.1	6.6
	300 m	9	3.2	1.9	2.4	1.8	4.6	1.1	6.6
PFS_s	100 m	7	2.2	1.0	1.8	1.3	3.0	1.1	3.9
	300 m	20	2.6	1.1	2.4	1.9	3.4	1.1	5.2

Figure 7.8: Distribution of mean $\delta^{18}O\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley across the artificial diffuse (D_s) and the organic point N source subcategories (PS_s, PF_s, PFS_s) within **a)** 100 m and **b)** 300 m radius. *($\delta^{18}O$ is reported in ‰ against V-SMOW) (dashed lines represent the upper and the lower limits of the range reported by Durka et al. (1994) for nitrification)*



In the D_s category, groundwater sampling sites yielded nitrate with $\delta^{18}O\text{-}NO_3^-$ values that ranged between 0.7 ‰ and 7.2 ‰ within 100 m and 300 m radius. When compared with values expected for fertiliser nitrate (i.e. 18 ‰ to 22 ‰), it can be seen that there was no overlap, as the range displayed was at the very least 12 ‰ lower. On the other hand, there was a very large overlap with values expected for nitrate generated by nitrification (0 and 5 ‰). Similarly, category P_s and the organic point N source subcategories (i.e. PS_s, PF_s and PFS_s) had ranges of values stretching between 0.5 ‰ and 6.6 ‰, which matched the expected 0 to 5 ‰ range reported for Durka *et al.* (1994) for nitrification.

To make comparisons between the difference N sources categories, it was decided to examine medians rather than mean values because of some skewed distributions. The first observation was that all median $\delta^{18}O\text{-}NO_3^-$ values were within 1.0 ‰ of each other within 100 m and 300 m radius: the median of the D_s category was 1.4 ‰, whereas the medians of the P_s category and its three subcategories (i.e. PS_s, PF_s and PFS_s) ranged between 1.8 ‰ and 2.4 ‰. ANOVA tests, which were carried out on the $\delta^{18}O\text{-}NO_3^-$ log-transformed dependent variable and the N source groups with two categories (i.e. D_s and P_s) showed that there was no significant difference at the 0.05 level (2.1:1 ratio of the largest to smallest variance within 100 m and also 300 m radius). Equally, an ANOVA test on the N source group with four categories (i.e. D_s, PS_s, PF_s and PFS_s) showed that there was no significant N source effect at the 0.05 level within 100 m radius (3:1 ratio of the largest to smallest variance) and within 300 m radius (3.7:1 ratio of the largest to smallest variance).

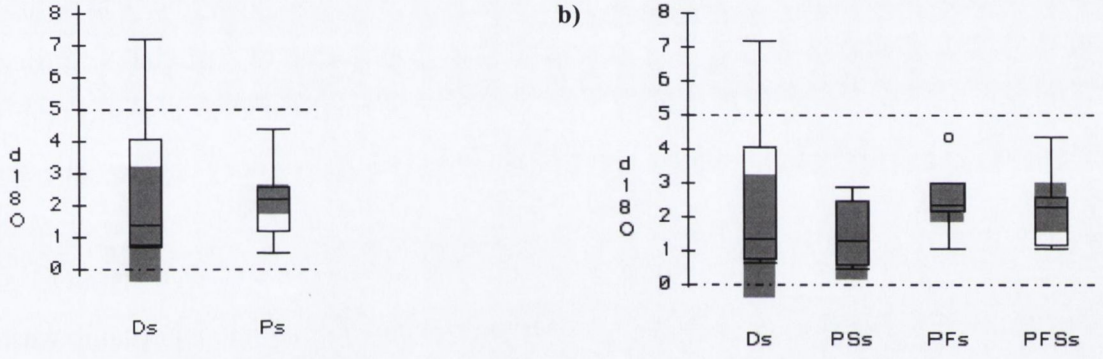
Figure 7.9a below shows how site mean $\delta^{18}O\text{-}NO_3^-$ values were distributed within 300 m radius within categories D_s (artificial diffuse N source) and P_s (organic point N source) at sites belonging to the 75-100 % tillage category. In figure 7.9b, the distinction is made between organic point N source subcategories, i.e. PS_s (septic tank source), PF_s (farmyard source) and PFS_s (septic tank and farmyard sources. Boxplots were used rather than dotplots in order to display median and interquartile values, which facilitates the comparison with table 7.9.

In comparison with values described by table 7.9, $\delta^{18}O\text{-}NO_3^-$ was little affected by restricting the study to the 75-100 % tillage category (within 300 m radius) in each category. Values in the P_s category were between 0.5 and 4.4 ‰ (median almost unchanged at 2.3 ‰), and the difference with the D_s category was not significant at the

0.05 level (1.9:1 ratio of the largest to smallest variance) when tested on the log-transformed variable with an ANOVA.

In the PS_s category, $\delta^{18}O\text{-}NO_3^-$ was still between 0.5 ‰ and 2.9 ‰, despite a slightly lower median value at 1.3 ‰. In the PF_s and PFS_s categories, the median remained unchanged around 2.3 ‰, but the range was slightly shortened between 1.1 ‰ and 4.4 ‰. In addition, an ANOVA test carried out on the log-transformed variable did not detect any significant N source effect at the 0.05 level (2.7:1 ratio of the largest to smallest variance).

Figure 7.9: Distribution of site mean $\delta^{18}O\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley within the 75-100 % tillage category (i.e. 300 m radius) across the following N source categories: **a)** D_s (n = 8) and P_s (n = 21), and **b)** D_s (n = 8), PS_s (n = 7), PF_s (n = 5) and PFS_s (n = 9). *($\delta^{18}O$ is reported in ‰ against V-SMOW) (dashed lines represent the upper and the lower limits of the range reported by Durka et al. (1994) for nitrification)*



7.3.5 Nitrate isotopic composition when site classifications based on hydrochemistry and N source groups agreed or disagreed

In section 6.4.4, the classification of high nitrate groundwater sampling sites (i.e. mean $[NO_3^-] \geq 25$ mg/l) based on hydrochemistry was compared with the site classification based on spatial characteristics taking into account the presence/absence (within 100 m and 300 m radius) of organic point N sources such as unsewered houses and/or farmyards. Several categories emerged from this comparison, the main distinction being made between sites where hydrochemistry agreed with spatial characteristics (suffix "cs" used in replacement of "c" or "s" in the category coding) and sites where there was disagreement:

- Category D_{cs}: sites with no organic point sources but only agricultural land (tillage and grassland) within 100 m or 300 m radius, where hydrochemistry showed evidence of artificial diffuse N source contamination.
- Category P_{cs}: sites with organic point N source (i.e. septic tank(s) and/or farmyard(s)) within a 100 m or 300 m radius, where hydrochemistry was linked to organic point N source contamination. This category was subdivided into PS_{cs}

(septic tank contamination), PF_{cs} (farmyard contamination) and PFS_{cs} (septic tank(s) and/or farmyard(s) contamination).

- Category D_c/P_s: sites where hydrochemistry was characteristic of artificial diffuse N source contamination, despite the presence of organic point N sources. This category was further-divided into D_c/PS_s, D_c/PF_s an D_c/PFS_s, depending on whether the type of organic point source present within 100 m or 300 m was septic tank(s), farmyard(s) or both. In addition, a category U_c/PS_s related to the only site with unclassifiable hydrochemistry despite the presence of septic tanks within 100 m and 300 m.

This section aims to analyse site mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values in groundwater nitrate where both hydrochemistry and spatial characteristics agreed, i.e. where the origin of the contamination was well identified as diffuse application of artificial N fertiliser (D_{cs} category) or organic point N source (P_{cs}), which was subdivided into septic tank (PS_{cs}), farmyard (PFcs) or undetermined point N source (PFS_{cs}). As done in previous sections, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were compared with predicted values that were reported in table 2.8 (section 2.6.6) for nitrate derived from artificial fertilisers (-4 ‰ $\leq \delta^{15}N\text{-}NO_3^- \leq$ 4 ‰, and 18 ‰ $\leq \delta^{18}O\text{-}NO_3^- \leq$ 22 ‰ in fertiliser nitrate) and animal/human organic wastes (10 ‰ $\leq \delta^{15}N\text{-}NO_3^- \leq$ 22 ‰ and 0 ‰ $\leq \delta^{18}O\text{-}NO_3^- \leq$ 5 ‰). Furthermore, comparisons were made between categories in order to see whether restricting data analysis to sites where both hydrochemistry and spatial characteristics agreed had improved the characterisation of artificial diffuse and organic point N source contamination. Attention was also given to sites where hydrochemistry and spatial characteristics disagreed, which were those where the hydrochemistry showed signs of artificial diffuse N source contamination while organic point N sources were present within a 100 m or 300 m radius (category D_c/P_s).

- <u>$\delta^{15}N\text{-}NO_3^-$ in groundwater nitrate</u>

Table 7.10 describes $\delta^{15}N\text{-}NO_3^-$ data at sites where hydrochemistry agreed with spatial characteristics within 100 m radius and 300 m radius. In addition to this table, the results are also presented in figure 7.10 as a dotplot, which highlights the differences in $\delta^{15}N\text{-}NO_3^-$ values between categories D_{cs}, P_{cs} and also D_c/P_s, and shows the distribution of mean values at each site. It should be noted that categories D_{cs}, P_{cs} and D_c/P_c being identical at 100 m and 300 m radius, figure 7.10 applies to both radii.

Table 7.10: Central values and spread of $\delta^{15}N\text{-}NO_3^-$ in groundwater nitrate at the Barrow Valley sites where chemistry and spatial characteristics within 100 m radius and 300 m radius agreed across the following categories: artificial diffuse contamination (D_{cs}) and organic point N source contamination (P_{cs}). *($\delta^{15}N$ is reported in ‰ against AIR)*

Group	Radius	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
D_{cs}	100 m	7	4.0	0.9	4.1	3.3	4.3	3.0	5.6
	300 m	7	4.0	0.9	4.1	3.3	4.3	3.0	5.6
P_{cs}	100 m	12	7.2	2.0	7.6	6.1	8.7	3.6	9.9
	300 m	12	7.2	2.0	7.6	6.1	8.7	3.6	9.9
PS_{cs}	100 m	5	7.4	2.1	8.3	6.6	8.6	3.8	8.9
	300 m	2	6.4	3.6	6.4	3.8	8.9	3.8	8.9
PF_{cs}	100 m	6	7.1	2.4	6.8	5.7	9.5	3.6	9.9
	300 m	1	3.6		3.6	3.6	3.6	3.6	3.6
PFS_{cs}	100 m	1	7.6		7.6	7.6	7.6	7.6	7.6
	300 m	9	7.8	1.4	7.6	7.0	8.8	5.7	9.9

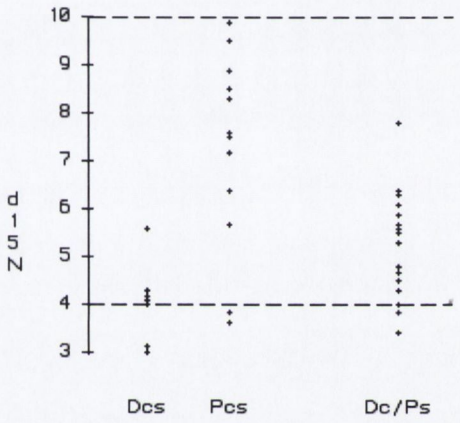


Figure 7.10: Distribution of mean $\delta^{15}N\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley, where i) hydrochemistry and spatial characteristics supported assumptions of artificial diffuse (D_{cs}, n = 7) or organic point source contamination (P_{cs}, n = 12), and where ii) hydrochemistry and spatial characteristics disagreed (D_c/P_c, n = 21), within 100m and 300 m radius. *($\delta^{15}N$ is reported in ‰ against AIR) (bottom dashed line represents the upper end of the range expected for artificial fertiliser-derived nitrate, top dashed line represents the lower end of the range expected for organic waste-derived nitrate)*

In comparison with D_c (table 7.4) or D_s categories (table 7.8), sites from the D_{cs} category showed a slightly more restricted range of $\delta^{15}N\text{-}NO_3^-$ values, between 3 ‰ to 5.6 ‰, which overlapped with the upper end of the range expected for artificial fertiliser-derived nitrate (-4 to 4 ‰) at two sites and the lower end of the range expected for organic soil N-derived nitrate (4 to 9 ‰) at the remaining five sites.

The range of $\delta^{15}N\text{-}NO_3^-$ values in the P_{cs} category, which went from 3.6 ‰ and 9.9 ‰, was identical to that of the P_c category (as the same twelve sites were involved) and slightly shorter than that of the P_s category. While values overlapped with the upper end of the range expected for artificial fertiliser-derived nitrate because of two sites, most of the observed $\delta^{15}N\text{-}NO_3^-$ values overlapped in fact with the whole range expected from soil organic N-derived nitrate, bordering on the lower end of the range expected for animal/human wastes derived nitrate.

The examination of organic point N source subcategories (i.e. PS_{cs}, PF_{cs} and PFS_{cs}) was made complicated because some categories contained no more than one or two sites. Therefore, it was decided to look only at categories PS_{cs} (five sites) and PF_{cs} (six sites)

within 100 m radius, and PFS_{cs} within 300 m radius (nine sites). These groups showed very little difference with the main P_{cs} category as the ranges were very similar, which implicated a large overlap with the range expected from soil organic N-derived nitrate.

Differences appeared between categories as the mean $\delta^{15}N\text{-}NO_3^-$ value of the D_{cs} category (4 ‰) was lower than that of the P_{cs} category (7.2 ‰) by more than 2 ‰. Interestingly, the mean of the D_c/P_s category was intermediate at 5.3 ‰. An ANOVA test, which was carried out on the $\delta^{15}N\text{-}NO_3^-$ log-transformed dependent variable and the N source group with three categories (i.e. D_{cs}, P_{cs} and D_c/P_s) as the independent variable, revealed that there was a significant N source effect at the 0.0001 level ($F_{2, 37} = 11.693$ and $p = 0.0001$ within 100 m and also 300 m radius; 2.5:1 ratio of the largest to smallest variance). LSD *Post-Hoc* tests showed that all the differences between the three categories were significant at the 0.05 level, i.e. not only the difference between D_{cs} and P_{cs} ($p \leq 0.0001$), but also the differences between D_{cs} and D_c/P_s ($p = 0.017$) or between P_{cs} and D_c/P_s ($p = 0.003$). If the two outliers in the P_{cs} category (values below 4 ‰) were excluded, the homogeneity of variance was greatly improved in conjunction with the significance of the N source effect on $\delta^{15}N\text{-}NO_3^-$ ($F_{2, 35} = 27.3, p \leq 0.0001$).
Finally, the means of the PS_{cs} (7.4 ‰) and PF_{cs} (7.1 ‰) categories within 100 m radius were very similar to that of the P_{cs} category, while higher than that of the D_{cs} category by slightly more than 2 ‰.

- $\delta^{18}O\text{-}NO_3^-$ in groundwater nitrate

Table 7.11 describes $\delta^{18}O\text{-}NO_3^-$ data at sites where hydrochemistry agreed with spatial characteristics within 100 m and 300 m radius. In addition, the $\delta^{18}O\text{-}NO_3^-$ values in categories D_{cs}, P_{cs} and also D_c/P_s are displayed in figure 7.11 as a dotplot, which helps visualise the distribution of mean values at each site. It should be noted that categories D_{cs}, P_{cs} and D_c/P_c being identical at 100 m and 300 m radius, figure 7.11 applies to both radii.

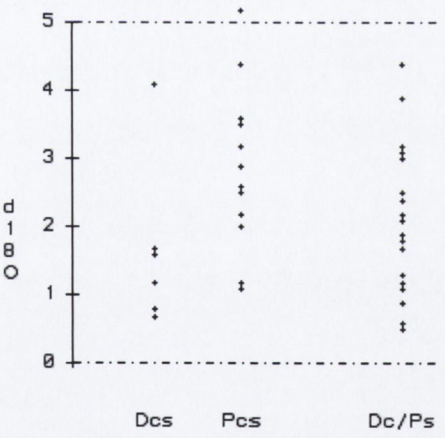
All but one site showed $\delta^{18}O\text{-}NO_3^-$ values that were within the 0 to 5 ‰ range for nitrification reported by Durka *et al.* (1994). Small differences emerged between categories, as the mean value of D_{cs} (1.6 ‰) was lower than the mean of P_{cs} (2.8 ‰) by 1.6 ‰, while the mean of the D_c/P_s category was intermediate at 2.1 ‰. Yet, an ANOVA test, which was carried out on the $\delta^{18}O\text{-}NO_3^-$ log-transformed dependent variable and the N source group with three categories (i.e. D_{cs}, P_{cs} and D_c/P_s) as the independent variable,

revealed that there was a significant N source effect affecting $\delta^{18}O\text{-}NO_3^-$ at the 0.05 level ($F_{2, 37} = 3.83$ and $p = 0.0306$ within 100 m and also 300 m radius; 1.7:1 ratio of the largest to smallest variance). LSD *Post-Hoc* tests showed that the only significant difference at the 0.05 level concerned the D_{cs} and P_{cs} categories ($p = 0.0104$).

Table 7.11: Central values and spread of $\delta^{18}O\text{-}NO_3^-$ in groundwater nitrate at the Barrow Valley sites where chemistry and spatial characteristics within 100 m radius and 300 m radius agreed across the following categories: artificial diffuse contamination (D_{cs}) and organic point N source contamination (P_{cs}). *($\delta^{18}O$ is reported in ‰ against V-SMOW)*

Group	Radius	n	Mean	SD	Median	25th %tile	75th %tile	Min	Max
D_{cs}	100 m	7	1.6	1.2	1.2	0.8	1.7	0.7	4.1
	300 m	7	1.6	1.2	1.2	0.8	1.7	0.7	4.1
P_{cs}	100 m	12	2.9	1.2	2.8	2.1	3.6	1.1	5.2
	300 m	12	2.9	1.2	2.8	2.1	3.6	1.1	5.2
PS_{cs}	100 m	5	3.4	1.2	3.5	2.7	4.0	2.0	5.2
	300 m	2	2.5	0.6	2.5	2.0	2.9	2.0	2.9
PF_{cs}	100 m	6	2.5	1.3	2.4	1.2	3.2	1.1	4.4
	300 m	1	1.1		1.1	1.1	1.1	1.1	1.1
PFS_{cs}	100 m	1	2.5		2.5	2.5	2.5	2.5	2.5
	300 m	9	3.2	1.2	3.2	2.4	3.8	1.2	5.2

Figure 7.11: Distribution of mean $\delta^{18}O\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley, where i) hydrochemistry and spatial characteristics supported assumptions of artificial diffuse (D_{cs}, n = 7) or organic point source contamination (P_{cs}, n = 12), and where ii) hydrochemistry and spatial characteristics disagreed (D_c/P_c, n = 21), within the 100m and 300 m radius. *($\delta^{18}O$ is reported in ‰ against V-SMOW) (dashed lines represent the upper and the lower limits of the range reported by Durka et al. (1994) for nitrification)*



7.3.6 Discussion of the comparison between groundwater nitrate isotopic composition and expected values from the literature

The first step in the isotopic data analysis undertaken in section 7.3 consisted of comparing site mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ with predicted values that were reported from the literature (see table 2.8 and section 2.6.2) for nitrate derived from artificial fertilisers (-4 ‰ $\leq \delta^{15}N\text{-}NO_3^- \leq$ 4 ‰, and 18 ‰ $\leq \delta^{18}O\text{-}NO_3^- \leq$ 22 ‰ in fertiliser nitrate) and from animal/human organic wastes (10 ‰ $\leq \delta^{15}N\text{-}NO_3^- \leq$ 22 ‰ and 0 ‰ $\leq \delta^{18}O\text{-}NO_3^- \leq$ 5 ‰). In the context of the Barrow Valley where tillage (hence artificial diffuse N sources) is ubiquitous, two types of sites were studied:

- Sites associated with artificial diffuse N source contamination based on i) hydrochemistry (category D_c), ii) the absence of organic point sources within 100 m and 300 m radius (category D_s), and iii) the convergence of hydrochemistry with the absence of organic point sources in 100 m and 300 m radius (category D_{cs}).
- Sites associated with organic point N source contamination based on i) hydrochemistry (category P_c), ii) the presence within 100 m and 300 m radius of organic point sources (category P_s) such as septic tanks (category PS_s) or farmyards (category PF_s) or both (category PFS_s), and iii) the convergence of hydrochemistry with the presence of organic point sources within 100 m and 300 m radius (category P_{cs} subcategorised into PS_{cs}, PF_{cs} and PFS_{cs}).

- Comparison of site mean $\delta^{15}N\text{-}NO_3^-$ with values from the literature

As seen in section 7.3, few sites associated with artificial diffuse contamination had mean $\delta^{15}N\text{-}NO_3^-$ within the -4 ‰ to 4 ‰ range expected for artificial fertiliser-derived nitrate. Most values were in fact within the 4 ‰ to 9 ‰ range predicted for soil organic N derived nitrate. In category D_c, i.e. where hydrochemistry showed signs of artificial diffuse contamination (based on assumptions made in section 6.3.2), $\delta^{15}N\text{-}NO_3^-$ ranged between 3.0 ‰ and 7.8 ‰, but only four sites out of twenty-eight had values lower than 4 ‰ (see section 7.3.2). In the category D_s, where no organic point source and only tillage/grassland was present within 100 m and 300 m radius (based on table 3.8), $\delta^{15}N\text{-}NO_3^-$ ranged between 3.0 ‰ and 7.4 ‰, with only two sites out of eight sites having $\delta^{15}N\text{-}NO_3^-$ values lower than 4 ‰ (see section 7.3.4). Likewise, sites associated with organic point sources showed mean $\delta^{15}N\text{-}NO_3^-$ within the 4 ‰ to 9 ‰ range predicted for soil organic N-derived nitrate, i.e. below the 10 ‰ to 22 ‰ range expected for animal/human waste-derived nitrate. In category P_c, i.e. where hydrochemistry showed signs of organic point source contamination (based on assumptions made in section 6.3.2), all twelve sites showed $\delta^{15}N\text{-}NO_3^-$ below 10 ‰ as values ranged between 3.6 ‰ and 9.9 ‰ (see section 7.3.2). In category P_s, i.e. where organic point sources like unsewered houses and/or farmyards were present within 100 m and 300 m radius (based on table 3.8), only one site out of thirty-eight showed $\delta^{15}N\text{-}NO_3^-$ higher than 10 ‰, with values ranging between 3.4 ‰ and 10.9 ‰ (see section 7.3.4). This single P_s site with mean $\delta^{15}N\text{-}NO_3^-$ above 10 ‰ belonged to category PF_s (presence of a farmyard within 100 m and 300 m radius), and therefore, no site from the other organic point source subcategories (i.e. PS_s and PFS_s within 100 m and 300 m radius) showed values above 10 ‰. When examining P_s sites within the 75-100 %

tillage category only (within 300 m radius), the range of site mean $\delta^{15}N\text{-}NO_3^-$ values was slightly shortened with all values below 10 ‰.

A direct consequence of the above results was that, where the origin of the contamination was considered beyond reasonable doubts as either artificial diffuse or organic point because hydrochemistry agreed with spatial characteristics, most site mean $\delta^{15}N\text{-}NO_3^-$ values lay also within the 4 ‰ to 9 ‰ range expected for soil organic matter. In the category D_{cs} (artificial diffuse contamination), which derives from categories D_c and D_s, values ranged from 3.0 ‰ to 5.6 ‰ and only two sites out of seven showed $\delta^{15}N\text{-}NO_3^-$ below 4 ‰ (see section 7.3.5). In the category P_{cs} (i.e. organic point source contamination from septic tanks and/or farmyards), which derives from categories P_c and P_s, all twelve sites showed $\delta^{15}N\text{-}NO_3^-$ below 10 ‰ as values ranged between 3.6 ‰ and 9.9 ‰ (see section 7.3.5). These results showed striking similarities with the isotopic data presented in section 5.3.1 for the unsaturated zone investigation in Moorepark RC, where it was seen that soil-water nitrate collected from the artificial fertiliser treatment plots overlapped with the upper end of the -4 ‰ to 4 ‰ range expected for artificial fertiliser while soil-water nitrate from the slurry treatment plots bordered on the lower end of the 10 ‰ to 22 ‰ range expected for animal waste-derived nitrate. As already suggested in section 5.3.5, these findings are consistent with soil organic N-derived nitrate ($4 ‰ \leq \delta^{15}N\text{-}NO_3^- \leq 9 ‰$) contributing significantly to the nitrate leaching process, as this would cause an increase of $\delta^{15}N\text{-}NO_3^-$ values where artificial fertiliser is the dominant N source, and a decrease of $\delta^{15}N\text{-}NO_3^-$ where organic point sources like septic tanks and farmyards provide most of the N input to soils. This large influence of soil organic matter in the Barrow Valley study areas may be a consequence of crop-residue incorporation during ploughing, which also stimulates mineralisation and nitrification. This is supported by the fact that, overall, six out of the seven sites with mean $\delta^{15}N\text{-}NO_3^-$ lower than 4 ‰ referred to in section 7.3.1 were surrounded by 75 to 100 % tillage (see section 7.3.3).

It should be noted that despite the possible influence of soil organic N-derived nitrate, higher $\delta^{15}N\text{-}NO_3^-$ values may have been expected from sites associated with organic point sources. Conditions around farmyards for instance, where soils are permanently soaked with animal organic wastes, favour a large ^{15}N-enrichment of the N substrate caused mainly by ammonia volatilisation. Nevertheless, rainy conditions may curtail this process (see section 2.4.4), resulting in $\delta^{15}N\text{-}NO_3^-$ values lower than expected.

To conclude, the use of $\delta^{15}N\text{-}NO_3^-$ as a tool to discriminate between artificial diffuse and organic point source contamination in the Barrow Valley study areas appears to be limited in regard of the isotopic composition of artificial fertilisers and animal/human wastes.

- Comparison of site mean $\delta^{18}O\text{-}NO_3^-$ with values from the literature

The results presented in section 7.3 showed that, regardless of the type of classification (hydrochemistry or spatial characteristics), sites associated with artificial diffuse contamination displayed consistently low mean $\delta^{18}O\text{-}NO_3^-$ that widely overlapped with the 0 ‰ to 5 ‰ range reported in the literature for nitrification. These values were far below the 18 ‰ to 22 ‰ expected for fertiliser nitrate. Values ranged between 0.5 ‰ and 4.4 ‰ in category D_c, and between 0.7 ‰ and 7.2 ‰ in the category D_s within 100 m and 300 m radius. A similar range of mean $\delta^{18}O\text{-}NO_3^-$ values was observed at sites associated with organic point source contamination, with values between 1.1 ‰ and 5.2 ‰ in category P_c, and between 0.5 ‰ and 6.6 ‰ in category P_s within 100 m and 300 m radius. Consequently for category D_{cs}, where the origin of the contamination was identified by both classification methods as artificial diffuse, site mean $\delta^{18}O\text{-}NO_3^-$ ranged between 0.7 ‰ and 4.1 ‰, matching very closely the 1.1 ‰ to 5.2 ‰ range of category P_{cs}, where the origin of the contamination was identified as organic point sources (septic and/or farmyards).

As previously discussed in section 5.3.4, the use of $\delta^{18}O\text{-}NO_3^-$ to identify nitrate derived from artificial fertiliser is inherently limited by the fact that artificial N fertilisers contain a large fraction of nitrogen that is in a non-nitrate form (see table 2.5) and that will undergo nitrification once in the soil. For this reason, the 18 ‰ to 22 ‰ range expected for artificial fertilisers seems high, and one might expect, at most, values: around 15 ‰ for a fertiliser like CAN (75 % N in nitrate form), and around 10 ‰ for a fertiliser like ammonium nitrate (50 % N in nitrate form).

In fact, values in categories D_{cs} and P_{cs} were far lower than the range predicted for ammonium nitrate. Again, similarities with the results displayed in section 5.3.1 for soil-water nitrate are striking. As suggested earlier in section 5.3.5, the reason for this levelling of $\delta^{18}O\text{-}NO_3^-$ may be the occurrence of Mineralisation-Immobilisation Turnover processes (MIT), which involve the immobilisation of nitrate by bacteria and its subsequent mineralisation/nitrification (section 2.4.1). From the isotopic point of view, it means that any nitrate undergoing the processes would eventually display $\delta^{18}O\text{-}NO_3^-$ characteristic of

nitrification (see section 2.6.3), which was quoted by Mengis *et al.* (2001) as the main obstacle to the use of $\delta^{18}O\text{-}NO_3^-$ as a tool to identify artificial fertiliser nitrate in groundwater (see section 2.6.4).

To conclude, $\delta^{18}O\text{-}NO_3^-$ does not help in any way to discriminate between artificial diffuse and organic point source contamination.

7.3.7 Discussion of the effects of N source (based on hydrochemistry and/or spatial characteristics) and % tillage on groundwater nitrate isotopic composition

In sections 7.3.2 to 7.3.5, the isotopic composition of groundwater nitrate was examined in two ways. First, site mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were compared with predicted values reported from the literature for artificial fertiliser and animal/human waste-derived nitrate. These results were discussed in section 7.3.6. Thereafter, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were compared between different categories for each site classification, which amounted to studying the following effects:

- N source effects based on i) hydrochemistry (section 7.3.2), ii) spatial characteristics (section 7.3.4), and iii) the convergence of hydrochemistry with spatial characteristics (section 7.3.5).
- % tillage effect (section 7.3.3).

After establishing the limited worth of isotopic analyses in isolation for the identification of nitrate sources in groundwater (see section 7.3.6), the second step in the testing of the isotopic technique consisted of investigating its use in conjunction with other tools, as a follow up to chapter 6, where site classifications based on hydrochemistry and spatial characteristics were examined. In section 6.3.3, sites were classified according to their groundwater chemistry, in regard of the exceedance (or non-exceedance) of contamination thresholds. But uncertainty remained as to the reliability of this classification for identifying groundwater nitrate sources, which was further discussed in section 6.3.5. In section 6.4.3, where groundwater chemistry was analysed in relation to site classification based on spatial characteristics (presence/absence of organic point sources in tillage and grassland areas), the significantly higher sodium levels at sites located nearby organic point sources gave credence to the assumptions that the mere presence of organic point sources within 100 m and 300 m radius had an impact on groundwater chemistry. But, as

stressed in section 6.4.6, the extent of the organic point sources contribution to nitrate contamination, which depends on many factors, remained unclear. In section 6.4.4, the comparison of both classifications highlighted some contradictions as hydrochemistry and spatial characteristics agreed for a small number of sites, which was discussed in section 6.4.7. The analysis of N source effects across section 7.3 aimed to answer these contradictions and find evidence that would support the validity of one site classification over the other.

The interest for analysing the % tillage effect on site mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values was motivated by the fact that a significant % tillage effect on nitrate concentrations was detected in section 6.4.2. Higher nitrate levels were associated with higher % tillage.

- N source effect on site mean $\delta^{15}N\text{-}NO_3^-$: comparison between artificial diffuse and organic point source categories

Despite all categories widely overlapping with the 4 ‰ to 9 ‰ range expected for soil organic N-derived nitrate (see section 7.3.6), the results in section 7.3 showed that mean (log-transformed) $\delta^{15}N\text{-}NO_3^-$ values were systematically lower at sites associated with artificial diffuse contamination than at sites associated with organic point sources. However, important differences were observed between site classifications. In section 7.3.4, the difference between categories D_s and P_s within 100 m and 300 m radius (based on spatial characteristics) was significant at the 0.05 level ($p = 0.0113$), and this difference remained significant when restricting the study to sites that belong to the 75-100 % tillage category ($p = 0.0316$). In comparison, the difference between categories D_c and P_c (based on hydrochemistry) in section 7.3.2 was significant at the 0.0005 level ($p = 0.0004$). In section 7.3.5, where both site classifications were compared, the LSD *Post-Hoc* tests revealed that the difference between categories D_{cs} and P_{cs} within 100 m and 300 m radius (based on the convergence of hydrochemistry with spatial characteristics) strengthened to be significant at the 0.0001 level ($p \leq 0.0001$).

In section 7.3.4, the N source effect based on spatial characteristics was still significant when comparing the D_s category and the three organic point source subcategories (i.e. D_s, PS_s, PF_s and PFS_s) within 100 m (p 0.0265) and 300 m radius ($p = 0.0087$). But the LSD *Post-Hoc* tests revealed that the significance of the N source effect was mainly accounted for by the lower site mean (log-transformed) $\delta^{15}N\text{-}NO_3^-$ values in the D_s category. In fact, only once was a significant difference detected at the 0.05 level between two organic point

source categories (PS_s and PFS_s within 300 m radius). In addition, little difference was observed when comparing categories PS_{cs} and PF_{cs} within 100 m radius (see section 7.3.5) as they showed similar means and ranges.

The literature has reported that $\delta^{15}N\text{-}NO_3^-$ measured underneath fields subjected to applications of artificial fertiliser is often lower by a few permils than in areas subjected to animal waste applications or septic tank contamination (see section 2.6.4). Similar results were observed during soil-water nitrate investigation in section 5.3.2, where experimental plots treated with artificial fertiliser yielded soil-water nitrate that was ^{15}N-depleted in comparison with the unfertilised controls or with plots subjected to applications of organic wastes (dairy wastewater or slurry).

Regardless of the site classification, the same pattern was observed during groundwater nitrate investigation, as mean $\delta^{15}N\text{-}NO_3^-$ was significantly lower (at least at the 0.05 level) at sites associated with artificial diffuse contamination in comparison with sites associated with organic point source contamination. At first sight, this consistency with the literature gives some credence to both site classification based on hydrochemistry and spatial characteristics. However, the significance of the difference between sites associated with artificial diffuse and organic point source contamination was much higher with the former classification than with the latter. This can be seen when comparing figure 7.2 with figures 7.6a and 7.6b. In figure 7.2, the overlap between artificial diffuse source subcategories (i.e. D_{c1} to D_{c4}) and organic point source subcategories (i.e. P_{c1} and P_{c2}) involved only five sites out of forty. In comparison, the overlap in figures 7.6a and 7.6b between category D_s and the organic point source subcategories (i.e. PS_s, PF_s and PFS_s) was extensive within 100 m and 300 m radius. Incidentally, this may support the use of hydrochemistry and contamination thresholds (as defined in section 6.3.1) rather than spatial characteristics to discriminate between artificial diffuse and organic point sources of nitrate.

An additional element came to support the validity of site classification based on hydrochemistry. As may have been expected, the greatest difference in mean $\delta^{15}N\text{-}NO_3^-$ values was observed between categories D_{cs} and P_{cs}, i.e. where the origin of the contamination was considered beyond reasonable doubt as artificial diffuse or organic point source. In category D_c/P_s, where the hydrochemistry reflected artificial diffuse contamination and nearby organic point sources, site mean $\delta^{15}N\text{-}NO_3^-$ values were found to be intermediate between D_{cs} and P_{cs} values, as better seen in figure 7.10. However, the LSD *Post-Hoc* tests in section 7.3.5 showed that the difference of log-transformed values

was more significant with category P_{cs} (p = 0.003) than with category D_{cs} (p = 0.017). In other words, when hydrochemistry and spatial characteristics disagreed, $\delta^{15}N\text{-}NO_3^-$ were more in disagreement with site classification based on spatial characteristics than on hydrochemistry. Nevertheless, the fact that values in category D_c/P_s were significantly higher than values in category D_{cs} corresponded with the assumption made in section 6.4.6 that organic point sources had some influence on nitrate contamination.

In sections 7.3.4 and 7.3.5, the examination of mean $\delta^{15}N\text{-}NO_3^-$ values at sites associated with septic tank and farmyard contamination did not reveal any significant difference, which was consistent with the literature (see section 2.6.2). Although a study by Fogg *et al.* (1998) reported some significant difference in $\delta^{15}N\text{-}NO_3^-$ values between both types of N sources, this is rarely observed in most studies addressing this topic.

- N source effect on site mean $\delta^{18}O\text{-}NO_3^-$: comparison between artificial diffuse and organic point source categories

In section 7.3.4, no significant difference in site mean $\delta^{18}O\text{-}NO_3^-$ was observed at the 0.05 level between categories D_s and P_s within 100 m and 300 m radius, and the difference remained insignificant when restricting the study to sites that belong to the 75-100 % tillage category ($p > 0.05$). Distinctively, site mean $\delta^{18}O\text{-}NO_3^-$ values in category P_c were significantly higher at the 0.05 level (p = 0.0234) than values in categories D_c (section 7.3.2). In section 7.3.5, where hydrochemistry and spatial characteristics were compared, the LSD *Post-Hoc* tests showed that site mean $\delta^{18}O\text{-}NO_3^-$ in category P_{cs} was significantly higher at the 0.05 level (p = 0.0104) than values in category D_{cs}.

Despite the significance of some differences, categories associated with artificial diffuse and organic point source contamination largely overlapped with the 0 ‰ to 5 ‰ range predicted by Durka *et al.* (1994) for nitrification, regardless of the classification (see figures 7.3, 7.8 and 7.11). This levelling of $\delta^{18}O\text{-}NO_3^-$, which was also observed in section 5.3.2 during soil-water investigations, supports the idea that most fertiliser nitrate probably undergoes the MIT processes, which were described in sections 2.4.1 and 2.6.3.
The fact that mean $\delta^{18}O\text{-}NO_3^-$ were significantly higher at sites associated with organic point source contamination may be attributed to the occurrence of some very partial denitrification, which would cause residual nitrate to be ^{18}O-enriched. As animal/human wastes contain large quantities of carbon, denitrification may be slightly favoured where

organic point sources are at the origin of nitrate contamination. This was suggested by soil-water investigations in section 5.3.3, where evidence of denitrification (using correlation between $\delta^{18}O\text{-}NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$) was observed in plots subjected to dairy wastewater applications but not in plots subjected to applications of artificial fertiliser (see discussion in section 5.3.7).

- % tillage effect on site mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$

In section 7.3.3, no significant % tillage effect on site mean (log-transformed) $\delta^{15}N\text{-}NO_3^-$ was detected, as all categories overlapped widely with one another. However, mean (log-transformed) $\delta^{18}O\text{-}NO_3^-$ were significantly lower ($p = 0.0404$) at sites belonging to the 50-100 % tillage category in comparison with sites from the 0-50 % tillage category.

The absence of % tillage effect on $\delta^{15}N\text{-}NO_3^-$ came as a relative surprise considering that in section 6.4.2, nitrate concentrations in the 50-100 % tillage category were significantly higher at the 0.005 level than the 0-50 % tillage category. Therefore, one may have expected mean $\delta^{15}N\text{-}NO_3^-$ to be lower where the nitrate concentrations were the highest, i.e. in the 50-100 % tillage category where the artificial diffuse N source was more important. However, there is a possibility that the soil organic N-derived nitrate, released after the ploughing-in of organic residues, masks this effect.
The significance of the % tillage effect on $\delta^{18}O\text{-}NO_3^-$ may be attributed to the occurrence of partial denitrification, which could be limited where soils are well aerated (see section 2.4.3), i.e. at sites with high % tillage.

7.5 Case studies: use of $\delta^{15}N$, $\delta^{18}O$, and correlations to identify NO_3^- sources and denitrification in the study areas

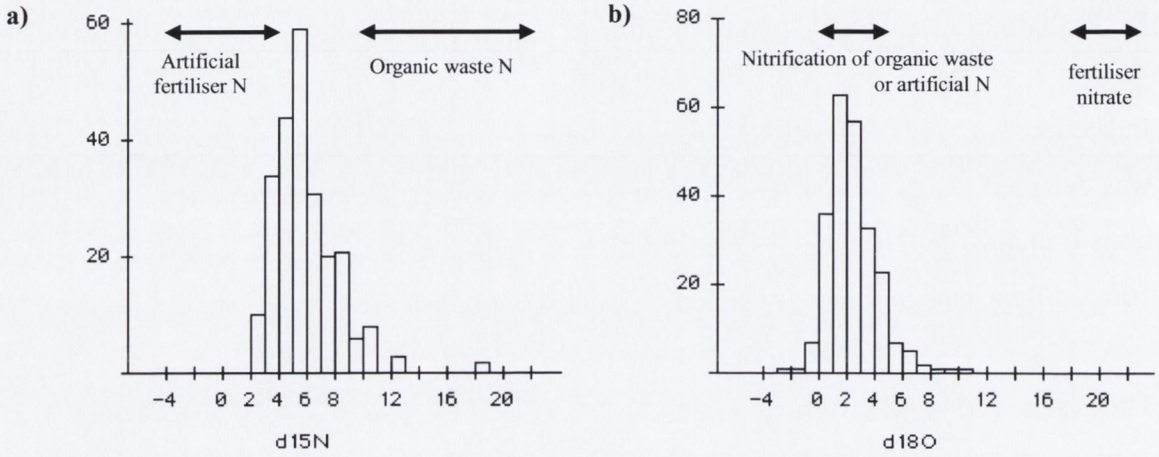
7.5.1 The Barrow Valley

- Overview

Figures 7.12a and 7.12b describe in more detail than section 7.2.1 the respective distributions of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values for groundwater nitrate from the Barrow Valley study areas. In addition, $\delta^{15}N$ values are compared with the ranges of values reported in the literature for artificial fertiliser and organic waste-derived nitrate, whereas

$\delta^{18}O$ values are compared with the ranges reported for nitrification and fertiliser nitrate (see table 2.8 in section 2.6.6).

Figure 7.12: Distribution of **a)** $\delta^{15}N\text{-}NO_3^-$ (n = 238) and **b)** $\delta^{18}O\text{-}NO_3^-$ (n = 238) in groundwater nitrate analysed for forty-six sites in the Barrow Valley, and comparisons with the ranges of values reported in the literature for nitrate derived from artificial fertiliser and organic wastes. *(on the x-axis are reported $\delta^{15}N$ and $\delta^{18}O$ in ‰ against AIR and V-SMOW respectively; the frequency is reported on the y-axis)*



As already noted in section 7.2.1, most groundwater nitrate samples from the Barrow showed $\delta^{15}N\text{-}NO_3^-$ values lying between the -4 ‰ to 4 ‰ range expected for artificial fertiliser and the 10 ‰ to 22 ‰ range predicted for animal/human waste-derived nitrate. Nonetheless, figure 7.12a shows a larger overlap with the artificial than the organic waste range.

On the other hand, all groundwater nitrate sample showed $\delta^{18}O\text{-}NO_3^-$ values within the range expected for nitrification, far below the 18 ‰ to 22 ‰ range expected for fertiliser nitrate.

- Correlations between $\delta^{15}N\text{-}NO_3^-$, $\delta^{18}O\text{-}NO_3^-$ and physico-chemical parameters

Table 7.12 displays Spearman's rank correlation coefficients between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ variables for each sampling event carried out in the Barrow Valley study areas between February 2002 and June 2004.

The results show that $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were significantly correlated at the 0.001 level in all but the first sampling event. Apart from September 2002, all regression slopes for the other sampling events were between 0.42 and 0.57.

Table 7.12: Spearman's rank r_s values between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ and regression slopes for each sampling event carried out in the Barrow Valley ($p \leq 0.05$ in bold, $p \leq 0.01$ in bold and single-underlined, $p \leq 0.001$ and double-underlined).

	$\delta^{18}O\text{-}NO_3^-$	Slope
Sep-02	0.319	0.28
Feb-03	**0.646**	0.49
Jun-03	**0.606**	0.48
Sep-03	**0.688**	0.57
Feb-04	**0.723**	0.56
Jun-04	**0.582**	0.42

Tables 7.13 and 7.14 display Spearman's rank correlation coefficients between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ respectively, and other chemical variables for each sampling event carried out in the Barrow Valley.

Table 7.13: Spearman's rank r_s values between $\delta^{15}N\text{-}NO_3^-$ and other chemical variables for each sampling event carried out in the Barrow Valley ($p \leq 0.05$ in bold, $p \leq 0.01$ in bold and single-underlined, $p \leq 0.001$ and double-underlined).

	$[NO_3^-]$	$[Cl^-]$	$[K^+]$	$[Na^+]$	$[SO_4^{2-}]$	$[Mg^{2+}]$	$[Ca^{2+}]$	Alkalinity	pH	Conductivity
Sep-02	-0.013	0.082	**0.519**	0.193	0.325	-0.054	**0.443**	**0.65**	**-0.46**	**0.571**
Feb-03	-0.053	**0.381**	0.276	**0.57**	**0.425**	0.13	**0.334**	**0.524**	**-0.468**	**0.59**
Jun-03	-0.14	**0.381**	0.275	**0.605**	**0.477**	0.162	0.276	**0.454**	**-0.421**	**0.558**
Sep-03	-0.099	**0.363**	**0.443**	**0.548**	**0.416**	0.072	**0.345**	**0.433**	**-0.446**	**0.494**
Feb-04	-0.237	**0.339**	0.28	**0.397**	**0.388**	0.101	**0.368**	**0.616**	**-0.604**	**0.571**
Jun-04	-0.231	**0.512**	**0.377**	**0.567**	**0.411**	0.12	**0.339**	0.267	**-0.454**	**0.501**

Table 7.14: Spearman's rank r_s values between $\delta^{18}O\text{-}NO_3^-$ and other chemical variables for each sampling event carried out in the Barrow Valley ($p \leq 0.05$ in bold, $p \leq 0.01$ in bold and single-underlined, $p \leq 0.001$ and double-underlined).

	$[NO_3^-]$	$[Cl^-]$	$[K^+]$	$[Na^+]$	$[SO_4^{2-}]$	$[Mg^{2+}]$	$[Ca^{2+}]$	Alkalinity	pH	Conductivity
Sep-02	-0.378	-0.08	0.046	-0.012	-0.153	**0.41**	0.245	**0.521**	-0.391	0.187
Feb-03	**-0.371**	0.007	0.098	0.26	**0.348**	0.159	0.13	**0.489**	**-0.32**	0.219
Jun-03	-0.213	0.242	0.26	0.275	**0.332**	-0.041	0.242	**0.313**	**-0.437**	**0.382**
Sep-03	**-0.366**	0.013	0.061	0.172	0.038	0.051	0.126	**0.48**	**-0.568**	0.247
Feb-04	**-0.358**	0.16	-0.059	0.166	0.265	0.164	0.151	**0.434**	**-0.336**	0.293
Jun-04	-0.127	**0.356**	0.012	0.202	**0.374**	0.255	0.19	**0.577**	-0.184	0.291

The results show that $\delta^{15}N\text{-}NO_3^-$ was significantly (positively) correlated at least at the 0.05 level with i) chloride concentration on five occasions, ii) potassium on three occasions, and iii) sodium on five occasions. On the other hand, $\delta^{15}N\text{-}NO_3^-$ was negatively correlated with pH at least at the 0.05 level on every occasion.

Fewer correlations were observed between $\delta^{18}O\text{-}NO_3^-$ and other physico-chemical parameters. Noticeably, it was negatively correlated with pH at least at the 0.05 level on four occasions.

- Assumptions about the origin of the nitrate contamination and the occurrence of denitrification in the Barrow Valley

From figure 7.12a, it appears evident that the use of $\delta^{15}N\text{-}NO_3^-$ cannot help determine for sure whether groundwater contamination in the Barrow Valley study areas was mainly caused by diffuse applications of artificial fertiliser or by organic point sources (i.e. farmyards and unsewered houses). At first sight, a simplistic reason for most $\delta^{15}N\text{-}NO_3^-$ values to lie within the range expected for soil organic N-derived nitrate may be that most leached nitrate originates from the nitrification of soil organic N. This would be consistent with the ubiquitous presence of tillage where large quantities of crop residues are ploughed in after harvest. Furthermore, this assumption could also explain why higher % tillage was associated with significantly higher nitrate concentrations (section 6.4.2), but not with significantly lower $\delta^{15}N\text{-}NO_3^-$ values (section 7.3.3).

Seemingly, $\delta^{15}N\text{-}NO_3^-$ values leaned more towards the range expected for artificial fertiliser-derived nitrate than towards the range predicted for animal/human waste-derived nitrate (figure 7.12a). This may be an indication that the leaching of artificial fertiliser-derived nitrate had some impact on groundwater contamination. It may also be that crop residues undergoing nitrification were slightly ^{15}N-depleted due to the incorporation of fertiliser N with lower $\delta^{15}N\text{-}TN$, which would result in a slight lowering of $\delta^{15}N\text{-}NO_3^-$ values (Choi *et al.* (2002) - in section 6.4.2).
As additional supporting evidence for artificial diffuse contamination, most sites had the hydrochemistry characteristic of artificial diffuse contamination, and these sites showed $\delta^{15}N\text{-}NO_3^-$ significantly lower than sites with hydrochemistry associated with organic point source contamination. However, this does not confirm whether nitrate was derived from artificial fertiliser or from ^{15}N-depleted crop residues.

Figure 7.12b shows clearly that $\delta^{18}O\text{-}NO_3^-$ does not help answer the ambiguities, as most values lay within the range reported in the literature for nitrification. The main limitation to the usage of $\delta^{18}O\text{-}NO_3^-$ was attributed in section 5.3.5 to the occurrence of Mineralisation-Immobilisation Turnover (MIT) processes, involving the bacterial immobilisation of nitrate followed by remineralisation and resulting in a levelling of all $\delta^{18}O\text{-}NO_3^-$ values regardless of the type of N source. As suggested by Mengis *et al.* (2001), the extent of MIT processes is probably curtailed at low temperatures during winter, which would result in higher $\delta^{18}O\text{-}NO_3^-$ values where artificial fertiliser has been applied. Consequently, one may have

expected $\delta^{18}O\text{-}NO_3^-$ values to be higher during sampling events in February 2002 and 2003, if artificial fertiliser were the main source of contamination in the Barrow Valley. However, the narrow range of $\delta^{18}O\text{-}NO_3^-$ values observed in the sampling area may indicate that winter soil temperatures did not fall far enough to noticeably affect MIT (see air temperature in figure 3.5).

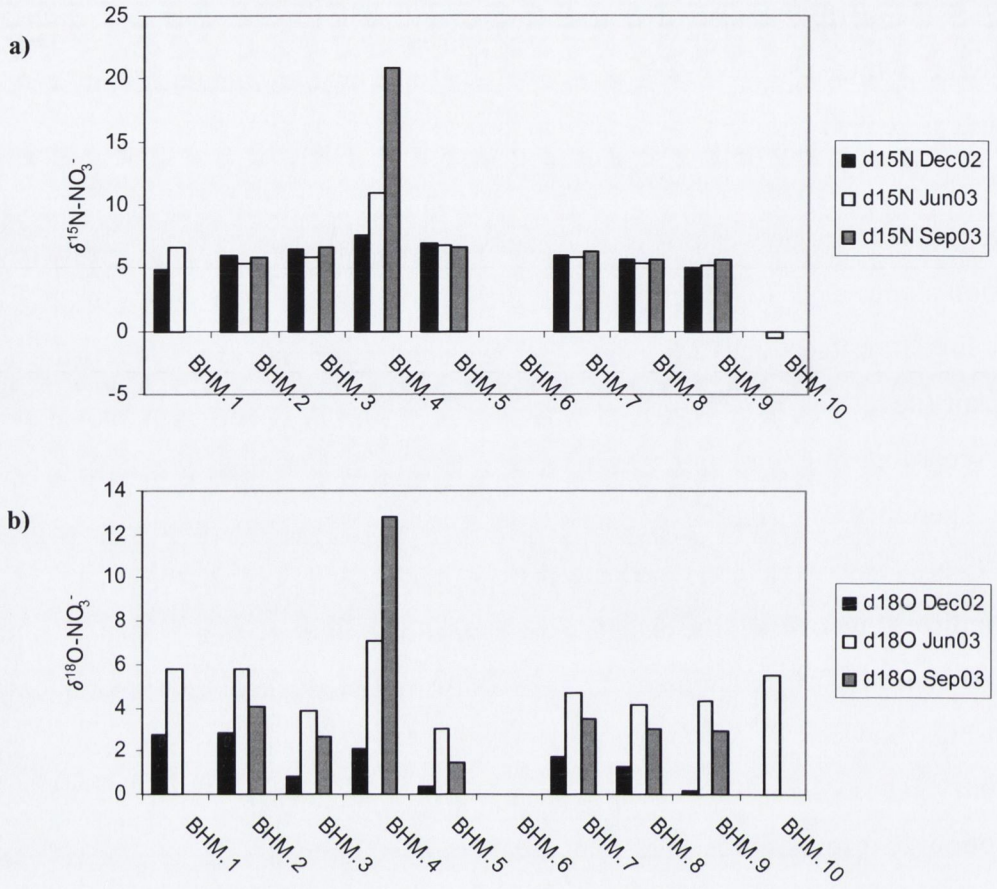
Positive correlations between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ (table 7.12), in conjunction with regression slopes close to 0.5, strongly suggest the occurrence of denitrification, according to the literature (sections 2.6.3 and 2.6.4). This assumption is consistent with the significant (negative) correlations between pH and $\delta^{15}N\text{-}NO_3^-$, and between pH and $\delta^{18}O\text{-}NO_3^-$. According to equation 2.5 (see section 2.4.3), one by-product of denitrification is HCO_3^-. Therefore, one could expect pH to decrease as the reaction goes on and $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ increase. However, the narrow ranges of low $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values indicate that overall, the extent of the denitrification process may be very limited.
The examination of correlations in table 7.13 also revealed some significant and positive relationships between $\delta^{15}N\text{-}NO_3^-$ and indicators of organic contamination (i.e. chloride, potassium and sodium). This supports the idea that, whatever the extent of their contribution to groundwater contamination, organic point sources probably cause the leaching of important quantities of nitrate. It should also be noted that none of the relationships characteristic of the artificial fertiliser treatments, i.e. nitrate concentration negatively correlated with $\delta^{15}N\text{-}NO_3^-$ and positively correlated with $\delta^{18}O\text{-}NO_3^-$ (see section 5.3.3), were observed in the groundwater study area. However, this does not disqualify artificial fertiliser as a major source of nitrogen in the Barrow Valley. In fact, such relationships may be expected in small scale experiments with a controlled single source of nitrogen, but the context is far more complex in large geographical areas where different types of sources are found.

7.5.2 Moorepark RC

- Overview

In Moorepark RC, the smaller number of samples allowed results to be analysed for each site on a sample basis. Figures 7.13a and 7.13b display $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values measured in groundwater nitrate collected from the ten boreholes located in Curtin's farm.

Figure 7.13: a) $\delta^{15}N\text{-}NO_3^-$ (n = 24) and **b)** $\delta^{18}O\text{-}NO_3^-$ values (n = 24) measured in groundwater nitrate at Moorepark RC on three different sampling occasions. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*



In figure 7.15a, all boreholes except for BHM.4 and BHM.10 yielded nitrate with very similar $\delta^{15}N\text{-}NO_3^-$ values confined between 5 ‰ and 7 ‰, i.e. within the range expected for soil organic N-derived nitrate. Distinctively from other sites, $\delta^{15}N\text{-}NO_3^-$ at BHM.4 increased between December 2002 and June 2003.

It can bee seen in figure 7.15b that $\delta^{18}O\text{-}NO_3^-$ values were influenced by seasons (except for BHM.4), with lower values in winter than during summer. Distinctively, $\delta^{18}O\text{-}NO_3^-$ at BHM.4 followed the same pattern than $\delta^{15}N\text{-}NO_3^-$, which values increasing between December 2002 and September 2003.

- Correlations between $\delta^{15}N\text{-}NO_3^-$, $\delta^{18}O\text{-}NO_3^-$ and physico-chemical parameters

Figure 7.14a and 7.14b display the plotting of nitrate concentration against $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ respectively, while figure 7.14c displays the plotting of $\delta^{15}N\text{-}NO_3^-$ against $\delta^{18}O\text{-}NO_3^-$.

Figure 7.14: Variation of **a)** NO_3^- concentration with $\delta^{15}N\text{-}NO_3^-$ (n = 24), **b)** nitrate concentration with $\delta^{18}O\text{-}NO_3^-$ (n =24), and **c)** $\delta^{15}N\text{-}NO_3^-$ with $\delta^{18}O\text{-}NO_3^-$ (n = 24) in groundwater at Moorepark RC (hollow rounds are for site BHM.4). (*$\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively, nitrate concentration in mg/l NO_3^-)*

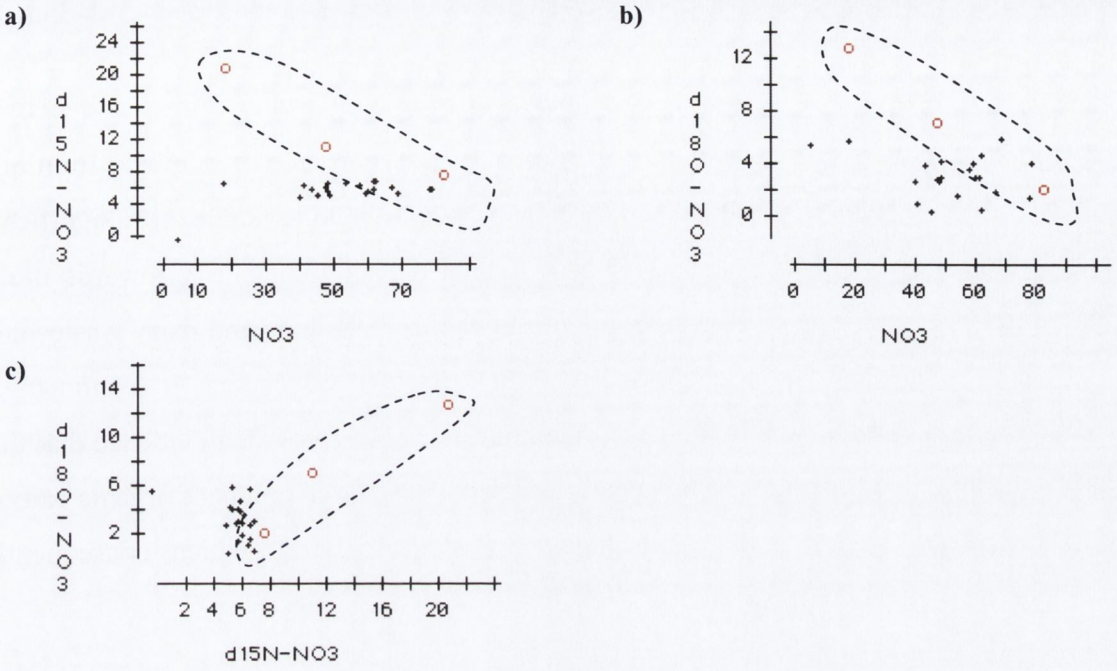


Figure 7.14a and 7.14b show that groundwater nitrate concentration was globally poorly correlated with $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$. Nevertheless, it can be seen that all boreholes did not behave the same. In the case of BHM.4, variables seemed to be correlated with one another, with lower nitrate concentrations associated with higher $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$

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Consequently, the plotting of $\delta^{15}N\text{-}NO_3$ against $\delta^{18}O\text{-}NO_3$ in figure 7.14c did not show any significant trend for any borehole except BHM.4, where an apparently linear relationship was observed.

- Assumptions about the origin of the nitrate contamination and the occurrence of denitrification at Moorepark RC

Figure 7.15a showed that most $\delta^{15}N\text{-}NO_3^-$ values lay within the range expected for soil organic N-derived nitrate, which suggests that soil organic matter plays an important role in nitrate leaching. This point was earlier discussed in relation to the unsaturated zone investigations (see section 5.3.5). The results seemed to disqualify slurry as a major source of nitrate, since its $\delta^{15}N\text{-}TN$ value was reported at 10.2 ‰ in table 5.4. On the other hand, the use of $\delta^{15}N\text{-}NO_3^-$ appeared very unlikely to help discriminate between contamination caused by artificial fertiliser and dairy wastewater as both materials exhibit similar $\delta^{15}N$-

TN values: δ^{15}N-TN in artificial fertilisers used by Teasgasc was measured between -2.4 and 2.0 ‰, while δ^{15}N-TN in dairy wastewater was measured at 3.8 ‰, i.e. less than 2 ‰ higher.

The relatively constant δ^{15}N-NO_3^- values (and also δ^{18}O-NO_3^- values to a lesser extent) observed in samples from most boreholes rules out the occurrence of denitrification at a farm scale. Nevertheless, the results from BHM.4 provided evidence of significant denitrification, with δ^{15}N-NO_3^- and δ^{18}O-NO_3^- increasing simultaneously towards much higher values. This was the closest borehole to the cattle shed/slurry and dairy wastewater tanks/silage storage, and the conventional chemical analyses discussed in section 6.5.2 including high potassium, sodium and chloride concentrations, provided evidence that this borehole was mainly contaminated by organic wastes. These large inputs of organic carbon may have created a favourable environment for denitrification, which consequently affected nitrate isotope composition locally.

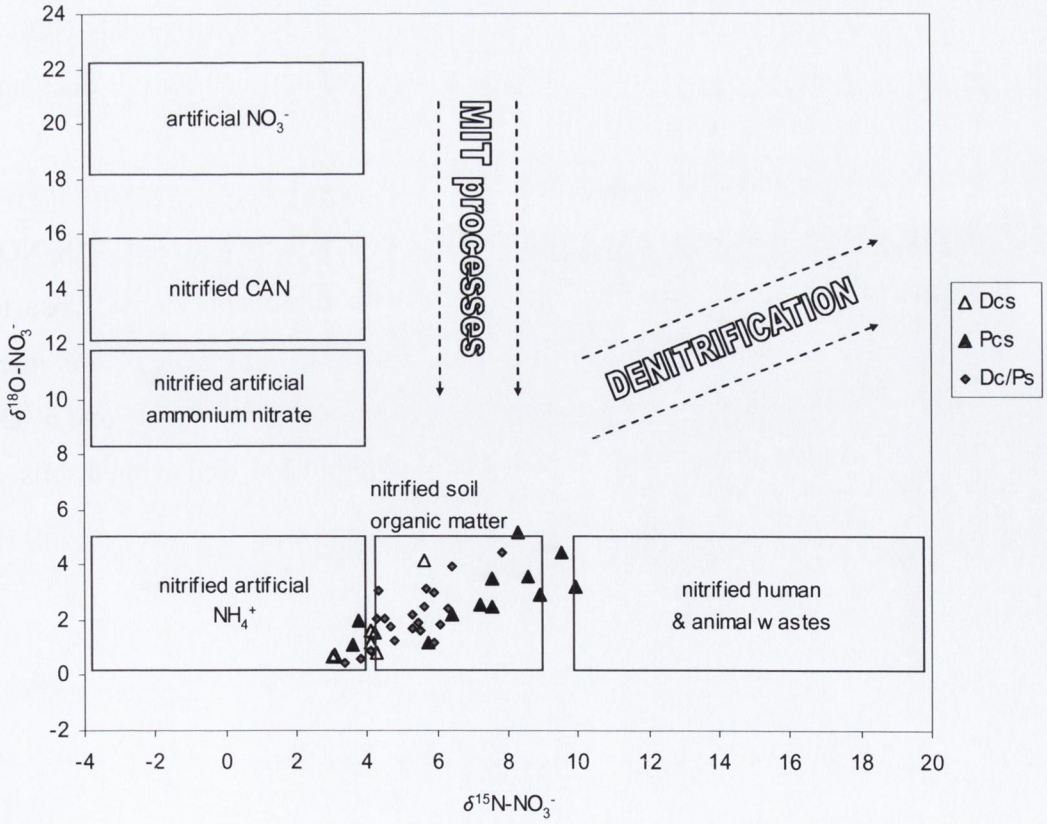
7.6 Conclusions

The analysis of soil-water nitrate isotopic composition in chapter 5 was greatly facilitated by the fact that, apart from soil organic matter, the main source of nitrogen in the experimental plots and lysimeters was known (either artificial fertiliser or animal organic wastes). In comparison, the examination of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- in groundwater nitrate was complicated by the presence of both artificial diffuse and organic point sources in the vicinity of most sampling wells. In this complex context of mixed N sources, a multi-step approach was required to test isotopic analysis in groundwater nitrate.
As a direct follow up to chapter 6, site mean δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values were analysed first in relation to site classification based on hydrochemistry, and then to site classification based on spatial characteristics, each site classification associating sites to either artificial diffuse or organic point source contamination.

The results established that regardless of the site classification and the type of associated N source, most values lay within the 4 ‰ to 9 ‰ range reported in the literature for soil organic N-derived nitrate, i.e. above the range expected for artificial fertiliser-derived nitrate (-4 ‰ to 4 ‰) and below the range predicted for animal/human waste-derived nitrate (10 ‰ to 22 ‰). Similar results observed in chapter 5 were attributed to the

leaching of soil organic N-derived nitrate, which is consistent with the context of the Barrow Valley as a high % tillage area where large quantities of crop residues are ploughed in after harvest. On the other hand, all $\delta^{18}O\text{-}NO_3^-$ values were consistently low, overlapping with the 0 ‰ to 5 ‰ range reported for nitrification by Durka *et al.* (1994). Results from soil-water investigations in chapter 5 suggest that the leveling of $\delta^{18}O\text{-}NO_3^-$ was caused by Mineralisation-Immobilisation Turnover processes (MIT). Consequently, the analysis of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in groundwater nitrate did not allow identifying artificial diffuse and organic point source contamination in regard of the values reported in the literature. These limitations are illustrated in figure 7.15, which plots mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ for high nitrate sites where hydrochemistry and spatial characteristics agreed (i.e. where the origin of the contamination was considered beyond reasonable doubts as either artificial fertiliser or organic point) or disagreed.

Figure 7.15: Scatterplot of mean $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values at the groundwater sampling sites of the Barrow Valley where i) hydrochemistry and spatial characteristics supported assumptions of artificial diffuse (D_{cs}, n = 7) or organic point source contamination (P_{cs}, n = 12), and where ii) hydrochemistry and spatial characteristics disagreed (D_c/P_c, n = 21), within 100m and 300 m radius; boxes delineate predicted values for nitrate derived from several N sources, and dashed lines represent the expected isotopic fraction caused by denitrification and MIT processes. *($\delta^{15}N$ and $\delta^{18}O$ are reported in ‰ against AIR and V-SMOW respectively)*



Despite these limitations, important differences in $\delta^{15}N\text{-}NO_3^-$ values were observed between site classifications. When sites were classified according to spatial characteristics

(i.e. presence/absence of organic point source within 100 m and 300 m radius), $\delta^{15}N\text{-}NO_3^-$ (log-transformed) values were significantly lower at the 0.05 level at sites associated with artificial diffuse than organic point source contamination. On the other hand, when sites were classified according to hydrochemistry (i.e. in regard of contamination thresholds), the significance of the difference between sites associated with artificial diffuse and organic point source contamination was improved to the 0.0005 level. The significance of this difference further improved to the 0.0001 level when comparing sites where hydrochemistry and spatial characteristics agreed. This can be seen in figure 7.15, sites associated with artificial diffuse source (D_{cs}) showing distinctively lower $\delta^{15}N\text{-}NO_3^-$ values than sites associated with organic point source contamination (P_{cs}). Therefore, these results suggest that the use of $\delta^{15}N\text{-}NO_3^-$ may be complementary to the use of hydrochemistry in order to discriminate between artificial diffuse and organic point source contamination.

It should be noted that $\delta^{15}N\text{-}NO_3^-$ was not influenced by % tillage, despite a significant effect affecting nitrate concentration in chapter 6. This may be due to the fact that large quantities of leached nitrate originated from nitrified soil organic matter. If considering that under uncontaminated conditions, $\delta^{15}N\text{-}NO_3^-$ should already be within the range expected for soil organic N-derived nitrate, this could explain why $\delta^{15}N\text{-}NO_3^-$ is not influenced by an increase in % tillage (and in nitrate leaching) and why it does not shift towards lower values characteristic of artificial fertiliser.

Finally, significant (at the 0.001 level) and positive correlations between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ on five sampling occasions out of six, with regression slopes close to 0.5, strongly suggest the occurrence of denitrification. However, the extent of this microbial reaction was probably limited as few samples displayed elevated $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values. This is consistent within the context of freely-draining and well aerated soils.

CHAPTER 8: CONCLUSIONS

8.1 Review of the thesis objectives

The primary aim of this project was to test the worth of $\delta^{15}N$ and $\delta^{18}O$ analyses in nitrate as a tool to determine the origin of nitrate contamination in Irish groundwaters. The context was that of unsewered dwellings and farms scattered in areas of intensive agriculture with a significant proportion of tillage land and relatively free-draining soils overlying shallow Carboniferous limestone and sand/gravel aquifers. Ultimately, the main output was to distinguish between the two main sources of nitrogen identified in the Barrow Valley test areas, which are i) artificial diffuse N sources (i.e. artificial N fertilisers) and ii) organic point N sources (i.e. septic tanks and farmyard effluents). Beforehand, preliminary work in chapter 6 consisted of testing conventional chemical analyses and examining more particularly concentrations of three contamination indicators: chloride, potassium and sodium. These ions are major compounds of artificial fertilisers and/or organic wastes, and are typically of low natural occurrence in Carboniferous limestone and sand/gravel aquifers. This approach was intended to both highlight the limitations of conventional analyses, and classify samples in prevision of forthcoming isotopic data analysis in chapter 7, for which several specific objectives were developed:

- Analyse soil-water (see chapter 5) and groundwater nitrate isotopic composition under different types of land use (grass and tillage) and N inputs (artificial diffuse or point/diffuse organic N sources), and compare with the isotopic composition of artificial fertilisers and animal organic wastes.
- Analyse groundwater nitrate isotopic composition in relation to hydrochemistry.
- Identify microbial processes likely to affect groundwater nitrate original isotopic composition.

8.2 Main findings

8.2.1 Critical evaluation of hydrochemistry analysis as a tool to determine nitrate sources

As a preliminary step before moving on to the use of stable isotope analyses in section 8.2.2, this section concludes on the worth of hydrochemistry analysis as a tool to identify

nitrate sources in groundwaters and to discriminate between artificial diffuse and organic point N sources in rural areas.

- Unsaturated zone investigation

Soil-water experiments conducted in the unsaturated zone highlighted the fact that high nitrate leaching can occur in early spring after artificial fertiliser or dairy wastewater has been applied to free-draining soils overlain by grassland or tillage, whether or not the application rate exceeds Teagasc recommendations. In the artificial fertiliser experiments, nitrate concentrations in soil-water were measured up to three times the 50 mg/l NO_3^- limit set in the new Drinking Water Directive (Council of the European Communities, 1998). Likewise, nitrate concentrations in soil-water twice as high as the 50 mg/l NO_3^- limit were observed in the dairy wastewater experiments. These results strongly contrasted with unfertilised controls where nitrate levels merely exceeded around 25 mg/l NO_3^- at most. In addition, the amount of N applied seemed to influence how much nitrate was leached, the higher the application rates the higher the nitrate concentrations in soil-water.

- Saturated zone investigation

Nitrate aside, the analysis of groundwater chemistry was carried out on sites' mean concentrations of contamination indicators (i.e. chloride, potassium and sodium). The following independent factors were then investigated:

  - Exceedance / non-exceedance of contamination thresholds calculated for chloride, potassium and sodium (sites with similar groundwater chemistry were then grouped and associated with either artificial diffuse or organic point source contamination).
  - Presence / absence of organic point sources within 100 m and 300 m radius (it should be noted that tillage and associated artificial diffuse N sources were ubiquitous within these two radii, independently of organic point N sources occurrence).
  - % tillage within 300 m.

Based on the exceedance / non-exceedance of contamination thresholds, results suggested at first that contamination at most sites was of artificial fertiliser origin: out of forty-six high nitrate sites (i.e. mean $[NO_3^-] \geq 25$ mg/l), thirty-two showed hydrochemistry characteristic of artificial diffuse N source contamination, whereas only thirteen sites

showed hydrochemistry associated with organic point N source contamination. Evidence supporting the importance of agricultural diffuse contamination came from the investigation of % tillage effect on site mean concentration of nitrate. As most sites (forty-one out of fifty-one sampled) were surrounded by more than 50 % tillage within 300 m radius, nitrate concentration in the high % tillage group (i.e. tillage > 50 %) was significantly higher ($p \leq 0.005$) than in the lower % tillage group (i.e. tillage $\leq$ 50 %). However, such result should be interpreted cautiously as this does not unequivocally relate nitrate contamination to artificial N fertiliser. In fact, this may just suggest that crop residues ploughed in (and subsequently mineralised and nitrified) in tillage areas are strongly implicated into the nitrate leaching process.

Limitations to the use of contamination thresholds for contamination indicators exist. Firstly, chloride, potassium and sodium are less (or far less for potassium and sodium) mobile than nitrate, hence they cannot not fully account for the origin of nitrate. Secondly, question marks remain on how correctly contamination thresholds, based on the assumption of free-draining soils (made in section 6.3.2), can apply to a large area that shows large lateral and horizontal variations in terms of soil, subsoil, bedrock permeability.

Based on the presence / absence of organic point sources within 100 m and 300 m radius, the analysis of sodium levels strongly suggested that hydrochemistry at most sites was systematically impacted by organic point sources (septic tanks and/or farmyards). In contrast with the forty-two sites (out of fifty-one sampled) that have organic point sources present within 100 m radius (forty-three sites within 300 m radius), only nine sites have exclusively artificial diffuse sources within this radius (eight sites within 300 m radius). The concentration of sodium, which is a major constituent of organic wastes but is present at low level in one of the artificial fertilisers used in the study area, was significantly higher ($p \leq 0.001$) at sites where point sources were present within 100 m or 300 m radius, in comparison with sites with only artificial diffuse sources present with these two radii.

However, it is important to recognise the serious limitations of this qualitative approach. The conditions for a sampling well to intercept a plume of contamination coming from an organic point source are complex, which makes the use of sites' spatial characteristics alone perhaps too uncertain for a reliable determination of nitrate sources. Furthermore, no quantitative information can be gained the quantities of nitrate coming from different sources.

The above contradictions regarding nitrate sources among highly contaminated sites (i.e. mean $[NO_3^-] \geq 25$ mg/l) were highlighted after comparing classifications based on i) hydrochemistry alone (i.e. exceedance / non exceedance of contamination thresholds) and ii) sites' spatial characteristics (i.e. presence / absence of organic point sources within 100 m and 300 m radius). While 100 % of high nitrate sites with no other N source than artificial fertiliser within 100 m or 300 m radius (eight out of eight within 100 m radius, seven out of seven within 300 m radius) showed hydrochemistry indicative of artificial diffuse contamination, only 34 % of high nitrate sites with organic point sources present within 100 m or 300 m radius (thirteen out of thirty-eight within 100 m radius, thirteen out of thirty-nine within 300 m radius) showed groundwater chemistry indicative of contamination by organic point N sources (i.e. septic tank and/or farmyard).

Despite showing some real credence, both classifications, which associated sites to either artificial diffuse or organic point source contamination, had inherent limitations that confirmed the need for additional tools for the reliable identification of groundwater nitrate sources.

8.2.2 Critical evaluation of stable isotope analysis as a tool to determine nitrate sources

The list of specific objectives listed under the primary aim in section 1.2 is answered in bulleted conclusions in this section.

- Soil-water and groundwater nitrate isotopic composition under different types of land use and N inputs

Table 5.4 showed earlier that artificial fertilisers, dairy wastewater and slurry applied to experimental plots and lysimeters during this project had different isotopic compositions with respect to their ^{15}N content. With a -2.4 to 2 ‰ range, artificial fertilisers (total nitrogen and nitrate fraction) had the lowest $\delta^{15}N$ values, whereas dairy wastewater was comparatively slightly more ^{15}N-enriched with a mean value of 3.8 ‰, and slurry displayed the greatest ^{15}N-enriched material of all with $\delta^{15}N$ of 10.2 ‰. Results of soil-water investigations reveal that soil-water nitrate collected from plots at Moorepark (permanent grassland), Knockbeg (tillage) and from Oak Park soil lysimeters (permanent grassland) poorly reflected the original ^{15}N content of the above nitrogenous sources that

had been applied (see section 5.3.1). First, soil-water nitrate collected from plots subjected to applications of artificial fertilisers was found to be consistently ^{15}N-enriched in comparison with the fertiliser. With dairy wastewater applications, the range of δ^{15}N-NO_3^- in soil-water was likewise slightly higher than δ^{15}N-TN of dairy wastewater itself. In contrast, soil-water from the slurry treatment plots contained δ^{15}N-NO_3^- lower than δ^{15}N-TN in slurry. The reason for this pattern was attributed to the leaching of nitrate derived from soil organic matter, which could be expected to display δ^{15}N-NO_3^- between 4 ‰ and 9 ‰, i.e. lower than animal wastes but higher that artificial fertiliser.

As previously discussed in section 5.3.4, the use of δ^{18}O-NO_3^- to identify nitrate derived from artificial fertiliser is inherently limited by the fact that artificial N fertilisers contain a large fraction of nitrogen that is in a non-nitrate form (see table 2.5) and that will undergo nitrification once in the soil. For this reason, the 18 ‰ to 22 ‰ range expected for artificial fertilisers seems high, and one might expect, at most values around 15 ‰ for a fertiliser like CAN (75 % N in nitrate form), and around 10 ‰ for a fertiliser like ammonium nitrate (50 % N in nitrate form). However, δ^{18}O-NO_3^- values observed during soil-water experiments were far below these ranges. In the Moorepark experiments, all samples from the artificial fertiliser plots fell within a narrow range of -1.4 to 2.9 ‰, which happened to be similar to that displayed by soil-water samples from the control or from other plots subjected to applications of animal organic wastes. This result supports the idea that most fertiliser nitrate applied to soils was immobilised and remineralised through the Mineralisation-Immobilisation Turnover processes (MIT), which were reported by Mengis *et al.* (2001) as a major limitation to the use of δ^{18}O for the identification of nitrate of artificial origin. Nevertheless, experiments at Knockbeg showed that direct leaching of fertiliser nitrate is possible (section 5.3.1), as two soil-water nitrate samples from two low rate- spring barley plots showed low δ^{15}N-NO_3^- values (-0.4 ‰ each) in conjunction with high δ^{18}O-NO_3^- values (15.1 and 17 ‰).

Groundwater nitrate investigations gave some similar results to soil-water investigations. In the multi-step approach destined to test the worth of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- analysis in nitrate, groundwater sampling sites in the Barrow Valley were classified according to spatial characteristics and the absence/presence or unsewered houses and/or farmyards within 100 m and 300 m radius. The results showed that most δ^{15}N-NO_3^- values lay within the 4 ‰ to 9 ‰ range reported in the literature for soil organic N-derived nitrate, whether sites were located near or away from organic point sources. Nevertheless, δ^{15}N-NO_3^- were significantly higher (at the 0.05 level) when organic point sources were present within 100

m and 300 m radius (section 7.3.4). In addition, all $\delta^{18}O\text{-}NO_3^-$ widely overlapped with the 0 ‰ to 5 ‰ range reported in the literature for nitrification. Based on spatial characteristics $\delta^{15}N\text{-}NO_3^-$ was not influenced by % tillage, despite a significant effect affecting nitrate concentration in chapter 6. This may be due to the fact that large quantities of leached nitrate originated from nitrified soil organic matter. If considering that under uncontaminated conditions, $\delta^{15}N\text{-}NO_3^-$ should already be within the range expected for soil organic N-derived nitrate, this could explain why $\delta^{15}N\text{-}NO_3^-$ is not influenced by an increase in % tillage (and in nitrate leaching) and why it does not shift towards lower values characteristic of artificial fertiliser.

- Groundwater nitrate isotopic composition in relation to hydrochemistry

When sites were classified according to contamination thresholds, the difference of $\delta^{15}N\text{-}NO_3^-$ between sites associated with artificial diffuse and organic point source contamination was significant at the 0.0005 level. The significance of this difference further improved to the 0.0001 level when comparing sites where hydrochemistry and spatial characteristics referred to above agreed. Therefore, these results suggest that the use of $\delta^{15}N\text{-}NO_3^-$ may be complementary to the use of hydrochemistry in order to discriminate between artificial diffuse and organic point source contamination.

- Microbial processes likely to affect groundwater nitrate original isotopic composition

As mentioned earlier, the levelling of all $\delta^{18}O\text{-}NO_3^-$ values was consistent with the occurrence of Mineralisation-Immobilisation Turnover, as reported by Mengis *et al.* (2001). This microbial process consists of immobilising nitrate, which is subsequently remineralised. This means that fertiliser nitrate, which typically displays $\delta^{18}O\text{-}NO_3^-$ between 18 ‰ and 22 ‰, would eventually display a $\delta^{18}O\text{-}NO_3^-$ value characteristic of organic waste-derived nitrate if undergoing this process.
Denitrification is also likely to cause some important isotopic fractionation. However, the limited ranges of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values suggests that if occurring, its extent is very limited.

8.2.3 Origin of nitrate and denitrification in the study areas

The list of specific objectives listed under the secondary aim in section 1.2 is answered in bulleted conclusions in this section.

- Origin of nitrate in the groundwater sampling areas

The use of $\delta^{15}N\text{-}NO_3^-$ alone cannot help determine for sure whether groundwater contamination in the Barrow Valley study areas was mainly caused by diffuse applications of artificial fertiliser or by organic point sources (i.e. farmyards and unsewered houses), as reported in section 7.5.1. At first sight, a reason for most $\delta^{15}N\text{-}NO_3^-$ values to lie within the range expected for soil organic N-derived nitrate may be that most leached nitrate originates from the nitrification of soil organic N. Nonetheless, $\delta^{15}N\text{-}NO_3^-$ values leaned more towards the range expected for artificial fertiliser-derived nitrate than towards the range predicted for animal/human waste-derived nitrate, which may be an indication that the leaching of artificial fertiliser-derived nitrate had some impact on groundwater contamination. It may also be that crop residues undergoing nitrification were slightly ^{15}N-depleted due to the incorporation of fertiliser N with lower $\delta^{15}N\text{-}TN$, which would result in a slight lowering of $\delta^{15}N\text{-}NO_3^-$ values. As additional supporting evidence for artificial diffuse contamination, most sites had the hydrochemistry characteristic of artificial diffuse contamination, and these sites showed $\delta^{15}N\text{-}NO_3^-$ significantly lower than sites with hydrochemistry associated with organic point source contamination. However, this does not confirm whether nitrate was derived from artificial fertiliser or from ^{15}N-depleted crop residues. In addition, the results presented in section 7.5.1 shows clearly that $\delta^{18}O\text{-}NO_3^-$ does not help answer the ambiguities, as most values lay within the range reported in the literature for nitrification.

On the other hand, the use of $\delta^{15}N\text{-}NO_3^-$ in Moorepark RC appeared very unlikely to help discriminate between contamination caused by artificial fertiliser and dairy wastewater, which are two important sources of nitrogen in this intensive dairy farm. The reason is that both materials exhibit similar $\delta^{15}N\text{-}TN$ values: $\delta^{15}N\text{-}TN$ in artificial fertilisers used by Teasgasc was measured between -2.4 and 2.0 ‰, while $\delta^{15}N\text{-}TN$ in dairy wastewater was measured at 3.8 ‰, i.e. less than 2 ‰ higher.

- Information on denitrification processes in Irish soils and aquifer materials

In the Barrow Valley, positive correlations were observed between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$, in conjunction with regression slopes close to 0.5, which strongly suggested the occurrence of denitrification, according to the literature.

In Moorepark RC, the only evidence of denitrification was observed at a borehole located downgradient a farmyard, where large inputs of organic carbon may have created a favourable environment for denitrification.

8.3 Recommendations and scope for future research

The anion exchange resin procedure, designed to extract nitrate from freshwater samples and convert it into solid silver nitrate prior to IRMS analysis, proved to be extremely labour and time consuming. Therefore, methods to maximise time efficiency and ease laboratory work for researchers who deal with a large number of samples are needed. One solution suggested in this thesis was to slightly deviate from the methodology of Silva *et al.* (2000) by removing sulphate before the sample is passed through the anion exchange resin. Consequently, nitrate eluted from the column and converted into $AgNO_3$ would be ready for both $\delta^{15}N$ and $\delta^{18}O$ IRMS analyses.

This requires, as detailed in 4.4.2, the addition of barium chloride to the water sample prior to the nitrate extraction step, which may seem surprising at first since 4 ml of 1M $BaCl_2$ represents 8 meq of chloride and widely exceeds the 2.4 meq capacity of the column. However, Silva *et al.* (2000) pointed out that 'since the [Bio-Rad] AG 1-X8 resin has a higher affinity for NO_3^- than Cl^- and is in chloride form, incomplete adsorption of NO_3^- [generating isotopic fractionation] can only be caused by displacement of the NO_3^- and not by exceeding the exchange capacity of the resin with Cl^-'. In their experiments, they observed that '1000 ml of solution with chloride concentration up to 200 mg/l [5.6 meq] can be passed through the column without causing significant isotopic fractionation of the NO_3^-', while 'higher chloride concentrations can be tolerated in smaller-volume samples'. This last point was also confirmed by our experiments. Presented in table 4.5, the addition of barium chloride (8 meq Cl^-) to 125 ml standard solutions of KNO_3 (with nitrate concentrations of 50 mg/l NO_3^-) did not cause significant isotopic fractionation.

Another analytical recommendation relates to the use of on-line IRMS (in place of off-line combustion and dual inlet systems) for both $\delta^{15}N$ and $\delta^{18}O$ IRMS analyses. This enabled a substantial reduction in laboratory time required to analyse large numbers of samples.

Finally, the method involving denitrifying bacteria (Sigman *et al.*, 2001; Casciotti *et al.*, 2002) appears to be the most promising way to further reduce time spent in the laboratory, potentially enabling the processing of many more samples in a shorter time. The alternative cadmium reduction method (McIlvin and Altabet, 2005) is also very appealing, but has the drawback of requiring hazardous chemical usage.

Last but not least, the immense advantage of this recent denitrifier technique (or its cadmium reduction alternative) over the anion extraction method used in this thesis is that it allows for the first time the measurement of $\delta^{18}O\text{-}NO_3^-$ in seawater nitrate (Wankel *et al.*, 2006). Clearly, this opens a new field of investigation that allows the tracing of nitrate sources in brackish water and a better understanding of the N cycle.

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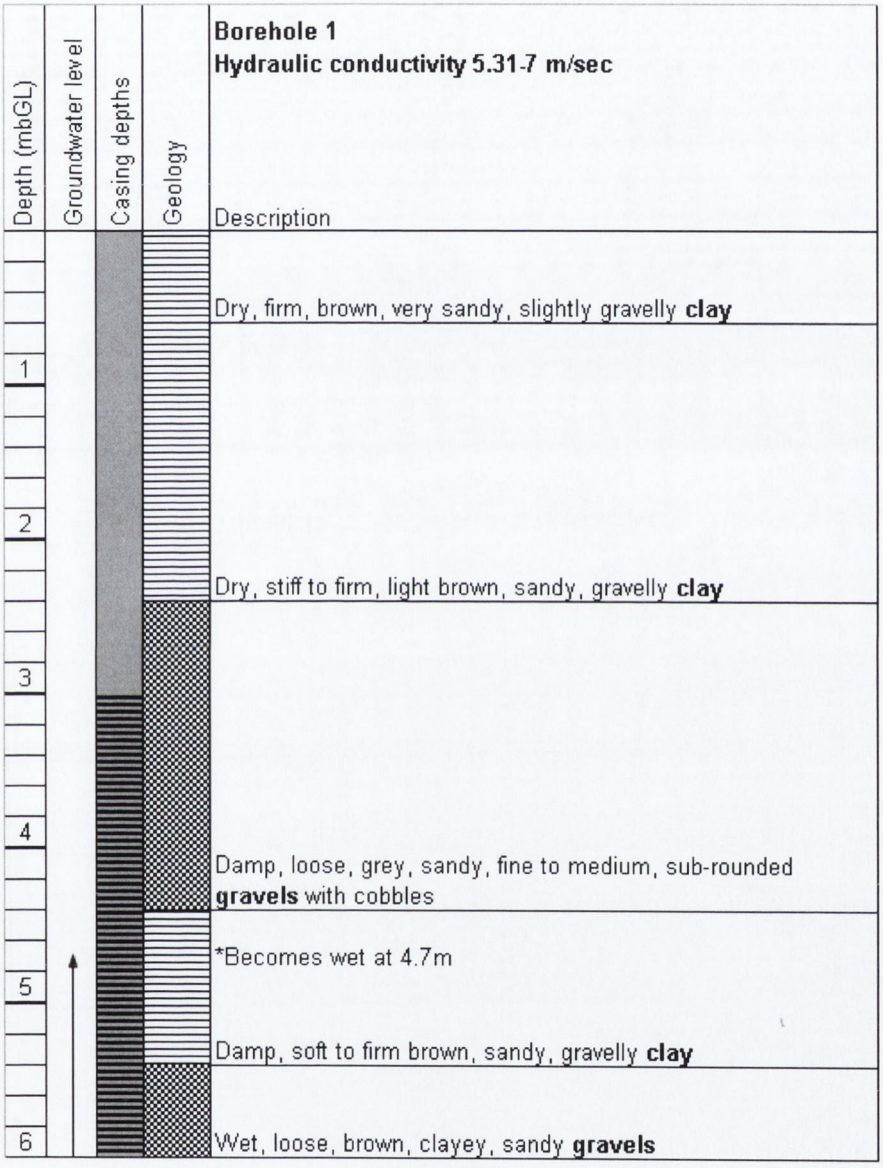
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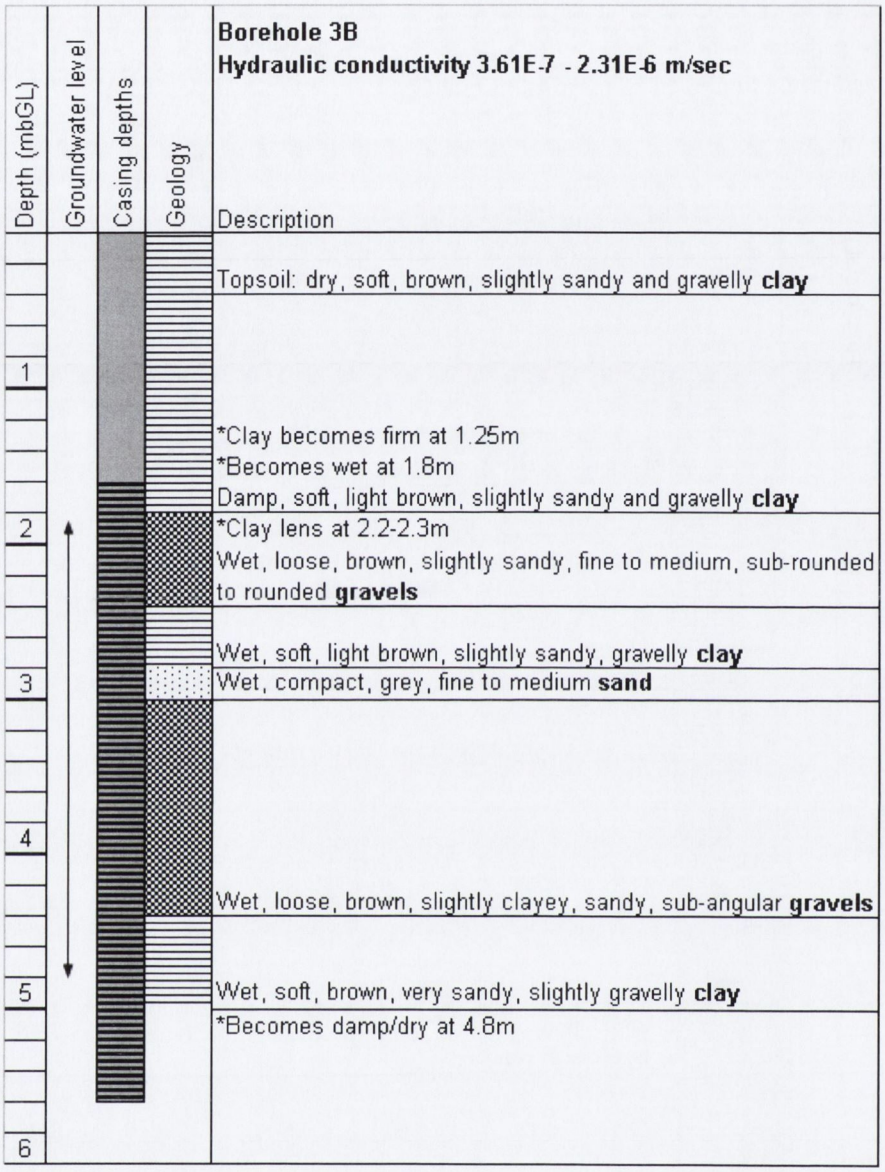
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APPENDICES

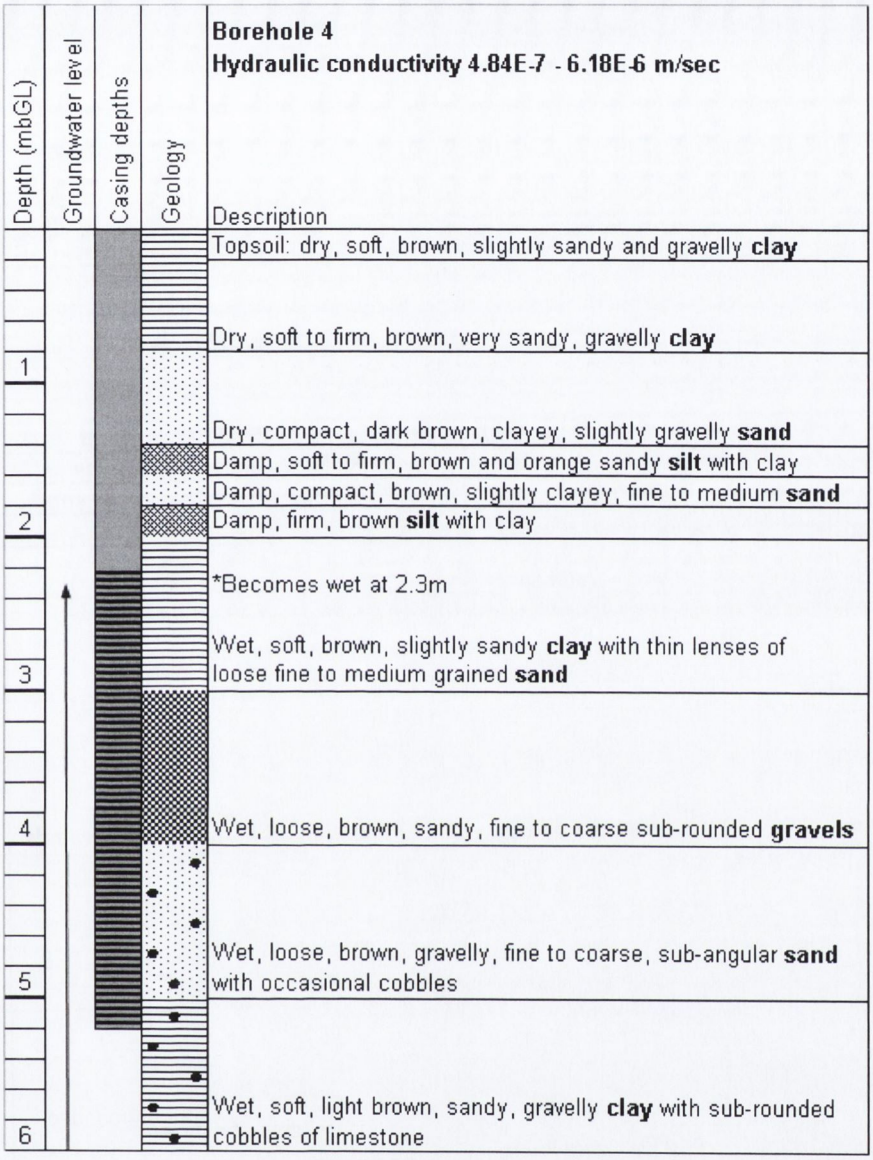
Appendix 1: Borehole log of BHO.1 at Oak Park Research Centre, and hydraulic conductivity (Hooker (2005), adapted from Minerex Environmental Ltd (2002)).



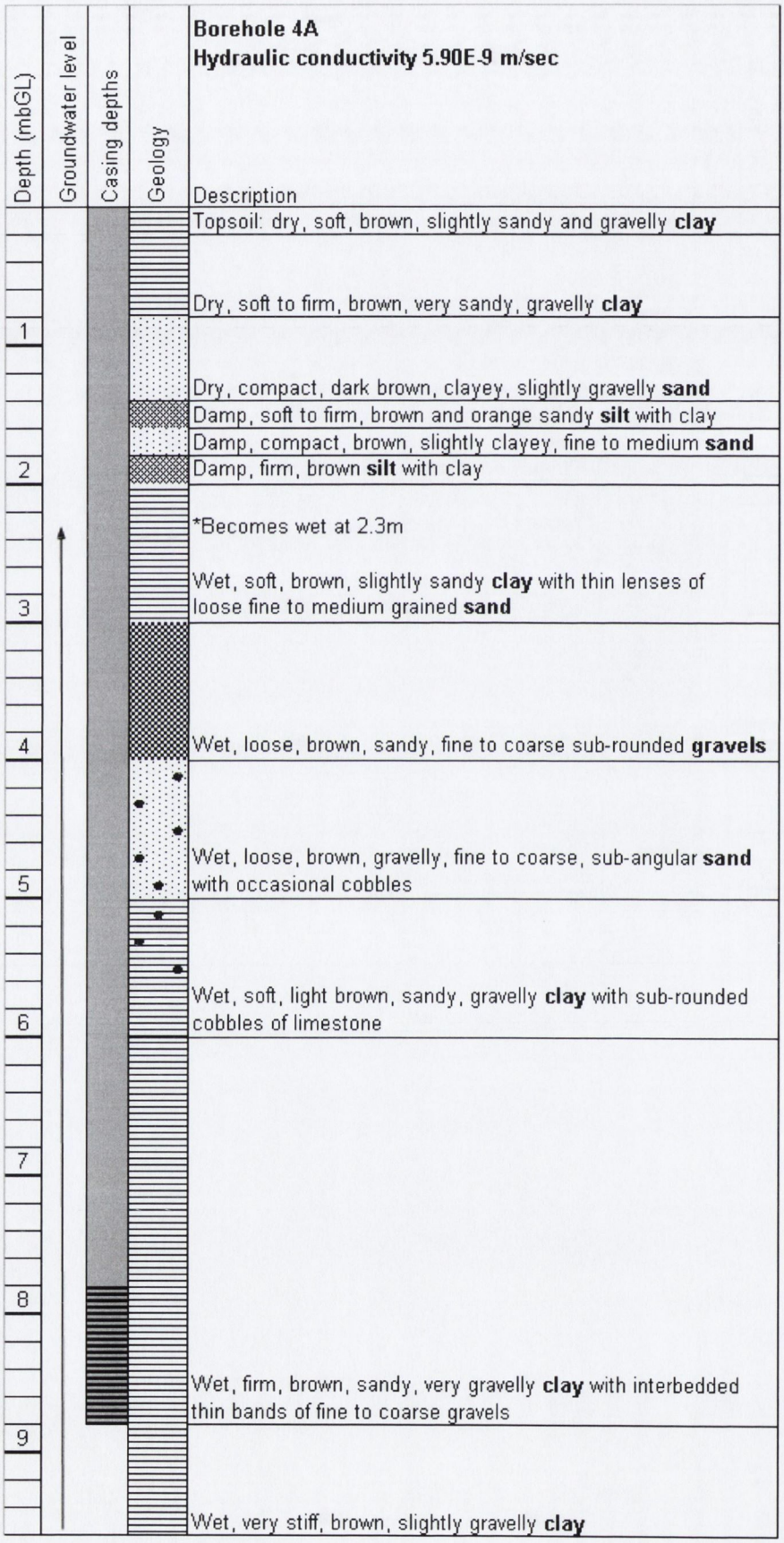
Appendix 1 (continued): Borehole log of BHO.3B at Oak Park Research Centre, and hydraulic conductivity.



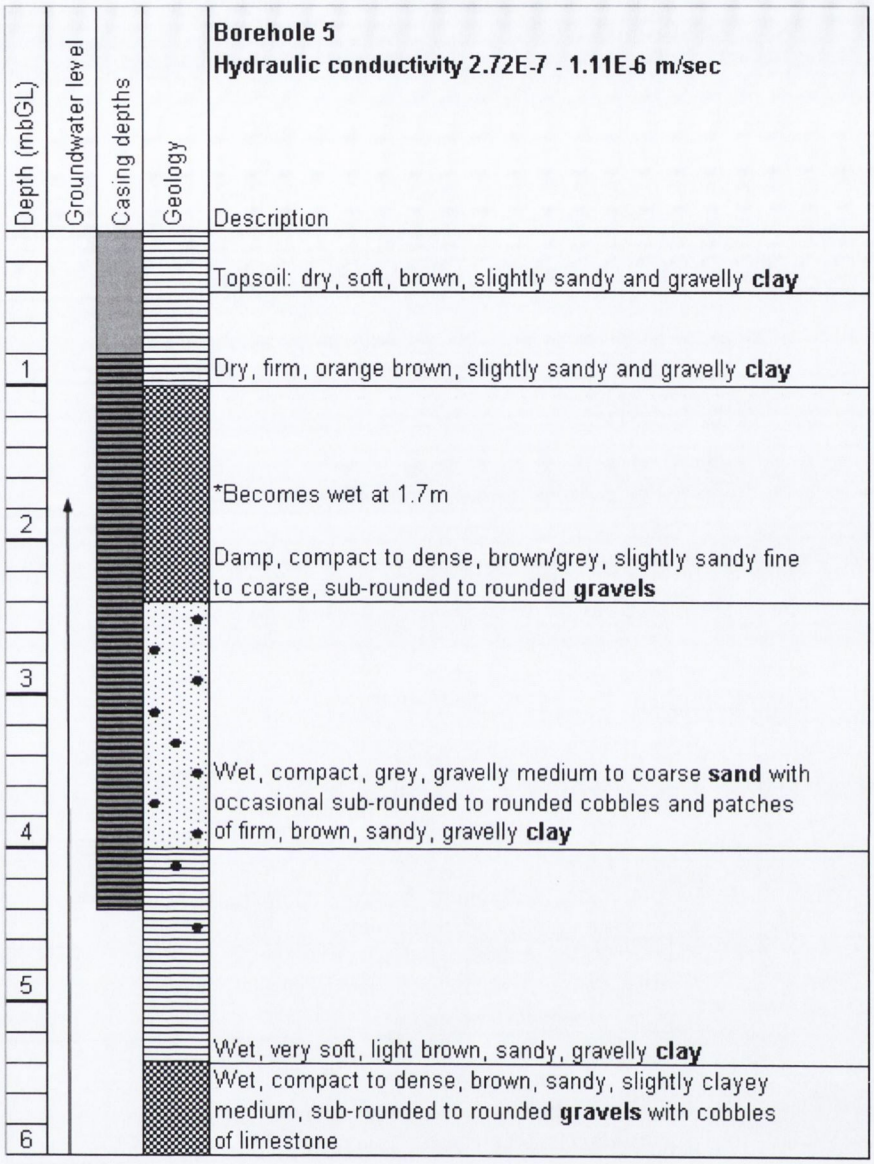
Appendix 1 (continued): Borehole log of BHO.4 at Oak Park Research Centre, and hydraulic conductivity.



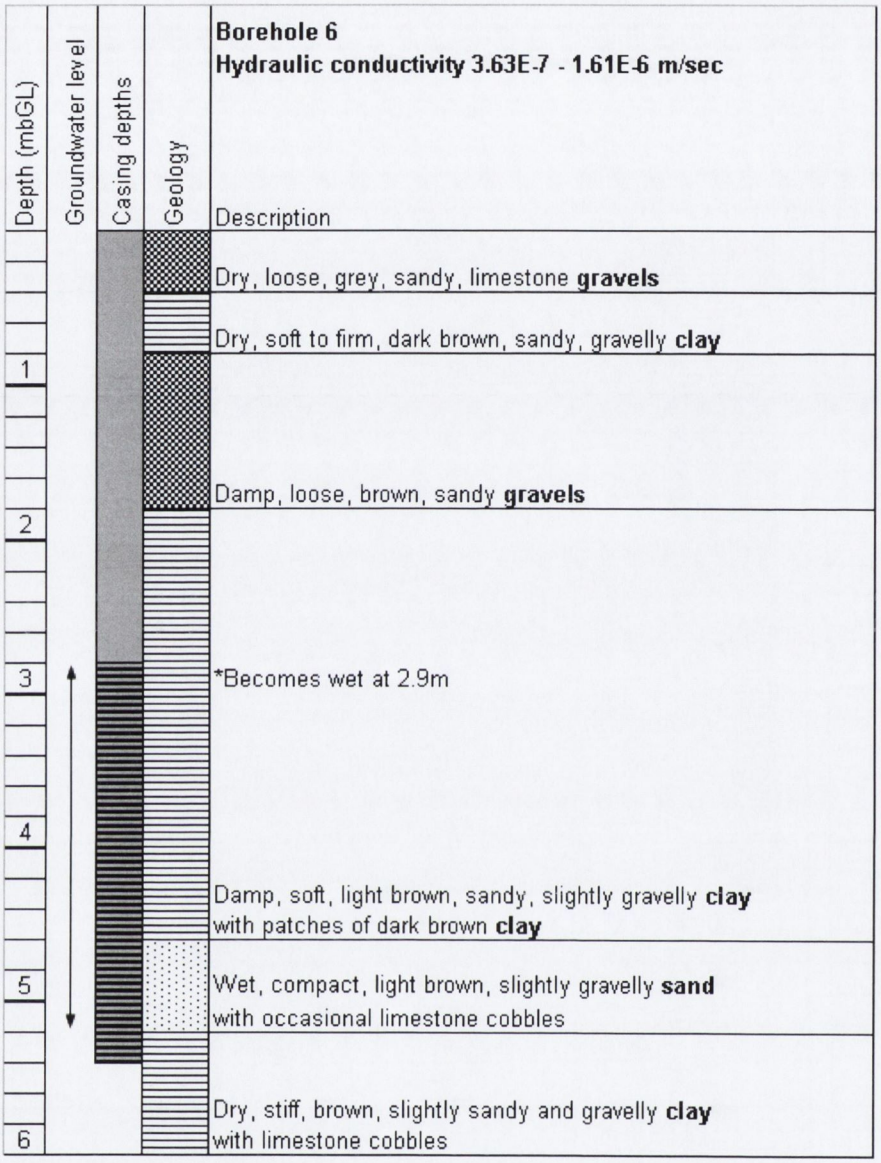
Appendix 1 (continued): Borehole log of BHO.4A at Oak Park Research Centre, and hydraulic conductivity.



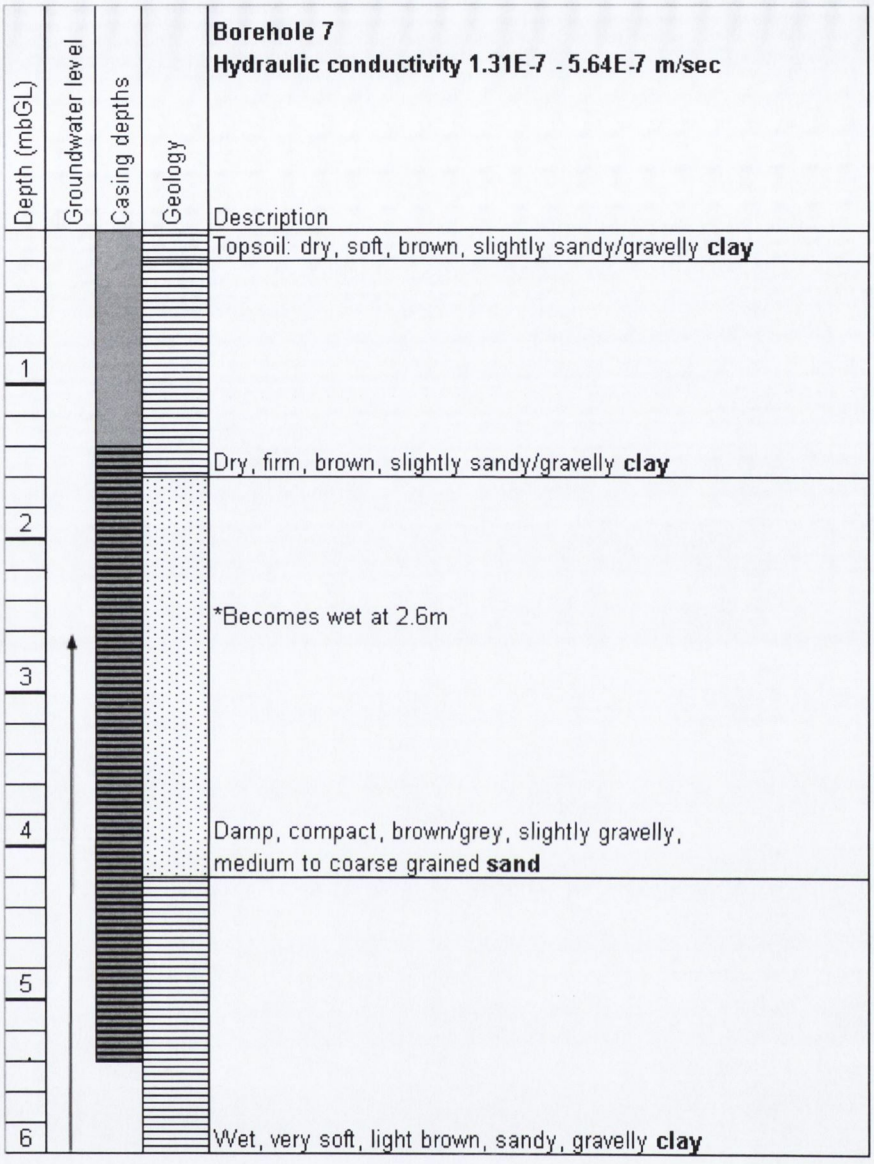
Appendix 1 (continued): Borehole log of BHO.5 at Oak Par Research Centre, and hydraulic conductivity.



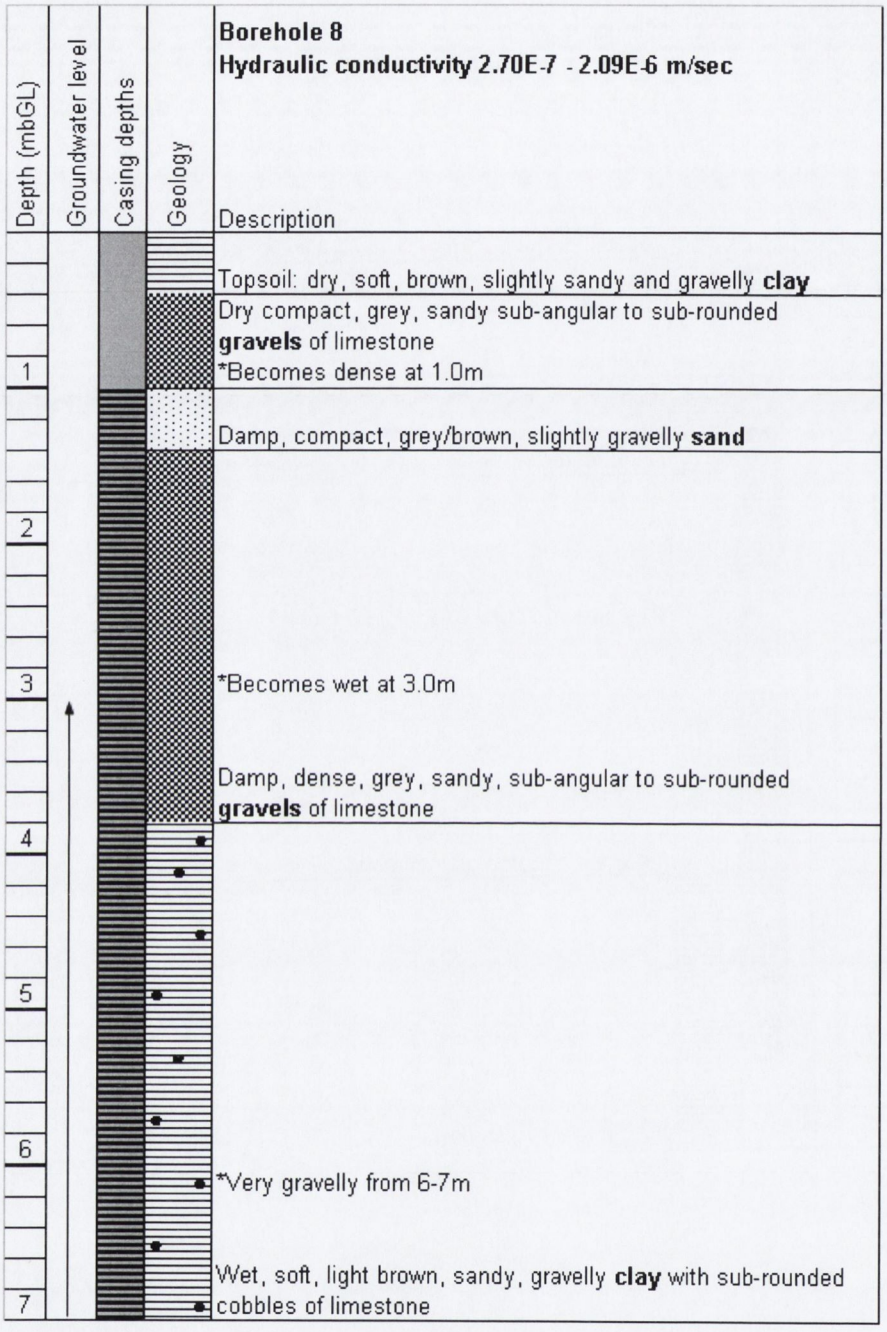
Appendix 1 (continued): Borehole log of BHO.6 at Oak Par Research Centre, and hydraulic conductivity.



Appendix 1 (continued): Borehole log of BHO.7 at Oak Par Research Centre, and hydraulic conductivity.



Appendix 1 (continued): Borehole log of BHO.8 at Oak Par Research Centre, and hydraulic conductivity.



Appendix 2: Soil-water chemistry and nitrate isotopic data in experiments carried out on Moorepark Research Centre (MOOR), Knockbeg (KNO) and Oak Park (OAK) soils.

In Moorepark, sample codes start with one or two letters followed by a number. Letter C means unfertilised control, letters L-M-H relate to the application rates low-medium-high as detailed in section 3.3.1, and the second letters F-D-S stand for the type of nitrogenous material applied, i.e. artificial fertiliser-dairy wastewater-slurry. Knockbeg codes relate to the plot number and treatment (L and H for low and high application rates respectively; sb and ww for spring barley and winter wheat respectively), which are given in section 3.3.2. Oak Park soil lysimeter codes contain a letter C or F, which relate to the treatment (i.e. unfertilised control or fertilised lysimeter respectively), followed by a number, which is the lysimeter replicate number (see section 3.3.3). *($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ are reported with their standard deviation (SD) in permils ‰ against AIR and V-SMOW respectively, % N refers to the mass percentage of nitrogen measured in $AgNO_3$ while % C relates to the mass percentage of C-bearing impurities measured in $AgNO_3$, nitrate and sulphate concentrations are reported in mg/l NO_3^- and mg/l SO_4^{2-} respectively, chloride concentration is in mg/l)*

Code	Soil	Time	$\delta^{15}N\text{-}NO_3^-$	SD $\delta^{15}N$	$\delta^{18}O\text{-}NO_3^-$	SD $\delta^{18}O$	% N	% C	$[NO_3^-]$	$[Cl^-]$	$[SO_4^{2-}]$
C1.0	MOOR	Dec-02							20.1	4.4	25.0
C1.0	MOOR	Jun-03	7.2	< 0.1	0.7	0.6	6.3	< 0.1	23.1		
C1.0	MOOR	Apr-04	5.9	< 0.1	1.6	< 0.1	6.7	< 0.1	34.0	7.8	31.6
C1.0	MOOR	May-04	5.9	0.1	0.6	0.7	7.1	< 0.1	31.4	7.5	15.4
C2.5	MOOR	Dec-02							19.7	6.5	23.9
C2.5	MOOR	Jun-03	6.8	< 0.1	1.6	0.2	6.9		23.5		
C2.5	MOOR	Apr-04							25.7	9.1	32.8
C2.5	MOOR	May-04	5.1	< 0.1	0.0	0.2	7.7	< 0.1	27.0	8.1	17.5
HD1.0	MOOR	Jun-03	6.1	0.1	0.2	0.2	7.4	< 0.1	24.2	11.5	18.9
HD1.0	MOOR	Apr-04	4.9	< 0.1	1.1	0.5	7.8	< 0.1	108.8	41.8	31.5
HD1.0	MOOR	May-04	4.5	0.1	0.9	0.3	7.8	< 0.1	76.2	31.2	15.4
HD2.5	MOOR	Jun-03	4.9	< 0.1	0.4	0.2	8.1	< 0.1	49.9	20.1	22.5
HD2.5	MOOR	Apr-04	7.6	< 0.1	2.8	0.8	7.7	< 0.1	56.4	30.0	37.0
HD2.5	MOOR	May-04	6.5	0.1	1.8	0.2	7.7	< 0.1	60.5	29.1	15.5
HF1.0	MOOR	Jun-03	2.9	< 0.1	1.2	< 0.1	7.8		101.9		
HF1.0	MOOR	Apr-04	2.7	< 0.1	2.3	0.5	7.8	< 0.1	136.3	10.5	51.4
HF1.0	MOOR	May-04	2.4	< 0.1	2.9	0.2	7.7	< 0.1	150.0	10.3	34.3
HF2.5	MOOR	Jun-03	2.5	< 0.1			8.2	< 0.1	112.2	10.2	30.4
HF2.5	MOOR	Apr-04	2.6	< 0.1	2.7	0.1	7.6	< 0.1	136.3	12.4	43.9
HF2.5	MOOR	May-04	2.7	0.1	2.9	0.5	7.7	< 0.1	143.7	12.8	24.6
HS1.0	MOOR	Jun-03							7.4		
HS1.0	MOOR	Apr-04	6.1	< 0.1	0.6	1.0	3.9	< 0.1	7.4	17.1	28.4
HS1.0	MOOR	May-04	5.1	< 0.1	1.0	0.2	3.2	< 0.1	5.2		
HS2.5	MOOR	Jun-03	5.9	0.1	0.0	0.1	7.1	< 0.1	22.9		
HS2.5	MOOR	Apr-04	6.0	0.1	0.7	0.3	5.0	< 0.1	19.3	16.4	28.2
LF1.0	MOOR	Jun-03	4.9	0.1	0.5	0.2	8.0	< 0.1	27.9	3.7	18.9
LF2.5	MOOR	Jun-03	4.4	< 0.1	-1.0	0.8	8.1	< 0.1	43.4	3.9	21.3
LS1.0	MOOR	Dec-02							4.0	4.6	21.4
LS1.0	MOOR	Jun-03							3.5	2.7	7.6
LS2.5	MOOR	Dec-02							17.0	6.0	39.3
LS2.5	MOOR	Jun-03	9.2	< 0.1	2.0	0.1	2.7		5.7		
MD1.0	MOOR	Dec-02	4.3	< 0.1	-0.6	< 0.1	7.3	< 0.1	21.0	8.9	34.9
MD1.0	MOOR	Apr-04	4.9	0.1	1.4	1.0	7.6	< 0.1	48.4	25.8	49.5
MD1.0	MOOR	May-04	6.1	< 0.1	1.8	0.6	6.4	< 0.1	20.0	19.6	19.7
MD2.5	MOOR	Dec-02	5.1	< 0.1	1.3		7.9	< 0.1	49.7	28.3	47.9
MD2.5	MOOR	Apr-04	4.5	0.1	1.0	0.7	7.7	< 0.1	63.4	19.0	43.9
MD2.5	MOOR	May-04	4.6	0.2	0.4	0.4	7.7	< 0.1	59.9	18.9	29.8
MF1.0	MOOR	Dec-02	4.3	< 0.1	0.3	0.8	7.9	< 0.1	35.4	5.3	20.1
MF1.0	MOOR	Jun-03	3.4	< 0.1	1.6	< 0.1	7.9	< 0.1	51.9	5.5	18.9
MF1.0	MOOR	Apr-04	1.8	< 0.1	1.5	0.5	7.7	< 0.1	115.0	11.3	37.6
MF1.0	MOOR	May-04	4.2	< 0.1	0.6	0.4	7.7	< 0.1	44.9	11.3	16.3
MF2.5	MOOR	Dec-02	4.1	< 0.1	-1.4	0.2	7.9	< 0.1	89.9	9.6	33.6
MF2.5	MOOR	Jun-03	3.9	< 0.1	-0.1	0.1	8.0	< 0.1	69.6	6.0	23.5
MF2.5	MOOR	Apr-04	4.1	0.1	0.8	0.8	7.8	< 0.1	89.2	10.4	38.1
MF2.5	MOOR	May-04	3.9	0.1	0.0	0.7	7.7	< 0.1	89.6	10.7	21.5
MS1.0	MOOR	Jun-03	5.7	0.1	2.3	0.3	6.8	< 0.1	16.0		
MS2.5	MOOR	Jun-03	6.2	< 0.1	-1.0	0.1	7.8	< 0.1	30.0		

Appendix 2 (continued): Soil-water chemistry and nitrate isotopic data in experiments carried out on Moorepark Research Centre (MOOR), Knockbeg (KNO) and Oak Park (OAK) soils.
In Moorepark, sample codes start with one or two letters followed by a number. Letter C means unfertilised control, letters L-M-H relate to the application rates low-medium-high as detailed in section 3.3.1, and the second letters F-D-S stand for the type of nitrogenous material applied, i.e. artificial fertiliser-dairy wastewater-slurry. Knockbeg codes relate to the plot number and treatment (L and H for low and high application rates respectively; sb and ww for spring barley and winter wheat respectively), which are given in section 3.3.2. Oak Park soil lysimeter codes contain a letter C or F, which relate to the treatment (i.e. unfertilised control or fertilised lysimeter respectively), followed by a number, which is the lysimeter replicate number (see section 3.3.3). *($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ are reported with their standard deviation (SD) in permils ‰ against AIR and V-SMOW respectively, % N refers to the mass percentage of nitrogen measured in $AgNO_3$ while % C relates to the mass percentage of C-bearing impurities measured in $AgNO_3$, nitrate and sulphate concentrations are reported in mg/l NO_3^- and mg/l SO_4^{2-} respectively, chloride concentration is in mg/l)*

Code	Soil	Time	$\delta^{15}N\text{-}NO_3^-$	SD $\delta^{15}N$	$\delta^{18}O\text{-}NO_3^-$	SD $\delta^{18}O$	% N	% C	$[NO_3^-]$	$[Cl^-]$	$[SO_4^{2-}]$
K7-Lsb	KNO	Mar-04	-0.4	< 0.1	17.0	1.1	7.4	< 0.1	152.2		
K57-Lsb	KNO	Mar-04	-0.4	0.3	15.1	0.1	7.7	< 0.1	129.5		
K19-Hsb	KNO	Mar-04	2.0	< 0.1	7.4	0.2	7.6	< 0.1	87.0		
K71-Hsb	KNO	Mar-04	2.6	0.1	5.5	0.3	7.6	< 0.1	84.6		
K25-Lww	KNO	Mar-04	4.2	0.1	0.7	0.3	7.5	< 0.1	48.9		
K49-Lww	KNO	Mar-04	6.6	0.1	3.8	0.1	7.4	< 0.1	61.4		
K13-Hww	KNO	Mar-04	3.7	< 0.1	1.5	0.7	7.6	< 0.1	68.6		
K37-Hww	KNO	Mar-04	3.5	0.1	1.0	0.2	7.5	< 0.1	71.0		
K63-Hww	KNO	Mar-04	5.6	< 0.1	3.1	1.1	6.2	< 0.1	13.2		
OAK C1	OAK	Nov-03	2.9	0.1	1.5	0.3	1.7	< 0.1	2.6		
OAK C2	OAK	Nov-03	2.7	0.1	-1.0	0.6	4.9	< 0.1	11.4		
OAK C3	OAK	Nov-03	2.3	0.1	-1.2	0.1	4.1	< 0.1	6.5		
OAK F1	OAK	Nov-03	1.1	0.1	4.9	0.4	6.9	< 0.1	29.7		
OAK F2	OAK	Nov-03	0.4	< 0.1	5.4	0.2	6.9	< 0.1	35.6		
OAK F3	OAK	Nov-03	0.4	0.1			7.7	< 0.1	60.5		

Appendix 3: Groundwater chemistry measured between February 2002 and June 2004 in samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *(Nitrate and sulphate concentrations are in mg/l NO_3^- and mg/l SO_4^{2-} respectively, other concentrations are in mg/l, $[K^+]/[Na^+]$ is the potassium to sodium ratio, conductivity is in µS/cm, temperature is in °C, alkalinity in mg/l $CaCO_3$, total and faecal coliforms are in number of bacteria by 100 ml sample – A = 0, 0 < B ≤ 10, 10 < C ≤ 50 and D > 50, and IBE is the Ion Balance Error)*

Site	Time	$[NO_3^-]$	$[Cl^-]$	$[K^+]$	$[Na^+]$	$[K^+]/[Na^+]$	$[SO_4^{2-}]$	$[Mg^{2+}]$	$[Ca^{2+}]$	pH	Conduct.	Temp.	Alk.	TC	FC	IBE
B.1	Feb-02	74.1	39.2	3.9	9.8	0.39	20.4	16.6	146.1	7.2			351			-3.0
B.1	Sep-02	48.4	41.8	3.8	11.8	0.32	20.5	19.0	141.0	7.1	928	12.8	332			1.0
B.2	Feb-02	49.1	58.3	0.4	22.9	0.02	31.9	11.9	117.6	7.8			245			-0.9
B.2	Sep-02	64.6	56.7	0.5	19.5	0.03	34.5	20.0	116.0	7.5	823	12.0	245			0.2
B.2	Feb-03	62.9	35.2	0.3	19.1	0.02	29.0	11.2	124.3	7.4	806	5.5	249			2.4
B.2	Jun-03	67.5	49.0	0.4	18.0	0.02	41.9	19.0	126.0	7.4	831	13.0	254	D	C	1.3
B.2	Sep-03	61.6	54.5	0.5	18.0	0.03	38.3	19.0	111.0	7.4	811	12.4	252	D	D	-2.8
B.2	Feb-04	72.0	55.8	0.5	19.0	0.03	48.5	21.0	110.0	7.3	824	7.5	222	C	A	-0.8
B.2	Jun-04	64.0	52.0	0.4	20.0	0.02	28.6	16.0	111.0	7.3	791	12.9	297	B	A	-7.8
B.3	Feb-02	50.0		1.1	9.1	0.12		21.6	110.6	7.9			307			
B.3	Sep-02	39.7	32.4	1.4	11.6	0.12	24.2	20.0	114.0	7.3	786	12.9	297			-0.8
B.3	Feb-03	51.6	24.2	1.2	10.2	0.12	32.1	20.4	112.6	7.4	780	10.0	307			-3.5
B.3	Jun-03	47.5	26.4	1.2	9.0	0.13	31.4	23.0	110.0	7.3	775	12.7	300	C	A	-2.3
B.3	Sep-03	45.0	28.1	1.2	10.0	0.12	30.8	23.0	110.0	7.3	766	11.8	312	A	A	-3.5
B.3	Feb-04	50.6	31.4	1.2	9.0	0.13	39.1	22.0	107.0	7.3	771	9.1	302	A	A	-6.1
B.3	Jun-04	45.7	29.4	1.2	9.0	0.13	23.4	23.0	108.0	7.2	766	11.8	360	A	A	-9.1
B.4	Feb-02	48.2	27.7	0.9	9.4	0.09	22.7	18.8	118.2	7.6			307			-1.9
B.4	Sep-02	37.8	28.1	1.0	10.0	0.10	23.5	20.0	113.0	7.3	749	12.1	288			0.6
B.4	Feb-03	61.1	28.3	1.0	11.9	0.08	24.9	17.5	114.7	7.2	762	8.3	280			-1.3
B.4	Jun-03	53.3	5.1	0.8	10.0	0.08	31.4	20.0	122.0	7.3	749	12.0	285	D	B	5.4
B.4	Sep-03	44.0	28.2	1.0	10.0	0.10	31.0	19.0	106.0	7.3	746	12.8	294	D	B	-4.6
B.4	Feb-04	46.7	35.1	1.0	10.0	0.10	35.5	20.0	105.0	7.3	743	10.4	296	C	A	-6.7
B.4	Jun-04	45.8	29.4	1.0	10.0	0.10	18.7	20.0	106.0	7.1	747	13.3	290	D	A	-2.4
B.5	Feb-02	57.6	32.9	3.4	13.4	0.25	17.5	13.3	136.2	7.5			333			-1.8
B.5	Sep-02	55.5	32.5	3.6	13.0	0.28	19.0	14.0	139.0	7.2	856	10.8	332			-0.6
B.5	Feb-03	67.5	19.3	3.3	11.1	0.30	26.3	13.5	140.7	7.2	849	10.0	340			-1.5
B.5	Jun-03	57.7	28.6	3.6	12.0	0.30	29.8	14.0	142.0	7.2	872	10.8	340	C	A	-1.7
B.5	Sep-03	55.1	28.9	4.0	12.0	0.33	29.0	14.0	144.0	7.1	861	10.5	351	B	A	-2.0
B.5	Feb-04	49.1	29.7	3.7	11.0	0.34	34.5	14.0	131.0	7.2	832	10.2	346			-5.7
B.5	Jun-04	51.6	27.4	3.8	11.0	0.35	21.0	14.0	135.0	7.0	827	10.6	393	A	A	-7.8
B.6	Feb-02	47.3	29.1	1.8	10.7	0.16	24.2	16.5	132.2	7.7			336			-2.0
B.6	Sep-02	38.3	28.3	1.4	9.5	0.15	20.8	17.0	131.0	7.2	828	12.9				
B.6	Feb-03	53.5	19.1				26.1			7.2	845	10.2	350			
B.6	Jun-03	52.8	26.8	1.6	10.0	0.16	29.7	17.0	136.0	7.2	835	10.6	335	B	A	-1.5
B.6	Sep-03	50.5	27.8	1.6	10.0	0.16	28.3	17.0	136.0	7.1	830	10.5	348	C	A	-2.7
B.6	Feb-04	45.8	29.9	1.6	10.0	0.16	36.5	17.0	124.0	7.1	820	10.0	337			-5.9
B.6	Jun-04	47.4	29.6	1.4	10.0	0.14	21.6	18.0	130.0	7.1	821	10.6	393	A	A	-8.0
B.7	Feb-02	44.0	29.6	2.5	7.2	0.35	22.7	12.2	141.9	7.8			331			-1.0
B.7	Sep-02	34.1	30.6	0.4	7.9	0.05	23.8	13.0	142.0	7.2	815	12.3	327			0.3
B.7	Feb-03	42.5	23.9	0.4	7.9	0.05	30.5	12.9	139.8	7.2	815	7.2	332			-1.4
B.7	Jun-03	38.9	27.2	0.4	8.0	0.05	30.4	12.0	135.0	7.3	803	12.1	323	B	A	-2.5
B.7	Sep-03	53.7	28.2	0.5	8.0	0.06	29.3	11.0	105.0	7.1	792	11.6	332	A	A	-15.6
B.7	Feb-04	37.4	32.1	0.4	7.0	0.06	38.1	12.0	128.0	7.2	801	10.6	320			-6.2
B.7	Jun-04	37.5	33.5	0.4	8.0	0.05	19.9	13.0	134.0	7.2	810	12.3	326	C	A	-2.3
B.8	Feb-02	81.7	24.0	0.2	6.0	0.03	36.0	8.9	139.2	7.8			282			-2.7
B.8	Sep-02	67.8	22.9	0.3	6.9	0.04	34.7	10.0	137.0	7.3	797	11.0	275			0.0
B.8	Feb-03	92.2	21.8	0.3	7.4	0.04	44.4	10.0	144.5	7.2	839	10.1	282			-1.8
B.8	Jun-03	93.6	23.8	0.2	7.0	0.03	62.3	11.0	149.0	7.4	850	10.6	278	D	B	-2.2
B.8	Sep-03	85.6	26.0	0.4	7.0	0.06	66.3	10.0	149.0	7.2	864	11.4	282	D	A	-3.2
B.8	Feb-04	87.5	27.8	0.2	7.0	0.03	68.8	10.0	141.0	7.2	853	10.7	285	B	A	-6.6
B.9	Feb-02	37.2	36.9	37.9	16.2	2.34	53.6	15.1	114.4	7.3	887	9.5	301			-0.9
B.9	Sep-02	54.5	48.2	53.0	15.0	3.53	38.2	15.0	129.0	7.2	988	12.1	336			-0.4
B.9	Feb-03	26.6	34.3	2.8	18.6	0.15	53.6	13.8	111.2	7.3	815	9.7	291			-4.9
B.9	Jun-03	68.8	57.8	63.0	18.0	3.50	47.6	16.0	134.0	7.1	1083	11.7	358	D	C	-2.4
B.9	Sep-03	54.1	40.9	47.0	14.0	3.36	42.1	14.0	134.0	7.2	937	11.6	338	D	B	0.0
B.9	Feb-04	49.5	42.1	57.0	16.0	3.56	45.8	14.0	119.0	7.2	959	10.6	358	B	A	-4.5
B.9	Jun-04	48.2	44.9	51.0	16.0	3.19	30.5	15.0	122.0	7.1	973	12.1	354	D	C	-2.3
B.10	Feb-02	33.8	40.3	2.1	10.9	0.19	29.2	26.3	106.3	7.1			293			-1.0

Appendix 3 (continued): Groundwater chemistry measured between February 2002 and June 2004 in samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *(Nitrate and sulphate concentrations are in mg/l NO_3^- and mg/l SO_4^{2-} respectively, other concentrations are in mg/l, $[K^+]/[Na^+]$ is the potassium to sodium ratio, conductivity is in µS/cm, temperature is in °C, alkalinity in mg/l $CaCO_3$, total and faecal coliforms are in number of bacteria by 100 ml sample – A = 0, 0 < B ≤ 10, 10 < C ≤ 50 and D > 50, and IBE is the Ion Balance Error)*

Site	Time	$[NO_3^-]$	$[Cl^-]$	$[K^+]$	$[Na^+]$	$[K^+]/[Na^+]$	$[SO_4^{2-}]$	$[Mg^{2+}]$	$[Ca^{2+}]$	pH	Conduct.	Temp.	Alk.	TC	FC	IBE
C.1	Feb-02	30.9	26.6	1.1	24.6	0.04	57.7	11.7	147.1	7.3	927	10.5	371			-2.4
C.1	Sep-02	30.2	24.4	7.0	13.0	0.54	53.6	12.0	141.0	7.2	849	11.0	337			-1.5
C.1	Feb-03	31.9	23.9	4.8	18.1	0.27	47.6	11.2	134.8	7.1	805	6.2	325			-0.7
C.1	Jun-03	47.1	21.4	8.0	21.0	0.38	55.6	13.0	137.0	7.2	862	14.2	324	D	D	0.1
C.1	Sep-03	38.3	22.1	7.0	20.0	0.35	53.4	11.0	127.0	7.2	823	13.3	336	D		-4.5
C.1	Feb-04	51.7	23.1	7.0	17.0	0.41	62.2	12.0	127.0	7.3	825	8.5	322	C	A	-5.6
C.1	Jun-04	41.8	21.6	7.0	20.0	0.35	44.7	13.0	132.0	7.3	853	12.9	341	D	A	-1.8
C.2	Feb-02	78.8	84.1	5.0	31.0	0.16	56.4	16.4	147.9	7.2	1184	7.5	346			-7.0
C.2	Sep-02	60.0	59.4	35.0	16.9	2.07	43.6	13.0	145.0	7.2	1012	11.7	323			-0.4
C.2	Feb-03	76.9	67.4	54.4	28.5	1.91	55.1	14.1	145.5	7.1	1117	7.9	343			-0.4
C.2	Jun-03	73.9	51.4	38.0	18.0	2.11	53.7	14.0	150.0	7.1	1037	12.5	330	D	D	0.2
C.2	Sep-03	67.1	56.8	38.0	17.0	2.24	47.4	12.0	136.0	7.2	994	12.6	334	D	A	-4.3
C.2	Feb-04	82.0	82.9	52.0	29.0	1.79	64.3	15.0	147.0	7.2	1206	9.0	365	A	A	-4.9
C.2	Jun-04	66.7	47.5	38.0	17.0	2.24	40.5	13.0	134.0	7.1	987	13.6	333	B	A	-2.4
C.3	Feb-02	52.0	23.9	6.6	9.9	0.66	23.2	9.4	130.3	7.4	784	10.5	312			-2.2
C.3	Sep-02	72.9	32.6	5.7	11.7	0.49	24.2	11.0	131.0	7.3	813	10.7	275			0.0
C.3	Feb-03	74.7	40.2	6.8	11.2	0.60	24.8	10.1	138.6	7.2	857	9.3	299			-2.5
C.3	Jun-03	74.9	37.3	5.4	11.0	0.49	32.5	10.0	130.0	7.3	825	11.9	270	B	B	-2.5
C.3	Sep-03	73.5	40.4	5.8	13.0	0.45	32.4	10.0	151.0	7.2	845	11.1	287	B	A	1.8
C.3	Feb-04	57.0	33.4	5.6	11.0	0.51	35.8	10.0	122.0	7.2	801	9.8	308	A	A	-7.6
C.3	Jun-04	73.3	33.5	4.9	11.0	0.45	19.7	11.0	123.0	7.4	789	12.2	275	C	A	-2.5
C.4	Feb-02	47.3	27.9	0.8	10.4	0.08	24.5	13.9	121.1	7.3	734	10.0	278			0.3
C.4	Sep-02	44.7	31.6	1.5	11.6	0.13	22.4	16.0	117.0	7.3	756	11.1	283			-0.3
C.4	Feb-03	43.0	31.5	1.5	12.4	0.12	27.6	15.0	116.2	7.2	756	8.6	289			-2.1
C.4	Jun-03	45.9	30.9	1.7	11.0	0.15	28.9	15.0	112.0	7.4	742	12.3	273	A	A	-2.2
C.4	Sep-03	43.4	32.7	1.2	10.0	0.12	29.3	14.0	122.0	7.3	727	11.6	279	A	A	-0.7
C.4	Feb-04	34.8	29.6	1.2	11.0	0.11	37.5	14.0	101.0	7.4	708	9.9	291	A	A	-8.8
C.4	Jun-04	39.0	32.0	1.7	11.0	0.15	19.7	15.0	111.0	7.2	741	12.8	286	A	A	-2.4
C.5	Feb-02	49.2	46.8	10.9	12.2	0.89	25.8	16.2	128.3	7.4	835	9.0	302			-0.9
C.5	Sep-02	50.1	46.3	19.0	15.5	1.23	26.1	14.0	137.0	7.1	916	11.1	332			-0.8
C.5	Feb-03	54.0	53.3	21.5	20.0	1.08	27.2	13.1	142.4	7.2	964	8.7	358			-2.5
C.5	Jun-03	56.0	42.8	18.0	13.0	1.38	35.3	15.0	127.0	7.1	903	16.1	320	B	A	-3.6
C.5	Sep-03	48.8	42.9	19.0	13.0	1.46	34.3	14.0	144.0	7.3	865	12.8	320	C	A	1.5
C.5	Feb-04	48.4	42.0	12.0	12.0	1.00	37.7	15.0	116.0	7.2	822	7.4	308	A	A	-6.3
C.5	Jun-04	51.5	45.2	17.0	15.0	1.13	23.0	14.0	129.0	7.1	888	13.3	323	B	A	-2.0
C.6	Feb-02	30.8	11.6	6.1	10.7	0.57	23.6	7.5	119.0	7.4	688	6.7	298			-0.6
C.6	Sep-02	42.0	35.2	4.7	13.7	0.34	31.7	17.0	115.0	7.3	776	11.2	271			0.7
C.6	Feb-03	34.8	15.9	6.9	10.7	0.64	15.5	8.1	117.5	7.6	688	7.4	298			-0.9
C.6	Jun-03	47.9	28.6	4.7	13.0	0.36	35.8	15.0	109.0	7.3	749	12.3	274	C	A	-2.9
C.6	Sep-03	51.1	36.1	4.5	14.0	0.32	39.0	16.0	113.0	7.2	774	11.1	278	D	C	-3.3
C.6	Feb-04	19.9	15.0	6.9	9.0	0.77	30.0	10.0	95.0	7.6	636	8.9	292	B	A	-8.1
C.7	Feb-02	58.4	27.8	0.5	9.2	0.05	24.0	9.9	133.2	7.4	767	9.5	284			-0.3
C.7	Sep-02	57.5	27.2	0.5	7.9	0.06	21.7	10.0	125.0	7.3	746	12.9	279			-2.1
C.7	Feb-03	74.7	29.5	1.1	10.0	0.11	26.2	9.5	138.6	7.2	804	7.2	282			-0.4
C.7	Jun-03	65.9	25.1	0.5	8.0	0.06	31.0	9.0	124.0	7.4	746	12.1	263	B	A	-2.6
C.7	Sep-03	54.9	28.4	0.5	9.0	0.06	31.2	10.0	127.0	7.4	746	12.0	276	D	A	-1.8
C.7	Feb-04	134.9	47.8	1.5	19.0	0.08	58.1	12.0	159.0	7.3	1005	10.1	288	D	A	-3.5
C.7	Jun-04	61.0	27.5	0.4	8.0	0.05	16.9	10.0	121.0	7.3	726	11.6	273	B	A	-2.4
C.8	Feb-02	79.4	45.1	1.3	25.4	0.05	42.6	12.2	134.0	7.3	913	10.0	299			-3.2
C.8	Sep-02	52.2	38.6	0.8	16.0	0.05	21.6	13.0	125.0	7.3	774	10.7	277			0.7
C.8	Feb-03	69.5	35.8	1.3	17.5	0.07	26.5	11.2	118.6	7.3	760	7.6	264			-2.2
C.8	Jun-03	54.5	32.9	1.1	21.0	0.05	35.1	12.0	121.0	7.3	783	14.0	278	D	B	-0.8
C.8	Sep-03	45.7	39.7	0.8	20.0	0.04	31.1	12.0	119.0	7.2	784	12.3	290	D	B	-3.1
C.8	Feb-04	78.6	41.2	1.5	21.0	0.07	43.6	13.0	128.0	7.3	853	10.1	291	C	A	-4.2
C.8	Jun-04	57.0	32.5	0.8	15.0	0.05	18.4	12.0	114.0	7.1	751	12.7	275	D	B	-2.4

Appendix 3 (continued): Groundwater chemistry measured between February 2002 and June 2004 in samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *(Nitrate and sulphate concentrations are in mg/l NO_3^- and mg/l SO_4^{2-} respectively, other concentrations are in mg/l, $[K^+]/[Na^+]$ is the potassium to sodium ratio, conductivity is in µS/cm, temperature is in °C, alkalinity in mg/l $CaCO_3$, total and faecal coliforms are in number of bacteria by 100 ml sample – A = 0, 0 < B ≤ 10, 10 < C ≤ 50 and D > 50, and IBE is the Ion Balance Error)*

Site	Time	$[NO_3^-]$	$[Cl^-]$	$[K^+]$	$[Na^+]$	$[K^+]/[Na^+]$	$[SO_4^{2-}]$	$[Mg^{2+}]$	$[Ca^{2+}]$	pH	Conduct.	Temp.	Alk.	TC	FC	IBE
C.9	Feb-02	32.6	18.4	3.2	7.7	0.42	12.5	11.6	119.9	7.3	689	8.2	302			0.1
C.9	Sep-02	23.6	15.2	2.1	7.8	0.27	14.6	13.0	112.0	7.3	696	11.7	311			-1.9
C.9	Feb-03	15.2	15.9	3.7	7.8	0.47	9.7	9.7	109.1	7.3	651	4.2	300			-1.6
C.9	Jun-03	8.7	8.8	1.5	8.0	0.19	19.9	12.0	113.0	7.2	687	14.6	330	C	A	-2.7
C.9	Sep-03	19.7	18.0	2.2	9.0	0.24	25.5	12.0	123.0	7.3	686	12.1	320	C	B	-1.2
C.9	Feb-04	22.5	22.7	2.5	8.0	0.31	25.9	13.0	110.0	7.4	695	6.6	314	B	A	-5.8
C.9	Jun-04	12.1	14.5	1.6	8.0	0.20	8.8	13.0	116.0	7.2	700	14.7	338	B	A	-2.1
C.10	Feb-02	85.6	28.5	4.6	8.8	0.53	21.0	12.2	149.2	7.5	835	11.0	302			1.6
C.10	Sep-02	56.3	48.5	8.0	19.3	0.41	26.9	13.0	135.0	7.2	884	11.5	301			-0.1
C.10	Feb-03	61.7	39.6	9.4	13.7	0.69	23.5	12.8	140.6	7.1	884	8.1	330			-1.6
C.10	Jun-03	63.9	46.8	8.0	21.0	0.38	35.7	13.0	123.0	7.4	876	12.3	291	D	D	-3.4
C.10	Sep-03	57.8	52.2	5.6	21.0	0.27	34.9	13.0	132.0	7.3	860	11.9	300	D	C	-2.3
C.10	Feb-04	53.3	30.1	6.9	12.0	0.58	35.2	12.0	121.0	7.2	798	10.0	317	B	A	-6.4
C.10	Jun-04	61.3	48.9	8.0	21.0	0.38	24.1	13.0	127.0	7.1	866	12.0	302	D	A	-2.3
C.11	Feb-02	27.3	60.7	4.8	27.3	0.18	26.7	15.0	131.7	7.3	917	10.0				
C.11	Sep-02	1.2	32.2	3.1	14.8	0.21	11.3	15.0	107.0	7.3	686	11.3	299			1.1
C.11	Feb-03	25.7	49.7	5.6	22.6	0.25	29.0	15.7	134.7	7.1	887	9.1	344			-0.8
C.11	Jun-03	10.8	43.6	5.1	20.0	0.26	29.2	15.0	116.0	7.2	774	11.8	304	D	D	-0.4
C.11	Sep-03	2.0	34.9	3.4	14.0	0.24	20.4	13.0	96.0	7.2	676	11.6	300	B	A	-6.3
C.11	Feb-04	17.6	60.3	5.1	22.0	0.23	36.4	17.0	132.0	7.1	904	9.5	355	A	A	-4.1
C.11	Jun-04	5.6	51.3	2.7	17.0	0.16	17.3	14.0	102.0	7.1	698	11.1	285	B	A	-3.7
C.12	Feb-02	27.5	15.5	0.4	10.7	0.03	33.0	9.4	121.6	7.3	714	11.0	302			-2.0
C.12	Sep-02	33.5	22.1	0.7	11.3	0.06	24.6	13.0	127.0	7.1	762	11.8	310			0.3
C.12	Feb-03	50.6	25.9	0.6	11.1	0.06	28.0	11.5	136.6	7.3	813	10.6	328			-2.5
C.12	Jun-03	48.3	21.1	0.7	10.0	0.07	33.9	12.0	127.0	7.3	759	12.6	303	A	A	-2.3
C.12	Sep-03	43.1	25.8	0.8	11.0	0.07	33.4	12.0	119.0	7.2	769	12.0	316	A	A	-6.4
C.12	Feb-04	39.5	24.4	0.7	10.0	0.07	39.0	12.0	125.0	7.2	750	11.6	316		A	-4.9
C.12	Jun-04	45.8	23.9	0.7	10.0	0.07	20.4	13.0	121.0	7.1	764	12.4	309	A	A	-3.0
C.13	Feb-02	43.2	31.9	9.5	14.9	0.64	24.2	12.0	122.5	7.3	780	9.0	300			-0.7
C.13	Sep-02	35.2	36.0	4.6	12.7	0.36	25.0	14.0	133.0	7.3	762	13.5	275			5.4
C.13	Feb-03	58.3	38.9	35.6	22.8	1.56	30.1	9.1	139.5	7.1	919	10.3	334			1.4
C.13	Jun-03	40.8	33.7	33.0	20.0	1.65	35.8	8.0	127.0	7.1	868	13.8	321	C	B	-0.4
C.13	Sep-03	34.8	38.2	33.0	20.0	1.65	37.8	8.0	129.0	7.1	863	13.9	325	C	B	-0.7
C.13	Feb-04	55.3	38.0	29.0	17.0	1.71	39.4	9.0	112.0	7.2	864	10.2	319	A	A	-8.0
C.13	Jun-04	49.3	39.8	29.0	19.0	1.53	25.7	9.0	124.0	7.1	864	12.6	317	D	B	-1.7
C.14	Feb-02	43.4	31.2	2.2	11.3	0.20	23.1	11.5	111.8	7.3	717	9.0	270			-2.6
C.15	Feb-02	58.8	28.8	1.6	21.7	0.07	43.2	11.8	134.3	7.3	839	9.0	309			-1.0
C.15	Sep-02	122.5		2.5	42.0	0.06		17.0	155.0	7.1	1100	11.6	339			
C.15	Feb-03	71.2	39.7	1.9	18.3	0.10	38.2	13.7	138.5	7.2	891	9.5	310			-2.1
C.15	Jun-03	104.6	36.4	2.0	46.0	0.04	44.9	17.0	137.0	7.1	1017	12.9	350	C	C	-1.7
C.15	Sep-03	112.0	45.8	2.6	38.0	0.07	46.1	16.0	150.0	7.1	1049	12.0	347	D	A	-2.2
C.15	Jun-04	117.3	40.4	2.5	39.0	0.06	40.8	15.0	138.0	7.0	1012	12.2	332	C	A	-3.1
C.16	Feb-02	26.2	25.4	0.8	7.5	0.10	20.0	18.3	94.5	7.5	653	10.8	268			-2.6
C.16	Sep-02	23.6	25.5	0.8	8.5	0.09	19.0	15.0	95.0	7.4	655	11.3				
C.16	Feb-03	53.7	51.4	18.2	17.6	1.03	25.5	14.4	140.1	7.1	927	10.3	340			-1.3
C.16	Jun-03	28.8	5.1	0.9	8.0	0.11	27.6	20.0	94.0	7.4	658	12.0	264	B	A	1.8
C.16	Sep-03	22.9	27.5	0.9	9.0	0.10	28.7	2.0	95.0	7.4	655	11.7	270	B	A	-14.6
C.16	Feb-04	24.0	29.4	0.9	8.0	0.11	31.6	19.0	88.0	7.4	650	11.0	270	A	A	-7.0
C.16	Jun-04	24.4	27.6	0.9	8.0	0.11	15.9	19.0	90.0	7.2	653	12.2	264	A	A	-2.8
C.17	Feb-02	10.0	21.6	0.8	8.3	0.10	16.8	14.0	94.4	7.6			270			-2.2
C.17	Sep-02	26.1	31.3	1.3	10.6	0.12	23.7	13.0	108.0	7.4	686	10.9	261			-0.4
C.17	Feb-03	46.3	38.9	3.6	10.9	0.33	30.1	10.6	118.2	7.3			260			-2.2
C.17	Jun-03	49.3	5.1	1.3	13.0	0.10	34.7	11.0	120.0	7.4	751	11.1	262	C	B	4.1
C.17	Sep-03	39.4	35.1	1.2	12.0	0.10	35.4	10.0	117.0	7.5	716	11.6	257	C	A	-1.9
C.17	Feb-04	30.8	48.6	1.5	11.0	0.14	34.3	12.0	103.0	7.3	698	10.4	287	B	A	-11.2
C.17	Jun-04	15.6	28.2	1.0	10.0	0.10	18.4	14.0	96.0	7.2	628	11.2	264	B	A	-2.4
C.18	Feb-02	43.4	35.8	1.6	10.8	0.15	23.7	13.7	122.2	7.1			282			-0.7
C.19	Feb-02	56.2	41.3	2.3	14.6	0.15	34.2	10.7	131.3	7.1			276			-1.1
C.20	Feb-02	43.2	36.7	1.7	9.9	0.17	24.0	11.9	120.4	7.3			281			-2.6

Appendix 3 (continued): Groundwater chemistry measured between February 2002 and June 2004 in samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *(Nitrate and sulphate concentrations are in mg/l NO_3^- and mg/l SO_4^{2-} respectively, other concentrations are in mg/l, $[K^+]/[Na^+]$ is the potassium to sodium ratio, conductivity is in µS/cm, temperature is in °C, alkalinity in mg/l $CaCO_3$, total and faecal coliforms are in number of bacteria by 100 ml sample – A = 0, 0 < B ≤ 10, 10 < C ≤ 50 and D > 50, and IBE is the Ion Balance Error)*

Site	Time	$[NO_3^-]$	$[Cl^-]$	$[K^+]$	$[Na^+]$	$[K^+]/[Na^+]$	$[SO_4^{2-}]$	$[Mg^{2+}]$	$[Ca^{2+}]$	pH	Conduct.	Temp.	Alk.	TC	FC	IBE
O.1	Feb-02	32.8	21.8	0.7	7.8	0.08	34.4		108.0	7.3	776	8.8	318			
O.1	Feb-03	32.7	16.9	0.7	8.3	0.08	41.5	27.0	107.3	7.3	767	10.0	320			-1.9
O.1	Jun-03	28.8	20.2	0.6	8.0	0.08	46.3	28.0	108.0	7.3	763	12.3	314	D	A	-1.4
O.1	Sep-03	30.9	21.9	0.7	9.0	0.08	44.6	24.0	118.0	7.3	779	12.1	328	D	A	-2.0
O.1	Feb-04	27.1	23.4	0.7	8.0	0.09	49.6	24.0	102.0	7.2	756	10.3	314			-6.1
O.1	Jun-04	28.5	22.9	0.6	8.0	0.08	34.6	25.0	106.0	7.1	759	12.5	381	A	A	-10.1
O.2	Feb-02	33.7	22.4	1.1	10.3	0.10	20.8	15.5	117.7	7.3	724	10.7	298			0.4
O.2	Feb-03	34.4	18.5	1.1	11.3	0.10	29.0	15.9	111.8	7.3	726	10.3	299			-1.7
O.2	Jun-03	32.4	23.1	1.2	10.0	0.12	29.8	16.0	112.0	7.4	712	12.4	291	B	A	-1.7
O.2	Sep-03	31.7	24.5	1.4	11.0	0.13	28.6	15.0	108.0	7.3	714	11.8	301	B	A	-4.5
O.2	Feb-04	30.7	28.1	1.2	11.0	0.11	37.1	15.0	107.0	7.3	718	10.8	298			-6.3
O.2	Jun-04	29.8	27.7	1.4	11.0	0.13	21.0	15.0	108.0	7.2	719	12.0	357	A	A	-10.7
O.3	Feb-02	37.9		2.7	11.4	0.24		14.1	121.4	7.3	754	8.0	299			
O.3	Feb-03	35.8	26.3	2.9	14.4	0.20	32.2	14.4	109.1	7.2	765	8.4	307			-5.2
O.3	Jun-03	37.4	30.7	2.8	14.0	0.20	30.1	15.0	116.0	7.4	760	12.9	300	C	A	-2.5
O.3	Sep-03	30.9	29.0	3.3	15.0	0.22	30.1	15.0	126.0	7.3	753	11.9	291	B	A	3.1
O.3	Feb-04	29.7	31.0	3.2	15.0	0.21	37.4	15.0	112.0	7.3	763	7.7	311			-5.0
O.3	Jun-04	39.2	35.8	3.3	16.0	0.21	26.4	15.0	114.0	7.2	785	12.5	360	A	A	-9.8
O.4	Feb-02	18.6	28.4	1.1	15.6	0.07	19.1	20.5	103.5	7.3	749	10.4	310			-0.9
O.4	Feb-03	39.3	61.5	1.9	35.5	0.05	36.0	16.1	134.7	7.2	965	10.8	333			-0.7
O.4	Jun-03	35.4	66.2	1.7	31.0	0.05	36.5	19.0	136.0	7.3	880	11.7	318	B	A	0.9
O.4	Sep-03	39.4	56.4	2.4	28.0	0.09	34.3	15.0	133.0	7.2	909	11.3	286	A	A	2.7
O.4	Feb-04	24.6	54.6	1.6	23.0	0.07	36.3	20.0	110.0	7.2	789	10.8	316			-4.9
O.4	Jun-04	18.3	38.1	1.3	19.0	0.07	19.0	21.0	96.0	7.2	713	11.4	369	A	A	-10.7
O.5	Feb-02	41.7	22.2	1.3	8.9	0.14	19.6	17.0	114.8	7.5	729	10.1	298			-0.8
O.5	Feb-03	33.0	19.1	1.3	8.7	0.15	29.2	16.9	111.1	7.4	733	9.6	302			-2.5
O.5	Jun-03	30.2	21.5	1.3	9.0	0.14	28.4	18.0	110.0	7.6	723	11.6	304	B	A	-2.5
O.5	Sep-03	29.6	22.3	1.6	9.0	0.18	27.8	16.0	113.0	7.3	713	11.1	292	A	A	-0.9
O.5	Feb-04	30.1	26.6	1.4	9.0	0.16	36.7	17.0	110.0	7.3	723	10.5	297			-4.1
O.5	Jun-04	29.1	25.8	1.7	9.0	0.19	23.8	17.0	112.0	7.3	725	11.0	369	A	A	-10.0
O.6	Feb-02	12.9	14.6	0.8	7.2	0.11	16.7	21.0	83.6	7.4	620	8.0	283			-3.1
O.6	Feb-03	16.3	12.2	0.9	7.8	0.12	25.0	21.6	93.0	7.4	649	8.9	295			-1.8
O.6	Jun-03	18.5	17.2	0.9	7.0	0.13	27.1	22.0	97.0	7.5	663	13.5	292	D	A	-1.5
O.6	Sep-03	10.7	18.0	1.0	8.0	0.13	26.2	21.0	88.0	7.4	638	12.7	298	D	A	-5.0
O.6	Feb-04	20.3	21.9	0.9	7.0	0.13	41.2	19.0	96.0	7.3	679	8.7	295			-7.1
O.6	Jun-04	22.1	22.8	0.9	7.0	0.13	23.3	19.0	103.0	7.3	683	12.3	352	C	A	-9.6
O.7	Feb-03	44.0	42.1	2.3	31.0	0.07	35.7	15.0	139.2	7.3	921	8.2	343			0.5
O.7	Jun-03	48.2	52.1	2.3	32.0	0.07	37.6	15.0	135.0	7.4	940	13.1	284	A	A	3.9
O.7	Sep-03	45.5	54.4	2.7	30.0	0.09	35.5	14.0	142.0	7.4	933	11.9	294	A	A	3.9
O.7	Feb-04	44.4	50.4	2.3	24.0	0.10	40.4	15.0	133.0	7.3	903	8.7	338			-4.1
O.7	Jun-04	44.3	62.3	2.6	31.0	0.08	27.5	15.0	135.0	7.1	958	12.0	399	A	A	-8.0
O.8	Feb-02	40.4	30.4	1.5	9.2	0.16	33.3	18.0	135.8	7.2	778	8.9	312			1.4
O.8	Feb-03	43.5	19.9	1.3	8.9	0.14	35.7	19.6	105.2	7.2	779	5.8	312			-6.2
O.8	Jun-03	34.8	24.3	1.2	9.0	0.13	36.9	20.0	117.0	7.3	763	14.6	303	C	A	-1.1
O.8	Sep-03	32.3	27.3	1.4	10.0	0.14	37.3	20.0	120.0	7.2	764	12.4	288	B	A	1.7
O.8	Feb-04	33.1	29.7	1.3	10.0	0.13	46.2	20.0	112.0	7.2	864	7.5	305			-4.5
O.8	Jun-04	31.9	29.7	1.2	9.0	0.13	30.2	20.0	112.0	7.2	763	13.9	365	B	A	-9.6
O.9	Feb-02	62.1	39.7	1.5	9.0	0.16	27.1	20.8	127.0	7.1	814	10.4	304			-1.7
O.9	Feb-03	61.4	25.8	1.3	9.5	0.13	31.3	21.8	123.1	7.2	817	9.8	307			-0.7
O.9	Jun-03	59.4	32.3	1.3	9.0	0.14	32.9	21.0	128.0	7.5	808	12.8	298	A	A	0.2
O.9	Sep-03	58.5	32.0	1.4	9.0	0.16	32.2	20.0	122.0	7.4	806	11.5	296	A	A	-1.7
O.9	Feb-04	57.1	33.7	1.4	10.0	0.14	39.4	20.0	118.0	7.4	801	9.8	300			-4.2
O.9	Jun-04	58.6	34.4	1.5	9.0	0.17	24.1	20.0	120.0	7.4	805	12.8	355	A	A	-8.2
O.10	Feb-02	10.0	26.3	0.8	10.2	0.08	22.1	14.9	94.6	7.2	645	10.2	277			-3.7
O.10	Feb-03	12.6	17.9	0.9	11.2	0.08	27.6	16.4	94.9	7.3	649	5.7	276			-1.6
O.10	Jun-03	15.6	25.6	0.8	12.0	0.07	30.7	18.0	94.0	7.4	641	13.7	262	B	A	-1.0

Appendix 3 (continued): Groundwater chemistry measured between February 2002 and June 2004 in samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *(Nitrate and sulphate concentrations are in mg/l NO_3^- and mg/l SO_4^{2-} respectively, other concentrations are in mg/l, $[K^+]/[Na^+]$ is the potassium to sodium ratio, conductivity is in µS/cm, temperature is in °C, alkalinity in mg/l $CaCO_3$, total and faecal coliforms are in number of bacteria by 100 ml sample – A = 0, 0 < B ≤ 10, 10 < C ≤ 50 and D > 50, and IBE is the Ion Balance Error)*

Site	Time	$[NO_3^-]$	$[Cl^-]$	$[K^+]$	$[Na^+]$	$[K^+]/[Na^+]$	$[SO_4^{2-}]$	$[Mg^{2+}]$	$[Ca^{2+}]$	pH	Conduct.	Temp.	Alk.	TC	FC	IBE
O.11	Feb-02	33.3	32.1	0.7	11.6	0.06	34.5	11.9	128.6	7.0	814	12.1	331			-5.1
O.11	Feb-03	36.6	31.8	6.9	13.1	0.53	36.1	12.0	153.0	7.2	782	18.5	306			5.7
O.11	Jun-03	32.6	28.4	7.0	12.0	0.58	38.5	15.0	126.0	7.3	782	17.3	306			-0.2
O.11	Sep-03	29.8	28.3	8.0	13.0	0.62	39.1	15.0	123.0	7.2	782	13.3	316			-1.6
O.11	Feb-04	28.2	30.2	8.0	12.0	0.67	46.7	14.0	124.0	7.2	794	15.4	327			-4.5
O.11	Jun-04	27.4	28.9	8.0	11.0	0.73	30.9	16.0	117.0	7.2	778	16.2				
O.12	Feb-02	65.3	40.9	2.4	10.0	0.24	27.5	16.5	126.5	7.1	838	8.5	306			-4.3
O.12	Feb-03	75.3	26.1	2.3	12.1	0.19	30.0	17.6	134.6	7.4	865	9.8	320			-1.3
O.12	Jun-03	75.2	41.6	2.8	12.0	0.23	34.2	18.0	135.0	7.3	863	12.8	300	A	A	-1.6
O.12	Sep-03	73.1	35.1	2.5	11.0	0.23	33.7	17.0	135.0	7.2	856	12.2	289	C	A	0.1
O.12	Feb-04	73.6	40.0	2.5	11.0	0.23	42.0	18.0	131.0	7.2	866	10.0	308			-4.4
O.12	Jun-04	59.1	39.6	2.6	11.0	0.24	26.6	18.0	126.0	7.2	858	12.0	357	A	A	-8.0
O.13	Feb-02	50.2	33.8	2.4	9.3	0.26	27.8	16.4	121.2	7.2	776	9.2	296			-2.5
O.13	Feb-03	32.8	20.0	4.3	9.2	0.46	29.6	16.8	116.0		743	10.3	311			-1.6
O.13	Jun-03	31.3	20.9	3.2	9.0	0.36	27.5	16.0	113.0	7.3	733	11.6	310		A	-2.9
O.13	Sep-03	29.9	21.5	2.9	9.0	0.32	27.5	15.0	106.0	7.3	715	11.5	290	B	A	-3.3
O.13	Feb-04	32.9	30.9	3.1	9.0	0.34	40.6	17.0	106.0	7.3	752	10.4	299			-6.9
O.13	Jun-04	28.6	25.2	3.4	9.0	0.38	22.2	17.0	109.0	7.3	723	11.2	362	A	A	-9.6
BHO.1	Feb-03	35.4	27.5	7.9	5.2	1.52	27.2	10.3	112.2	7.3	678	8.6	289			-5.6
BHO.1	Jun-03	44.8	18.7	11.0	6.0	1.83	37.7	11.0	128.0	7.2	765	14.7	316			-3.3
BHO.1	Sep-03	70.2	13.9	18.0	6.0	3.00	60.5	13.0	143.0	7.3	883	13.0	346			-4.1
BHO.1	Feb-04	67.6	12.2	11.0	5.0	2.20	55.3	12.0	136.0	7.3	810	9.8				
BHO.1	Jun-04	66.6	14.1	17.0	5.0	3.40	47.4	13.0	138.0	7.1	852	12.4				
BHO.3B	Feb-03	7.0	18.0	4.3	4.7	0.91	20.8	9.8	147.5	6.8	798	9.3	399			-3.1
BHO.3B	Jun-03	4.3	7.5	3.9	4.0	0.98	9.1	11.0	143.0	6.9	805	11.0	403			-1.2
BHO.3B	Sep-03	5.5	17.8	1.7	6.0	0.28	20.7	11.0	150.0	6.9	834	12.3	417			-3.7
BHO.3B	Feb-04	3.3	12.6	8.0	5.0	1.60	43.2	13.0	190.0	6.8	1032	9.1	526			-3.8
BHO.4	Feb-03	89.0	28.6	7.9	8.5	0.93	31.2	12.2	129.5	7.2	804	8.7	266			-1.1
BHO.4	Jun-03	83.6	27.4	5.6	7.0	0.80	34.2	12.0	116.0	7.3	743	10.9	250			-4.1
BHO.4	Sep-03	74.4	25.8	5.3	8.0	0.66	33.8	11.0	116.0	7.3	718	11.6	248			-2.9
BHO.4	Feb-04	90.0	27.1	13.0	8.0	1.63	40.3	11.0	111.0	7.3	738	9.5				
BHO.4	Jun-04	78.0	25.7	4.8	7.0	0.69	23.5	12.0	114.0	7.2	733	10.9				
BHO.4A	Feb-03	71.5	30.0	6.7	7.8	0.86	29.8	11.5	123.7	7.4	770	9.5	129			19.0
BHO.4A	Jun-03	79.8	30.7	6.7	7.0	0.96	32.5	12.0	121.0	7.5	763	13.4	276			-5.3
BHO.4A	Sep-03	75.6	29.6	7.0	8.0	0.88	32.6	11.0	120.0	7.5	755	11.8	264			-3.8
BHO.4A	Feb-04	77.1	27.7	6.3	8.0	0.79	38.7	12.0	120.0	7.3	755	10.5				
BHO.4A	Jun-04	74.9	27.4	6.1	7.0	0.87	24.6	11.0	114.0	7.3	744	11.5				
BHO.5	Feb-03	53.3	15.9	2.1	7.0	0.30	20.9	6.8	118.2	7.2	721	7.6	292			-5.3
BHO.5	Jun-03	69.5	15.4	6.6	6.0	1.10	26.7	10.0	135.0	7.3	770	12.2	321			-3.3
BHO.5	Feb-04	130.2	59.8	2.1	9.0	0.23	33.4	9.0	128.0	7.4	837	8.3				
BHO.6	Feb-03	49.8	17.4	0.4	6.4	0.06	24.0	12.4	119.7	7.4	684	9.1	291			-2.3
BHO.6	Jun-03	75.3	23.4	0.4	6.0	0.07	27.4	12.0	121.0	7.3	721	11.8	263			-2.8
BHO.6	Sep-03	79.6	26.2	0.5	7.0	0.07	28.7	12.0	117.0	7.3	750	13.1	272			-6.0
BHO.6	Feb-04	73.5	21.5	1.3	5.0	0.26	33.3	12.0	124.0	7.3	743	9.8				
BHO.6	Jun-04	62.6	23.8	0.5	6.0	0.08	17.4	13.0	122.0	7.3	748	12.0				
BHO.7	Feb-03	51.9	37.6	0.2	18.5	0.01	32.0	6.5	122.1	7.3	755	7.8	264			-2.7
BHO.7	Jun-03	66.3	42.3	0.2	8.0	0.03	30.6	8.0	139.0	7.4	779	12.6	275			-2.7
BHO.7	Sep-03	63.8	40.0	0.2	8.0	0.03	31.6	9.0	132.0	7.2	784	13.2	277			-4.2
BHO.7	Feb-04	51.7	37.8	0.2	16.0	0.01	37.7	7.0	124.0	7.4	770	8.7				
BHO.7	Jun-04	82.9	59.6	0.2	9.0	0.02	23.1	9.0	133.0	7.1	840	12.0				
BHO.8	Feb-03	100.3	32.4	4.6	10.3	0.44	34.2	8.0	124.6	7.3	775	8.3	242			-4.1
BHO.8	Jun-03	96.5	31.6	4.7	9.0	0.52	33.1	7.0	115.0	7.5	707	10.7	210			-3.6
BHO.8	Sep-03	94.9	32.2	5.0	10.0	0.50	32.6	7.0	113.0	7.4	709	12.1	215			-4.5
BHO.8	Feb-04	94.1	23.7	4.2	9.0	0.47	31.6	8.0	111.0	7.3	715	8.8				
BHO.8	Jun-04	52.5	17.4	4.0	7.0	0.57	15.4	7.0	95.0	7.3	584	10.8				

Appendix 3 (continued): Groundwater chemistry measured between February 2002 and June 2004 in samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *(Nitrate and sulphate concentrations are in mg/l NO_3^- and mg/l SO_4^{2-} respectively, other concentrations are in mg/l, $[K^+]/[Na^+]$ is the potassium to sodium ratio, conductivity is in µS/cm, temperature is in °C, alkalinity in mg/l $CaCO_3$, total and faecal coliforms are in number of bacteria by 100 ml sample – A = 0, 0 < B ≤ 10, 10 < C ≤ 50 and D > 50, and IBE is the Ion Balance Error)*

Site	Time	$[NO_3^-]$	$[Cl^-]$	$[K^+]$	$[Na^+]$	$[K^+]/[Na^+]$	$[SO_4^{2-}]$	$[Mg^{2+}]$	$[Ca^{2+}]$	pH	Conduct.	Temp.	Alk.	TC	FC	IBE
BHM.1	Feb-02	35.8		1.2	9.6	0.13		2.0	126.0	7.2	783	11.8				
BHM.1	Dec-02	40.5	25.6	0.5	6.1	0.07	39.6	14.4	153.2	7.0						
BHM.1	Jun-03	17.5	11.4	0.5	5.0	0.10		14.0	128.0	7.1	722	13.5				
BHM.2	Feb-02	81.1		1.2	8.0	0.15		10.0	148.0	6.9	850	12.0				
BHM.2	Dec-02	48.3	13.9	1.0	7.8	0.13	34.1	10.2	163.5	6.7						
BHM.2	Jun-03	67.4	14.4	0.9	8.0	0.11		10.0	158.0	6.8	886	12.7				
BHM.2	Sep-03	81.7	19.8	1.3	8.0	0.16	34.7	11.0	160.0	6.9	910	12.7				
BHM.3	Feb-02	94.5		22.0	13.2	1.67		18.0	175.0	6.9	1087	11.7				
BHM.3	Dec-02	41.6	13.5	13.4	0.9	15.76	30.5	15.3	164.3	7.0						
BHM.3	Jun-03	42.6	5.1	14.0	8.0	1.75		17.0	171.0	6.8	963	13.6				
BHM.3	Sep-03	49.6	14.0	16.0	9.0	1.78	26.5	17.0	167.0	6.9	977	12.9				
BHM.4	Feb-02	78.6		30.0	14.3	2.10		18.0	187.0	6.8	1203	12.5				
BHM.4	Dec-02	83.7	30.0	25.8	1.3	19.25	36.7	15.7	203.9	6.8						
BHM.4	Jun-03	46.4	36.6	25.0	15.0	1.67		22.0	186.0	6.7	1153	14.1				
BHM.4	Sep-03	19.1	43.8	37.0	17.0	2.18	21.9	23.0	184.0	6.9	1240	13.0				
BHM.5	Feb-02	62.9		0.5	7.0	0.07		15.0	125.0	7.1	782	12.1				
BHM.5	Dec-02	63.1	45.2	0.4	0.8	0.52	19.6	15.9	138.8	7.1						
BHM.5	Jun-03	60.2	5.4	0.5	8.0	0.06		16.0	132.0	7.1	813	13.0				
BHM.5	Sep-03	55.7	38.0	0.6	9.0	0.07	20.2	15.0	122.0	7.1	790	12.4				
BHM.6	Feb-02	212.0		1.1	11.0	0.10		17.0	174.0	7.0	1063	12.6				
BHM.7	Feb-02	95.7		3.4	11.0	0.31		16.0	147.0	7.0	875	12.6				
BHM.7	Dec-02	68.0	18.0	1.6	1.4	1.18	37.1	16.9	162.8	6.9						
BHM.7	Jun-03	60.6	16.8	1.3	11.0	0.12		16.0	149.0	6.9	909	12.8				
BHM.7	Sep-03	59.8	19.9	1.6	10.0	0.16	30.1	17.0	153.0	6.9	925	13.0				
BHM.8	Feb-02	94.5		5.2	11.3	0.46		17.0	145.0	7.0	879	12.0				
BHM.8	Dec-02	79.4	15.6	4.5	0.9	4.87	33.8	18.9	153.0	7.0						
BHM.8	Jun-03	58.2	5.3	4.9	9.0	0.54		19.0	141.0	6.9	927	13.1				
BHM.8	Sep-03	62.1	18.3	4.7	10.0	0.47	27.4	18.0	145.0	7.0	904	13.0				
BHM.9	Feb-02	60.8		2.6	8.6	0.30		11.0	136.0	7.1	785	12.0				
BHM.9	Dec-02	45.9	23.1	2.5	0.8	2.99	26.2	10.1	133.5	7.0						
BHM.9	Jun-03	47.7	5.3	2.5	8.0	0.31		11.0	128.0	7.0	786	13.0				
BHM.9	Sep-03	50.0	24.9	2.8	9.0	0.31	23.0	11.0	126.0	7.0	780	13.0				
BHM.10	Jun-03	5.7	3.2	3.9	2.1	1.86		3.0	88.0	7.3	495	14.4				

Appendix 4: Isotopic composition of groundwater nitrate and groundwater measured between September 2002 and June 2004 in samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *($\delta^{15}N\text{-}NO_3^-$ is reported with its standard deviation (SD) in permils ‰ against AIR, $\delta^{18}O\text{-}NO_3^-/\delta^{18}O\text{-}H_2O$ and $\delta^2H\text{-}H_2O$ in permils ‰ against V-SMOW, % N refers to the mass percentage of nitrogen measured in $AgNO_3$ samples while % C relates to the mass percentage of C-bearing impurities measured in $AgNO_3$)*

Site	Time	$\delta^{15}N\text{-}NO_3^-$	SD $\delta^{15}N$	$\delta^{18}O\text{-}NO_3^-$	SD $\delta^{18}O$	% N	% C	$\delta^{18}O\text{-}H_2O$	SD $\delta^{18}O$	$\delta^2H\text{-}H_2O$	SD δ^2H
B.1	Sep-02	4.3	0.0	3.1	0.1	7.9		-7.1	0.2	-44.6	0.7
B.2	Sep-02	3.6	0.0	0.9	0.1	6.9		-7.2	0.1	-43.5	0.5
B.2	Feb-03	2.7	0.1	-0.5	0.0	7.8	< 0.1	-7.1	0.1	-46.7	0.6
B.2	Jun-03	3.8	0.0	0.8	0.3	7.9		-7.2	0.1	-44.5	0.4
B.2	Sep-03	4.0	0.0	0.6	0.0	7.9					
B.2	Feb-04	4.4	0.1	1.2	1.1	7.6	< 0.1				
B.2	Jun-04	2.9	0.1	3.7	0.1	7.7	< 0.1				
B.3	Sep-02	5.5	0.0	1.7	0.1	7.9		-7.0	0.0	-43.7	0.2
B.3	Feb-03	5.2	0.1	1.1	0.4	7.9	< 0.1	-7.1	0.1	-42.6	0.5
B.3	Jun-03	5.2	0.0	2.0	0.2	8.2	< 0.1	-7.4	0.1	-46.0	1.1
B.3	Sep-03	5.0	0.0	2.0		8.0	< 0.1				
B.3	Feb-04	5.3	0.1	2.3	0.5	7.7	< 0.1				
B.3	Jun-04	5.5	0.0	4.0	0.5	7.8	< 0.1				
B.4	Sep-02	4.6	0.0	2.2	1.1	8.0	< 0.1	-7.0	0.0	-43.9	0.4
B.4	Feb-03	4.0	0.0	1.1	0.2	8.1		-8.9	0.4	-46.6	2.3
B.4	Jun-03	4.5	0.0	2.7	0.2	8.1	< 0.1	-7.7	0.1	-46.1	0.6
B.4	Sep-03	4.7	0.0	2.3	0.1	7.8					
B.4	Feb-04	4.5	0.1	2.3	0.4	7.6	< 0.1				
B.4	Jun-04	4.7	0.0	1.7	1.2	8.1	< 0.1				
B.5	Sep-02	5.5	0.1	1.3	0.1	8.0	< 0.1	-7.1	0.0	-45.2	0.5
B.5	Feb-03	5.0	0.0	1.4	0.1	8.0	< 0.1	-7.2	0.0	-46.0	0.4
B.5	Jun-03	5.3	0.0	1.4	0.4	8.1	< 0.1	-7.5	0.1	-43.0	0.4
B.5	Sep-03	5.6	0.0	1.9	0.1	7.9	< 0.1				
B.5	Feb-04	5.7	0.0	1.8	0.3	7.6	< 0.1				
B.5	Jun-04	5.7	0.0	3.6	0.4	7.9	< 0.1				
B.6	Sep-02	5.7	0.0	0.8	0.4	8.0	< 0.1	-7.1	0.0	-41.4	1.7
B.6	Feb-03	5.4	0.1	2.3	0.0	8.1	< 0.1	-7.4	0.0	-42.7	0.2
B.6	Jun-03	5.4	0.1	2.1	0.4	6.8		-7.4	0.2	-42.9	0.5
B.6	Sep-03	5.4	0.0	2.2	0.1	7.9	< 0.1				
B.6	Feb-04	5.7	0.0	2.8	0.6	7.7	< 0.1				
B.6	Jun-04	6.0	0.0	4.9	0.3	7.8	< 0.1				
B.7	Sep-02	7.6	0.0	4.2	0.6	6.9		-7.0	0.1	-42.5	0.2
B.7	Feb-03	7.7	0.0	4.2	0.5	8.0	< 0.1	-6.8	0.1	-43.2	0.8
B.7	Jun-03	7.4	0.0	3.9	0.3	8.1	< 0.1	-7.1	0.0	-42.8	0.5
B.7	Sep-03	7.3	0.0	4.3	0.5	7.9	< 0.1				
B.7	Feb-04	8.4	0.1	5.5	1.1	8.0	< 0.1				
B.7	Jun-04	8.6	0.1	4.5	0.3	8.1	< 0.1				
B.8	Sep-02	5.3	0.0	-0.2	0.1	6.8		-7.3	0.1	-46.1	0.7
B.8	Feb-03	6.3	0.0	2.6	0.2	8.0		-7.2	0.1	-42.6	1.0
B.8	Jun-03	6.6	0.0	2.7	0.1	7.6		-6.9	0.1	-42.9	1.1
B.8	Sep-03	6.8	0.1	3.2	0.3	7.8					
B.8	Feb-04	6.6	0.0	3.7	1.0	7.7	< 0.1				
B.9	Sep-02	10.2	0.1	1.5	0.0	8.0		-7.0	0.2	-45.0	0.5
B.9	Feb-03	8.1	0.1	3.7	0.2			-6.9	0.3	-44.8	1.5
B.9	Jun-03	11.9	0.1	4.9	0.2			-7.2	0.0	-40.8	0.9
B.9	Sep-03	8.6	0.1	3.0		7.8					
B.9	Feb-04	10.1	0.1	3.4	0.4	7.5	< 0.1				
B.9	Jun-04	10.4	0.1	2.9	0.8	7.8	< 0.1				
C.1	Sep-02	8.7	0.0	1.6	0.1	7.8		-7.2	0.2	-47.0	0.5
C.1	Feb-03	8.7	0.1	3.2	0.1	8.3	< 0.1	-7.2	0.1	-43.8	0.3
C.1	Jun-03	7.9	0.1	3.2	0.0	7.9		-7.2	0.2	-42.1	0.3
C.1	Sep-03	8.2	0.1	2.9	0.2	7.7					
C.1	Feb-04	8.0	0.0	2.0	0.2	7.8	< 0.1				
C.1	Jun-04	8.7	0.0	2.3	1.4	7.7	< 0.1				
C.2	Sep-02	6.7	0.0	0.0	0.1	8.2	< 0.1	-7.1	0.0	-44.8	0.8
C.2	Feb-03	7.8	0.1	4.2	0.1			-6.6	0.1	-43.6	0.4
C.2	Jun-03	7.0	0.1	4.3	0.0			-7.5	0.1	-45.6	0.8
C.2	Sep-03	6.9	0.1	2.1	0.3	7.9					
C.2	Feb-04	7.7	0.0	2.9	0.1	7.4	< 0.1				
C.2	Jun-04	6.9	0.0	2.1	1.0	7.8	< 0.1				

Appendix 4 (continued): Isotopic composition of groundwater nitrate and groundwater measured between September 2002 and June 2004 in samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *($\delta^{15}N\text{-}NO_3^-$ is reported with its standard deviation (SD) in permils ‰ against AIR, $\delta^{18}O\text{-}NO_3^-/\delta^{18}O\text{-}H_2O$ and $\delta^2H\text{-}H_2O$ in permils ‰ against V-SMOW, % N refers to the mass percentage of nitrogen measured in $AgNO_3$ samples while % C relates to the mass percentage of C-bearing impurities measured in $AgNO_3$)*

Site	Time	$\delta^{15}N\text{-}NO_3^-$	SD $\delta^{15}N$	$\delta^{18}O\text{-}NO_3^-$	SD $\delta^{18}O$	% N	% C	$\delta^{18}O\text{-}H_2O$	SD $\delta^{18}O$	$\delta^2H\text{-}H_2O$	SD δ^2H
C.3	Sep-02	5.3	0.0	-0.1	0.0	7.4		-7.2	0.1	-43.0	0.5
C.3	Feb-03	6.1	0.0	1.1	0.4			-7.2	0.1	-42.0	0.3
C.3	Jun-03	5.6	0.0	2.8				-7.2	0.1	-42.1	1.0
C.3	Sep-03	6.5	0.1	1.1	0.1	8.0					
C.3	Feb-04	5.7	0.0	0.4	0.2	7.8	< 0.1				
C.3	Jun-04	5.5	0.0	1.4	0.2	7.8	< 0.1				
C.4	Sep-02	3.2	0.1	0.5	1.1	6.9		-7.1	0.0	-41.7	0.5
C.4	Feb-03	3.6	0.0	0.4	0.0	8.0		-7.4	0.5	-46.0	1.6
C.4	Jun-03	3.3	0.0	0.7	0.2	8.2	< 0.1	-7.3	0.1	-45.8	0.7
C.4	Sep-03	3.1	0.0	0.6	0.0	8.0					
C.4	Feb-04	3.3	0.1	0.2	0.2	7.5	< 0.1				
C.4	Jun-04	3.8	0.0	0.6	0.6	7.7	< 0.1				
C.5	Sep-02	8.0	0.1	2.2	1.9	8.0		-7.1	0.2	-44.7	0.1
C.5	Feb-03	9.1	0.0	3.4				-7.0	0.1	-44.0	1.1
C.5	Jun-03	7.9	0.1	4.3	0.4			-7.1	0.0	-43.6	1.0
C.5	Sep-03	7.6	0.0	2.2	0.1	7.8					
C.5	Feb-04	5.3	0.0	0.4	0.3	7.7	< 0.1				
C.5	Jun-04	7.2	0.1	2.5	0.3	7.5	< 0.1				
C.6	Sep-02	5.2	0.1	-1.1	0.1	8.0	< 0.1	-7.1	0.1	-45.1	0.2
C.6	Feb-03	4.1	0.0	1.8	0.0	8.2	< 0.1	-6.6	0.1	-37.6	1.0
C.6	Jun-03	5.1	0.1	2.3	0.0	7.9		-7.7	0.1	-46.5	1.2
C.6	Sep-03	5.6	0.1	2.1	0.7	7.8					
C.6	Feb-04	3.9	0.1	1.2	0.1	7.2	< 0.1				
C.7	Sep-02	3.0	0.1	-2.4	0.2	7.1		-7.1	0.1	-45.2	0.4
C.7	Feb-03	4.2	0.0	0.7		8.2	< 0.1	-7.1	0.0	-42.3	0.4
C.7	Jun-03	3.5	0.0	1.2	0.0	8.1	< 0.1	-7.7	0.1	-46.1	0.4
C.7	Sep-03	3.6	0.0	0.6	0.1	7.9					
C.7	Feb-04	5.8	0.0	1.8	0.0	7.7	< 0.1				
C.7	Jun-04	2.7	0.1	1.9	0.3	7.6	< 0.1				
C.8	Sep-02	2.7	0.0	0.3	0.1	7.4		-7.5	0.1	-44.5	0.5
C.8	Feb-03	4.5	0.1	1.6	0.1	8.0		-7.0	0.1	-42.1	0.7
C.8	Jun-03	4.3	0.0	3.2	0.8	7.9	< 0.1	-7.3	0.1	-44.5	0.6
C.8	Sep-03	3.4	0.0	2.0	0.2	7.8					
C.8	Feb-04	4.7	0.0	3.0	0.8	7.5	< 0.1				
C.8	Jun-04	3.0	0.0	1.7	1.8	7.7	< 0.1				
C.9	Sep-02	5.9	0.0	1.6	0.1	7.4		-7.2	0.1	-45.5	0.6
C.9	Feb-03	5.3	0.0	1.9		7.4		-7.0	0.0	-47.0	0.5
C.9	Jun-03	6.5	0.0	1.7	0.3	7.6		-7.1	0.1	-44.5	1.1
C.9	Sep-03	5.8	0.0	2.9	0.1	7.8					
C.9	Feb-04	4.8	0.1	3.9	0.1	7.5	< 0.1				
C.9	Jun-04	5.9	0.0	1.8	0.5	7.2	< 0.1				
C.10	Sep-02	5.7	0.0	-0.7	0.1	8.0		-7.0	0.0	-44.5	0.4
C.10	Feb-03	5.8	0.0	1.7	0.1			-7.1	0.1	-45.8	0.7
C.10	Jun-03	5.6	0.1	2.6	0.1			-7.0	0.0	-42.7	0.8
C.10	Sep-03	5.6	0.1	1.1	0.2	7.9		-6.9	0.1	-41.6	0.1
C.10	Feb-04	5.2	0.1	1.8	0.4	7.7	< 0.1				
C.10	Jun-04	6.1	0.1	0.8	0.2	7.8	< 0.1				
C.11	Sep-02							-5.9	0.0	-36.4	0.4
C.11	Feb-03	7.8	0.1	2.0		7.8		-6.7	0.0	-43.5	1.0
C.11	Jun-03	8.6	0.1	4.4	0.3	7.3	< 0.1	-6.9	0.1	-45.2	0.3
C.11	Sep-03	18.4	0.0	10.9	0.6	2.3					
C.11	Feb-04	7.8	0.1	2.2	0.1	7.7	< 0.1				
C.11	Jun-04	12.1	0.0	6.8	0.3	4.0	< 0.1				
C.12	Sep-02	3.4	0.1	1.5	0.1	8.0		-7.4	0.1	-44.4	0.2
C.12	Feb-03	4.9	0.1	0.8	0.8	8.0		-7.0	0.1	-47.1	0.2
C.12	Jun-03	3.8	0.1	0.9	0.3	8.3	< 0.1	-7.2	0.1	-46.4	0.3
C.12	Sep-03	3.9	0.2	0.5	0.1	7.9					
C.12	Feb-04	4.1	0.1	0.7	0.4	7.8	< 0.1				
C.12	Jun-04	4.0	0.1	1.1	0.2	7.8	< 0.1				

Appendix 4 (continued): Isotopic composition of groundwater nitrate and groundwater measured between September 2002 and June 2004 in samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *$\delta^{15}N\text{-}NO_3^-$ is reported with its standard deviation (SD) in permils ‰ against AIR, $\delta^{18}O\text{-}NO_3^-/\delta^{18}O\text{-}H_2O$ and $\delta^2H\text{-}H_2O$ in permils ‰ against V-SMOW, % N refers to the mass percentage of nitrogen measured in $AgNO_3$ samples while % C relates to the mass percentage of C-bearing impurities measured in $AgNO_3$)*

Site	Time	$\delta^{15}N\text{-}NO_3^-$	SD $\delta^{15}N$	$\delta^{18}O\text{-}NO_3^-$	SD $\delta^{18}O$	% N	% C	$\delta^{18}O\text{-}H_2O$	SD $\delta^{18}O$	$\delta^2H\text{-}H_2O$	SD δ^2H
C.13	Sep-02	5.0	0.0	2.5	0.2	7.6					
C.13	Feb-03	9.5	0.1	5.0	1.0			-7.1	0.1	-45.2	0.3
C.13	Jun-03	12.1	0.1	7.0	0.1			-7.6	0.1	-46.1	0.3
C.13	Sep-03	10.0	0.0	3.6	0.0	8.0	< 0.1	-7.0	0.1	-44.9	0.1
C.13	Feb-04	9.3	0.1	3.3	0.2	7.6	< 0.1				
C.13	Jun-04	10.8	0.1	5.2	0.2	8.1	< 0.1				
C.15	Sep-02	10.1	0.0	2.4	0.4	8.0	< 0.1	-7.3	0.0	-43.7	0.3
C.15	Feb-03	5.6	0.1	2.3	0.1	8.1	< 0.1	-7.0	0.1	-45.7	0.3
C.15	Jun-03	10.1	0.0	4.0	0.2	7.9	< 0.1	-7.9	0.2	-48.0	1.0
C.15	Sep-03	10.3	0.0	3.5	0.1	7.6					
C.15	Jun-04	8.3	0.0	2.5	2.2	7.8	< 0.1				
C.16	Sep-02	4.4	0.1	1.2	0.9	8.0	< 0.1	-7.2	0.0	-44.8	0.5
C.16	Feb-03	8.6	0.1	2.2	0.7	8.1	< 0.1	-6.9	0.1	-45.7	0.8
C.16	Jun-03	4.8	0.0	2.4	0.5	7.7	1.6	-7.5	0.2	-42.7	0.8
C.16	Sep-03	5.3	0.1	1.8	0.1	8.1					
C.16	Feb-04	4.7	0.0	1.2	0.1	7.8	< 0.1				
C.16	Jun-04	5.1	0.0	1.1	0.8	8.1	< 0.1				
C.17	Sep-02	5.4	0.0	0.5	0.4	7.4		-7.1	0.0	-41.7	0.2
C.17	Feb-03	4.8	0.0	-0.1	0.1	8.2	< 0.1	-7.0	0.0	-45.0	0.4
C.17	Jun-03	6.2	0.0	1.9	0.8	8.0	< 0.1	-7.0	0.1	-43.0	0.2
C.17	Sep-03	5.4	0.0	0.9	0.2	8.1	< 0.1				
C.17	Feb-04	7.9	0.1	2.8	0.6	7.5	< 0.1				
C.17	Jun-04	5.9	0.0	1.2	1.4	7.7	< 0.1				
O.1	Feb-03	6.0	0.1	3.3	0.1	7.9	< 0.1	-7.1	0.1	-44.7	0.8
O.1	Jun-03	6.5	0.0	3.3	0.2	7.9		-7.1	0.1	-44.0	0.2
O.1	Sep-03	6.6	0.1	3.2	0.2	7.7					
O.1	Feb-04	6.5	0.0	5.2	0.4	7.7	< 0.1				
O.1	Jun-04	6.6	0.1	4.6	0.4	7.8	< 0.1				
O.2	Feb-03	5.4	0.0	3.0	0.1	8.0	< 0.1	-6.9	0.1	-44.1	0.5
O.2	Jun-03	5.5	0.0	2.4	0.3	7.7	< 0.1	-6.9	0.1	-42.4	0.2
O.2	Sep-03	5.8	0.0	2.9	0.0	7.6					
O.2	Jun-04	6.0	0.1	4.4	0.4	7.7	< 0.1				
O.3	Feb-03	6.4	0.1	2.2	0.5	7.7	< 0.1	-6.9	0.0	-44.3	0.4
O.3	Jun-03	5.6	0.2	0.7	0.2	8.1	< 0.1	-7.4	0.3	-45.3	1.3
O.3	Sep-03	6.1	0.0	1.2	0.2	7.6					
O.3	Feb-04	7.2	0.0	3.2	0.8	7.6	< 0.1				
O.3	Jun-04	6.9	0.0	3.6	0.2	7.8	< 0.1				
O.4	Feb-03	7.8	0.1	2.9	0.2	7.9		-8.0	1.4	-47.8	2.5
O.4	Jun-03	9.0	0.0	3.7	0.1	7.8		-7.6	0.2	-45.8	0.7
O.4	Sep-03	8.8	0.1	3.9	0.1	7.8					
O.4	Feb-04	8.6	0.0	4.3	0.3	7.6	< 0.1				
O.4	Jun-04	8.5	0.1	3.2	0.0	7.8	< 0.1				
O.5	Feb-03	4.0	0.0	1.4	0.2	7.8	< 0.1	-6.8	0.0	-44.3	0.5
O.5	Jun-03	4.2	0.1	1.0	0.5	7.7		-7.1	0.1	-43.3	0.7
O.5	Sep-03	4.4	0.0	1.2	0.1	7.8					
O.5	Feb-04	4.2	0.0	2.7	0.2	7.7	< 0.1				
O.5	Jun-04	4.5	0.1	4.2	1.4	7.7	< 0.1				
O.6	Feb-03	3.6	0.0	2.8	0.2			-6.8	0.1	-44.5	0.4
O.6	Jun-03	3.3	0.1	3.1	0.2			-7.8	0.1	-46.1	0.3
O.6	Sep-03	3.3	0.0	1.6	0.1	7.4					
O.6	Feb-04	3.5	0.0	1.1	0.0	7.7	< 0.1				
O.6	Jun-04	3.3	0.1	1.6	0.3	7.3	< 0.1				
O.7	Feb-03	7.4	0.1	2.5	0.5	8.2	< 0.1	-6.8	0.0	-44.4	0.1
O.7	Jun-03	7.3	0.1	3.8	0.0	8.2	< 0.1	-7.6	0.1	-45.9	0.7
O.7	Sep-03	7.7	0.0	2.4	0.3	7.8					
O.7	Feb-04	7.1	0.0	4.5	0.5	7.5	< 0.1				
O.7	Jun-04	8.1	0.1	4.5	0.8	7.8	< 0.1				

Appendix 4 (continued): Isotopic composition of groundwater nitrate and groundwater measured between September 2002 and June 2004 in samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *$\delta^{15}N\text{-}NO_3^-$ is reported with its standard deviation (SD) in permils ‰ against AIR, $\delta^{18}O\text{-}NO_3^-/\delta^{18}O\text{-}H_2O$ and $\delta^2H\text{-}H_2O$ in permils ‰ against V-SMOW, % N refers to the mass percentage of nitrogen measured in $AgNO_3$ samples while % C relates to the mass percentage of C-bearing impurities measured in $AgNO_3$)*

Site	Time	$\delta^{15}N\text{-}NO_3^-$	SD $\delta^{15}N$	$\delta^{18}O\text{-}NO_3^-$	SD $\delta^{18}O$	% N	% C	$\delta^{18}O\text{-}H_2O$	SD $\delta^{18}O$	$\delta^2H\text{-}H_2O$	SD δ^2H
O.8	Feb-03	5.6	0.0	4.2	0.3			-7.0	0.1	-45.8	0.9
O.8	Jun-03	5.7	0.0	2.1	0.0			-7.4	0.1	-42.1	0.6
O.8	Sep-03	6.1	0.0	2.4	0.2	7.8					
O.8	Feb-04	5.9	0.2	3.9	1.0	7.6	< 0.1				
O.8	Jun-04	6.1	0.1	2.5	0.2	7.8	< 0.1				
O.9	Feb-03	5.1	0.0	1.1	0.2	8.1	< 0.1	-7.1	0.1	-44.9	0.2
O.9	Jun-03	4.9	0.0	0.9	0.3	7.8					
O.9	Sep-03	5.4	0.0	1.0	0.1	7.9					
O.9	Feb-04	5.3	0.1	1.5	1.4	7.6	< 0.1				
O.9	Jun-04	5.6	0.0	4.2	0.3	7.9	< 0.1				
O.10	Feb-03	8.0	0.1	6.2	0.2	7.9	< 0.1	-6.9	0.1	-44.9	0.6
O.10	Jun-03	8.2	0.0	7.0	0.1	8.2	< 0.1	-7.5	0.1	-42.8	0.8
O.11	Feb-03	6.8	0.0	3.3	0.3	8.1	< 0.1	-6.7	0.0	-43.4	0.7
O.11	Jun-03	7.0	0.0	5.3	0.2	7.2	1.8	-7.5	0.2	-45.2	1.0
O.11	Sep-03	8.3	0.0	5.2	0.2	8.1	< 0.1	-7.3	0.2	-46.3	1.0
O.11	Feb-04	9.8	0.0	5.3	0.3	7.7	< 0.1				
O.11	Jun-04	9.4	0.1	6.7	0.1	7.6	< 0.1				
O.12	Feb-03	6.5	0.1	2.3	0.5	7.9	< 0.1	-6.9	0.2	-43.7	0.6
O.12	Jun-03	6.0	0.1	1.1	0.3	7.8		-6.8	0.1	-41.6	0.6
O.12	Sep-03	5.5	0.0	0.8	0.2	8.0	< 0.1				
O.12	Feb-04	6.2	0.0	1.1	0.4	7.7	< 0.1				
O.12	Jun-04	6.3	0.0	3.8	0.3	7.9	< 0.1				
O.13	Feb-03	4.4	0.0	1.5	0.4	7.9		-7.0	0.1	-45.4	0.5
O.13	Jun-03	4.5	0.0	1.5	0.2	8.0		-7.1	0.1	-42.2	0.9
O.13	Sep-03	4.5	0.0	1.2	0.0	7.6					
O.13	Feb-04	5.3	0.1	1.8	0.1	7.6					
O.13	Jun-04	4.7	0.0	2.8	0.8	7.4	2.5				
BHO.1	Feb-03	2.2	0.1	1.8	0.1			-6.5	0.0	-38.9	0.3
BHO.1	Jun-03	4.0	0.1	2.3	0.2			-8.0	0.1	-48.1	0.3
BHO.1	Sep-03	4.3	0.1	0.0	0.6	8.2	< 0.1	-7.9	0.2	-50.2	1.3
BHO.1	Feb-04	4.5	0.1	-0.2	0.7	7.6	< 0.1				
BHO.1	Jun-04	4.9	0.0	2.2	0.1	7.9	< 0.1				
BHO.3B	Feb-03	3.9	0.1	6.6	0.4	2.7	< 0.1	-6.9	0.1	-45.4	1.0
BHO.3B	Jun-03	3.4	0.0	8.0	0.2	2.8	1.6	-7.7	0.1	-46.4	0.9
BHO.3B	Sep-03	4.1	0.0	4.5		3.4		-7.4	0.1	-45.2	0.3
BHO.3B	Feb-04	18.6	0.1	9.8	0.3	5.0	< 0.1				
BHO.4	Feb-03	4.5	0.1	1.1	0.2	8.3		-6.7	0.0	-40.2	0.1
BHO.4	Jun-03	3.8	0.0	2.8	0.2	7.0	2.0	-7.6	0.0	-43.8	0.5
BHO.4	Sep-03	4.2	0.0	0.9	0.2	8.2	< 0.1	-7.3	0.0	-43.9	0.2
BHO.4	Feb-04	3.8	0.1	1.3	0.3	7.6	< 0.1				
BHO.4	Jun-04	4.2	0.1	2.2	1.1	7.9	< 0.1				
BHO.4A	Feb-03	4.4	0.1	0.6	0.0	8.0		-6.9	0.0	-44.2	0.6
BHO.4A	Jun-03	3.9	0.0	1.7	0.2	7.3	1.6	-7.4	0.0	-45.6	0.3
BHO.4A	Sep-03	4.4	0.1	1.2	0.1	8.2		-7.4	0.1	-45.2	0.6
BHO.4A	Jun-04	4.2	0.1	2.8	0.3	7.9	< 0.1				
BHO.5	Feb-03	5.5	0.0	0.4	0.7	8.1	< 0.1	-6.5	0.1	-38.3	0.1
BHO.5	Jun-03	4.2	0.1	1.0	0.4	7.4	1.7	-7.5	0.0	-45.2	0.4
BHO.5	Feb-04	3.1	0.0	1.1	0.2	7.6	< 0.1				
BHO.6	Feb-03	2.8	0.0	0.2	0.4			-7.9	0.7	-51.8	1.8
BHO.6	Jun-03	2.8	0.0	-0.5	0.3			-7.7	0.0	-47.3	0.8
BHO.6	Sep-03	3.1	0.1	1.5	1.7	8.2	< 0.1	-8.1	0.2	-49.5	0.5
BHO.6	Feb-04	3.4	0.1	0.7	0.2	7.6	< 0.1				
BHO.6	Jun-04	2.8	0.0	1.7	0.0	7.8	< 0.1				
BHO.7	Feb-03	5.7	0.1	4.0		8.0		-6.5	0.1	-41.9	0.4
BHO.7	Jun-03	4.8	0.0	4.3	0.0	7.4	1.6	-7.4	0.0	-45.7	0.6
BHO.7	Sep-03	5.1	0.0	2.8	0.1	8.3		-6.7	0.0	-36.1	0.4
BHO.7	Feb-04	5.6	0.1	3.4	0.5	7.6					
BHO.7	Jun-04	6.9	0.0	6.2	0.0	7.9	< 0.1				

Appendix 4 (continued): Isotopic composition of groundwater nitrate and groundwater measured between September 2002 and June 2004 in samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *$\delta^{15}N\text{-}NO_3^-$ is reported with its standard deviation (SD) in permils ‰ against AIR, $\delta^{18}O\text{-}NO_3^-/\delta^{18}O\text{-}H_2O$ and $\delta^2H\text{-}H_2O$ in permils ‰ against V-SMOW, % N refers to the mass percentage of nitrogen measured in $AgNO_3$ samples while % C relates to the mass percentage of C-bearing impurities measured in $AgNO_3$)*

Site	Time	$\delta^{15}N\text{-}NO_3^-$	SD $\delta^{15}N$	$\delta^{18}O\text{-}NO_3^-$	SD $\delta^{18}O$	% N	% C	$\delta^{18}O\text{-}H_2O$	SD $\delta^{18}O$	$\delta^2H\text{-}H_2O$	SD δ^2H
BHO.8	Feb-03	3.7	0.0	0.8	1.0	7.7		-6.5	0.1	-39.2	0.5
BHO.8	Jun-03	3.1	0.1	1.7	0.1	7.3	1.6	-7.4	0.1	-43.2	1.0
BHO.8	Sep-03	3.8	0.0	0.5	0.1	8.0	< 0.1	-7.4	0.0	-43.6	0.9
BHO.8	Feb-04	2.5	0.0	0.2	0.3	7.7	< 0.1				
BHO.8	Jun-04	2.4	0.1	0.6	0.1	7.8	< 0.1				
BHM.1	Dec-02	5.0	0.0	2.7	0.6	8.2	< 0.1	-6.3	0.0	-35.1	0.4
BHM.1	Jun-03	6.7	0.0	5.8	0.2	7.4	1.6	-6.7	0.2	-38.2	1.5
BHM.2	Dec-02	6.1	0.0	2.9	0.9	8.0	< 0.1	-6.2	0.1	-38.1	0.7
BHM.2	Jun-03	5.4	0.0	5.8	0.4	7.4	1.7	-6.4	0.0	-38.1	0.9
BHM.2	Sep-03	5.8	0.0	4.0	0.0	7.8		-7.1	0.1	-39.9	0.2
BHM.3	Dec-02	6.5	0.0	0.9	0.2	8.3	< 0.1		0.2		0.6
BHM.3	Jun-03	5.9	0.0	3.9	0.9	7.2	1.7	-6.7		-37.4	
BHM.3	Sep-03	6.6	0.0	2.7	0.0	7.8		-6.1	0.1	-35.5	0.4
BHM.4	Dec-02	7.6	0.0	2.1	0.3	8.0	< 0.1	-6.3	0.1	-35.6	1.0
BHM.4	Jun-03	11.0	0.0	7.1	0.1	7.5	1.6	-5.9	0.1	-33.4	0.5
BHM.4	Sep-03	20.8	0.0	12.8	0.0	7.6		-6.6	0.1	-36.0	0.4
BHM.5	Dec-02	6.9	0.1	0.4	0.2	7.8	< 0.1	-6.3	0.0	-35.2	0.4
BHM.5	Jun-03	6.9	0.0	3.1	0.3	7.4	1.7	-6.8	0.0	-38.4	0.6
BHM.5	Sep-03	6.7	0.1	1.4	0.2	8.1	< 0.1	-6.7	0.1	-38.0	0.9
BHM.7	Dec-02	6.1	0.0	1.7	0.4	8.1	< 0.1	-6.2	0.2	-34.2	1.0
BHM.7	Jun-03	5.9	0.0	4.7	0.3	7.3	1.7	-6.1	0.1	-35.1	0.9
BHM.7	Sep-03	6.3	0.0	3.5	0.1	7.4		-7.6	0.1	-45.8	0.5
BHM.8	Dec-02	5.8	0.0	1.3	0.2	8.0	< 0.1	-6.0	0.2	-32.3	0.9
BHM.8	Jun-03	5.4	0.1	4.1	0.1	7.4	1.7	-6.2	0.1	-33.4	0.4
BHM.8	Sep-03	5.7	0.0	3.0	0.1	8.1	< 0.1	-6.8	0.1	-38.1	0.2
BHM.9	Dec-02	5.1	0.0	0.2	0.7	8.2	< 0.1		0.0		0.3
BHM.9	Jun-03	5.1	0.1	4.3	0.3	7.4	1.8	-6.6		-36.3	
BHM.9	Sep-03	5.6	0.0	3.0	0.0	7.1		-7.3	0.1	-40.7	0.5
BHM.10	Jun-03	-0.5	0.1	5.5	0.2	4.8	1.9	-7.1	0.1	-40.0	0.9

Appendix 5A: Mean and median nitrate concentrations measured in groundwater samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *(nitrate concentration is reported in mg/l NO_3^-)*

Site	n	Mean	SD	Median	Min	Max
B.1	2	61.3	18.2	61.3	48.4	74.1
B.2	7	63.1	7.1	64.0	49.1	72.0
B.3	7	47.2	4.1	47.5	39.7	51.6
B.4	7	48.1	7.4	46.7	37.8	61.1
B.5	7	56.3	5.8	55.5	49.1	67.5
B.6	7	47.9	5.2	47.4	38.3	53.5
B.7	7	41.2	6.4	38.9	34.1	53.7
B.8	6	84.7	9.4	86.6	67.8	93.6
B.9	7	48.4	13.5	49.5	26.6	68.8
B.10	1	33.8		33.8	33.8	33.8
C.1	7	38.8	8.5	38.3	30.2	51.7
C.2	7	72.2	7.8	73.9	60.0	82.0
C.3	7	68.3	9.6	73.3	52.0	74.9
C.4	7	42.6	4.3	43.4	34.8	47.3
C.5	7	51.1	2.9	50.1	48.4	56.0
C.6	6	37.8	11.6	38.4	19.9	51.1
C.7	7	72.5	28.3	61.0	54.9	134.9
C.8	7	62.4	13.4	57.0	45.7	79.4
C.9	7	19.2	8.0	19.7	8.7	32.6
C.10	7	62.8	10.7	61.3	53.3	85.6
C.11	7	12.9	10.9	10.8	1.2	27.3
C.12	7	41.2	8.3	43.1	27.5	50.6
C.13	7	45.3	9.3	43.2	34.8	58.3
C.14	1	43.4		43.4	43.4	43.4
C.15	6	97.7	26.3	108.3	58.8	122.5
C.16	7	29.1	11.0	24.4	22.9	53.7
C.17	7	31.1	15.0	30.8	10.0	49.3
C.18	1	43.4		43.4	43.4	43.4
C.19	1	56.2		56.2	56.2	56.2
C.20	1	43.2		43.2	43.2	43.2
O.1	6	30.1	2.4	29.9	27.1	32.8
O.2	6	32.1	1.8	32.1	29.8	34.4
O.3	6	35.2	3.9	36.6	29.7	39.2
O.4	6	29.3	10.0	30.0	18.3	39.4
O.5	6	32.3	4.8	30.2	29.1	41.7
O.6	6	16.8	4.4	17.4	10.7	22.1
O.7	5	45.3	1.7	44.4	44.0	48.2
O.8	6	36.0	4.8	34.0	31.9	43.5
O.9	6	59.5	1.9	59.0	57.1	62.1
O.10	3	12.7	2.8	12.6	10.0	15.6
O.11	6	31.3	3.5	31.2	27.4	36.6
O.12	6	70.3	6.6	73.4	59.1	75.3
O.13	6	34.3	8.0	32.1	28.6	50.2
BHO.1	5	56.9	15.8	66.6	35.4	70.2
BHO.3B	4	5.0	1.6	4.9	3.3	7.0
BHO.4	5	83.0	6.8	83.6	74.4	90.0
BHO.4A	5	75.8	3.0	75.6	71.5	79.8
BHO.5	3	84.3	40.5	69.5	53.3	130.2
BHO.6	5	68.2	12.0	73.5	49.8	79.6
BHO.7	5	63.3	12.8	63.8	51.7	82.9
BHO.8	5	87.7	19.8	94.9	52.5	100.3

Site	n	Mean	SD	Median	Min	Max
BHM.1	3	31.3	12.2	35.8	17.5	40.5
BHM.2	4	69.6	15.7	74.3	48.3	81.7
BHM.3	4	57.1	25.2	46.1	41.6	94.5
BHM.4	4	57.0	30.2	62.5	19.1	83.7
BHM.5	4	60.5	3.4	61.6	55.7	63.1
BHM.6	1	212.0		212.0	212.0	212.0
BHM.7	4	71.0	16.9	64.3	59.8	95.7
BHM.8	4	73.6	16.7	70.8	58.2	94.5
BHM.9	4	51.1	6.7	48.9	45.9	60.8
BHM.10	1	5.7		5.7	5.7	5.7

Appendix 5B: Mean and median chloride concentrations measured in groundwater samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *(Chloride concentration is reported in mg/l Cl^-)*

Site	n	Mean	SD	Median	Min	Max
B.1	2	40.5	1.8	40.5	39.2	41.8
B.2	7	51.6	7.9	54.5	35.2	58.3
B.3	6	28.7	3.1	28.8	24.2	32.4
B.4	7	26.0	9.6	28.2	5.1	35.1
B.5	7	28.5	4.5	28.9	19.3	32.9
B.6	7	27.2	3.7	28.3	19.1	29.9
B.7	7	29.3	3.2	29.6	23.9	33.5
B.8	6	24.4	2.2	23.9	21.8	27.8
B.9	7	43.6	7.8	42.1	34.3	57.8
B.10	1	40.3		40.3	40.3	40.3
C.1	7	23.3	1.8	23.1	21.4	26.6
C.2	7	64.2	14.6	59.4	47.5	84.1
C.3	7	34.5	5.7	33.5	23.9	40.4
C.4	7	30.9	1.6	31.5	27.9	32.7
C.5	7	45.6	3.9	45.2	42.0	53.3
C.6	6	23.7	10.9	22.3	11.6	36.1
C.7	7	30.5	7.8	27.8	25.1	47.8
C.8	7	38.0	4.6	38.6	32.5	45.1
C.9	7	16.2	4.3	15.9	8.8	22.7
C.10	7	42.1	9.5	46.8	28.5	52.2
C.11	7	47.5	11.3	49.7	32.2	60.7
C.12	7	22.7	3.6	23.9	15.5	25.9
C.13	7	36.6	2.9	38.0	31.9	39.8
C.14	1	31.2		31.2	31.2	31.2
C.15	5	38.2	6.3	39.7	28.8	45.8
C.16	7	27.4	13.4	27.5	5.1	51.4
C.17	7	29.8	13.8	31.3	5.1	48.6
C.18	1	35.8		35.8	35.8	35.8
C.19	1	41.3		41.3	41.3	41.3
C.20	1	36.7		36.7	36.7	36.7
O.1	6	21.2	2.4	21.9	16.9	23.4
O.2	6	24.1	3.6	23.8	18.5	28.1
O.3	5	30.6	3.5	30.7	26.3	35.8
O.4	6	50.9	14.6	55.5	28.4	66.2
O.5	6	22.9	2.8	22.3	19.1	26.6
O.6	6	17.8	4.1	17.6	12.2	22.8
O.7	5	52.3	7.3	52.1	42.1	62.3
O.8	6	26.9	4.1	28.5	19.9	30.4
O.9	6	33.0	4.5	33.0	25.8	39.7
O.10	3	23.3	4.7	25.6	17.9	26.3
O.11	6	30.0	1.7	29.6	28.3	32.1
O.12	6	37.2	5.9	39.8	26.1	41.6
O.13	6	25.4	5.8	23.4	20.0	33.8
BHO.1	5	17.3	6.2	14.1	12.2	27.5
BHO.3B	4	14.0	5.0	15.2	7.5	18.0
BHO.4	5	26.9	1.2	27.1	25.7	28.6
BHO.4A	5	29.1	1.5	29.6	27.4	30.7
BHO.5	3	30.4	25.5	15.9	15.4	59.8
BHO.6	5	22.5	3.3	23.4	17.4	26.2
BHO.7	5	43.5	9.2	40.0	37.6	59.6
BHO.8	5	27.5	6.7	31.6	17.4	32.4

Site	n	Mean	SD	Median	Min	Max
BHM.1	2	18.5	10.0	18.5	11.4	25.6
BHM.2	3	16.0	3.3	14.4	13.9	19.8
BHM.3	3	10.9	5.0	13.5	5.1	14.0
BHM.4	3	36.8	6.9	36.6	30.0	43.8
BHM.5	3	29.5	21.2	38.0	5.4	45.2
BHM.6	0					
BHM.7	3	18.2	1.6	18.0	16.8	19.9
BHM.8	3	13.1	6.9	15.6	5.3	18.3
BHM.9	3	17.8	10.8	23.1	5.3	24.9
BHM.10	1	3.2		3.2	3.2	3.2

Appendix 5C: Mean and median potassium concentrations measured in groundwater samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *(Potassium concentration is reported in mg/l K^+)*

Site	n	Mean	SD	Median	Min	Max
B.1	2	3.9	0.1	3.9	3.8	3.9
B.2	7	0.4	0.1	0.4	0.3	0.5
B.3	7	1.2	0.1	1.2	1.1	1.4
B.4	7	1.0	0.1	1.0	0.8	1.0
B.5	7	3.6	0.2	3.6	3.3	4.0
B.6	6	1.6	0.2	1.6	1.4	1.8
B.7	7	0.7	0.8	0.4	0.4	2.5
B.8	6	0.3	0.1	0.3	0.2	0.4
B.9	7	44.5	20.0	51.0	2.8	63.0
B.10	1	2.1		2.1	2.1	2.1
C.1	7	6.0	2.4	7.0	1.1	8.0
C.2	7	37.2	16.1	38.0	5.0	54.4
C.3	7	5.8	0.7	5.7	4.9	6.8
C.4	7	1.4	0.3	1.5	0.8	1.7
C.5	7	16.8	3.9	18.0	10.9	21.5
C.6	6	5.6	1.1	5.4	4.5	6.9
C.7	7	0.7	0.4	0.5	0.4	1.5
C.8	7	1.1	0.3	1.1	0.8	1.5
C.9	7	2.4	0.8	2.2	1.5	3.7
C.10	7	7.2	1.6	8.0	4.6	9.4
C.11	7	4.3	1.2	4.8	2.7	5.6
C.12	7	0.7	0.1	0.7	0.4	0.8
C.13	7	24.8	12.4	29.0	4.6	35.6
C.14	1	2.2		2.2	2.2	2.2
C.15	6	2.2	0.4	2.3	1.6	2.6
C.16	7	3.3	6.6	0.9	0.8	18.2
C.17	7	1.5	0.9	1.3	0.8	3.6
C.18	1	1.6		1.6	1.6	1.6
C.19	1	2.3		2.3	2.3	2.3
C.20	1	1.7		1.7	1.7	1.7
O.1	6	0.7	0.1	0.7	0.6	0.7
O.2	6	1.2	0.1	1.2	1.1	1.4
O.3	6	3.0	0.3	3.1	2.7	3.3
O.4	6	1.7	0.5	1.7	1.1	2.4
O.5	6	1.4	0.2	1.4	1.3	1.7
O.6	6	0.9	0.1	0.9	0.8	1.0
O.7	5	2.4	0.2	2.3	2.3	2.7
O.8	6	1.3	0.1	1.3	1.2	1.5
O.9	6	1.4	0.1	1.4	1.3	1.5
O.10	3	0.8	0.1	0.8	0.8	0.9
O.11	6	6.4	2.9	7.5	0.7	8.0
O.12	6	2.5	0.2	2.5	2.3	2.8
O.13	6	3.2	0.6	3.2	2.4	4.3
BHO.1	5	13.0	4.3	11.0	7.9	18.0
BHO.3B	4	4.5	2.6	4.1	1.7	8.0
BHO.4	5	7.3	3.4	5.6	4.8	13.0
BHO.4A	5	6.6	0.4	6.7	6.1	7.0
BHO.5	3	3.6	2.6	2.1	2.1	6.6
BHO.6	5	0.6	0.4	0.5	0.4	1.3
BHO.7	5	0.2	0.0	0.2	0.2	0.2
BHO.8	5	4.5	0.4	4.6	4.0	5.0

Site	n	Mean	SD	Median	Min	Max
BHM.1	3	0.7	0.4	0.5	0.5	1.2
BHM.2	4	1.1	0.2	1.1	0.9	1.3
BHM.3	4	16.4	3.9	15.0	13.4	22.0
BHM.4	4	29.5	5.5	27.9	25.0	37.0
BHM.5	4	0.5	0.1	0.5	0.4	0.6
BHM.6	1	1.1		1.1	1.1	1.1
BHM.7	4	2.0	1.0	1.6	1.3	3.4
BHM.8	4	4.8	0.3	4.8	4.5	5.2
BHM.9	4	2.6	0.1	2.6	2.5	2.8
BHM.10	1	3.9		3.9	3.9	3.9

Appendix 5D: Mean and median sodium concentrations measured in groundwater samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *(Potassium concentration is reported in mg/l Na^+)*

Site	n	Mean	SD	Median	Min	Max
B.1	2	10.8	1.4	10.8	9.8	11.8
B.2	7	19.5	1.7	19.1	18.0	22.9
B.3	7	9.7	1.0	9.1	9.0	11.6
B.4	7	10.2	0.8	10.0	9.4	11.9
B.5	7	11.9	1.0	12.0	11.0	13.4
B.6	6	10.0	0.4	10.0	9.5	10.7
B.7	7	7.7	0.4	7.9	7.0	8.0
B.8	6	6.9	0.5	7.0	6.0	7.4
B.9	7	16.3	1.6	16.0	14.0	18.6
B.10	1	10.9		10.9	10.9	10.9
C.1	7	19.1	3.6	20.0	13.0	24.6
C.2	7	22.5	6.6	18.0	16.9	31.0
C.3	7	11.3	0.9	11.0	9.9	13.0
C.4	7	11.1	0.8	11.0	10.0	12.4
C.5	7	14.4	2.8	13.0	12.0	20.0
C.6	6	11.9	2.0	11.9	9.0	14.0
C.7	7	10.2	4.0	9.0	7.9	19.0
C.8	7	19.4	3.6	20.0	15.0	25.4
C.9	7	8.0	0.4	8.0	7.7	9.0
C.10	7	16.7	5.1	19.3	8.8	21.0
C.11	7	19.7	4.7	20.0	14.0	27.3
C.12	7	10.6	0.6	10.7	10.0	11.3
C.13	7	18.1	3.4	19.0	12.7	22.8
C.14	1	11.3		11.3	11.3	11.3
C.15	6	34.2	11.4	38.5	18.3	46.0
C.16	7	9.5	3.6	8.0	7.5	17.6
C.17	7	10.8	1.5	10.9	8.3	13.0
C.18	1	10.8		10.8	10.8	10.8
C.19	1	14.6		14.6	14.6	14.6
C.20	1	9.9		9.9	9.9	9.9
O.1	6	8.2	0.4	8.0	7.8	9.0
O.2	6	10.8	0.5	11.0	10.0	11.3
O.3	6	14.3	1.6	14.7	11.4	16.0
O.4	6	25.4	7.5	25.5	15.6	35.5
O.5	6	8.9	0.1	9.0	8.7	9.0
O.6	6	7.3	0.5	7.1	7.0	8.0
O.7	5	29.6	3.2	31.0	24.0	32.0
O.8	6	9.4	0.5	9.1	8.9	10.0
O.9	6	9.3	0.4	9.0	9.0	10.0
O.10	3	11.1	0.9	11.2	10.2	12.0
O.11	6	12.1	0.8	12.0	11.0	13.1
O.12	6	11.2	0.8	11.0	10.0	12.1
O.13	6	9.1	0.1	9.0	9.0	9.3
BHO.1	5	5.4	0.5	5.2	5.0	6.0
BHO.3B	4	4.9	0.8	4.9	4.0	6.0
BHO.4	5	7.7	0.7	8.0	7.0	8.5
BHO.4A	5	7.6	0.5	7.8	7.0	8.0
BHO.5	3	7.3	1.5	7.0	6.0	9.0
BHO.6	5	6.1	0.7	6.0	5.0	7.0
BHO.7	5	11.9	5.0	9.0	8.0	18.5
BHO.8	5	9.1	1.3	9.0	7.0	10.3
BHM.1	3	6.9	2.4	6.1	5.0	9.6
BHM.2	4	8.0	0.1	8.0	7.8	8.0
BHM.3	4	7.8	5.1	8.5	0.9	13.2
BHM.4	4	11.9	7.2	14.7	1.3	17.0
BHM.5	4	6.2	3.7	7.5	0.8	9.0
BHM.6	1	11.0		11.0	11.0	11.0
BHM.7	4	8.4	4.7	10.5	1.4	11.0
BHM.8	4	7.8	4.7	9.5	0.9	11.3
BHM.9	4	6.6	3.9	8.3	0.8	9.0
BHM.10	1	2.1		2.1	2.1	2.1

Appendix 5E: Mean and median potassium to sodium ratio (ratio of concentrations in mg/l) calculated in groundwater samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *(the dimentionless ratio is the ratio of potassium and sodium concentrations expressed in mg/l)*

Site	n	Mean	SD	Median	Min	Max
B.1	2	0.36	0.05	0.36	0.32	0.39
B.2	7	0.02	0.01	0.02	0.02	0.03
B.3	7	0.12	0.01	0.12	0.12	0.13
B.4	7	0.09	0.01	0.10	0.08	0.10
B.5	7	0.31	0.04	0.30	0.25	0.35
B.6	6	0.16	0.01	0.16	0.14	0.16
B.7	7	0.10	0.11	0.05	0.05	0.35
B.8	6	0.04	0.01	0.04	0.03	0.06
B.9	7	2.80	1.25	3.36	0.15	3.56
B.10	1	0.19		0.19	0.19	0.19
C.1	7	0.33	0.15	0.35	0.04	0.54
C.2	7	1.79	0.74	2.07	0.16	2.24
C.3	7	0.52	0.08	0.49	0.45	0.66
C.4	7	0.12	0.02	0.12	0.08	0.15
C.5	7	1.17	0.20	1.13	0.89	1.46
C.6	6	0.50	0.19	0.47	0.32	0.77
C.7	7	0.07	0.02	0.06	0.05	0.11
C.8	7	0.05	0.01	0.05	0.04	0.07
C.9	7	0.30	0.11	0.27	0.19	0.47
C.10	7	0.46	0.14	0.41	0.27	0.69
C.11	7	0.22	0.04	0.23	0.16	0.26
C.12	7	0.06	0.01	0.07	0.03	0.07
C.13	7	1.30	0.56	1.56	0.36	1.71
C.14	1	0.20		0.20	0.20	0.20
C.15	6	0.07	0.02	0.07	0.04	0.10
C.16	7	0.24	0.35	0.11	0.09	1.03
C.17	7	0.14	0.08	0.10	0.10	0.33
C.18	1	0.15		0.15	0.15	0.15
C.19	1	0.15		0.15	0.15	0.15
C.20	1	0.17		0.17	0.17	0.17
O.1	6	0.08	0.00	0.08	0.08	0.09
O.2	6	0.12	0.01	0.12	0.10	0.13
O.3	6	0.21	0.02	0.21	0.20	0.24
O.4	6	0.07	0.02	0.07	0.05	0.09
O.5	6	0.16	0.02	0.16	0.14	0.19
O.6	6	0.13	0.01	0.13	0.11	0.13
O.7	5	0.08	0.01	0.08	0.07	0.10
O.8	6	0.14	0.01	0.14	0.13	0.16
O.9	6	0.15	0.02	0.15	0.13	0.17
O.10	3	0.08	0.01	0.08	0.07	0.08
O.11	6	0.53	0.24	0.60	0.06	0.73
O.12	6	0.23	0.02	0.23	0.19	0.24
O.13	6	0.35	0.07	0.35	0.26	0.46
BHO.1	5	2.39	0.79	2.20	1.52	3.40
BHO.3B	4	0.94	0.54	0.95	0.28	1.60
BHO.4	5	0.94	0.40	0.80	0.66	1.63
BHO.4A	5	0.87	0.06	0.87	0.79	0.96
BHO.5	3	0.54	0.48	0.30	0.23	1.10
BHO.6	5	0.11	0.09	0.07	0.06	0.26
BHO.7	5	0.02	0.01	0.02	0.01	0.03
BHO.8	5	0.50	0.05	0.50	0.44	0.57

Site	n	Mean	SD	Median	Min	Max
BHM.1	3	0.10	0.03	0.10	0.07	0.13
BHM.2	4	0.14	0.02	0.14	0.11	0.16
BHM.3	4	5.24	7.01	1.77	1.67	15.76
BHM.4	4	6.30	8.64	2.14	1.67	19.25
BHM.5	4	0.18	0.23	0.07	0.06	0.52
BHM.6	1	0.10		0.10	0.10	0.10
BHM.7	4	0.44	0.50	0.24	0.12	1.18
BHM.8	4	1.59	2.19	0.51	0.46	4.87
BHM.9	4	0.98	1.34	0.31	0.30	2.99
BHM.10	1	1.86		1.86	1.86	1.86

Appendix 6A: Mean and median $\delta^{15}N\text{-}NO_3^-$ values in nitrate extracted from groundwater samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *($\delta^{15}N\text{-}NO_3^-$ is reported in ‰ against AIR).*

Site	n	Mean	SD	Median	Min	Max
B.1	1	4.3		4.3	4.3	4.3
B.2	6	3.6	0.7	3.7	2.7	4.4
B.3	6	5.3	0.2	5.3	5.0	5.5
B.4	6	4.5	0.3	4.6	4.0	4.7
B.5	6	5.5	0.3	5.6	5.0	5.7
B.6	6	5.6	0.2	5.6	5.4	6.0
B.7	6	7.8	0.5	7.7	7.3	8.6
B.8	5	6.3	0.6	6.6	5.3	6.8
B.9	6	9.9	1.4	10.2	8.2	12.1
B.10	0					
C.1	6	8.4	0.4	8.5	7.9	8.7
C.2	6	7.2	0.5	7.0	6.7	7.9
C.3	6	5.9	0.5	5.8	5.3	6.5
C.4	6	3.4	0.3	3.3	3.1	3.8
C.5	6	7.6	1.3	7.8	5.3	9.2
C.6	5	4.8	0.7	5.1	3.9	5.6
C.7	6	3.8	1.1	3.6	2.7	5.8
C.8	6	3.8	0.8	3.9	2.7	4.7
C.9	6	5.7	0.6	5.9	4.8	6.5
C.10	6	5.7	0.3	5.8	5.2	6.1
C.11	5	10.9	4.5	8.6	7.8	18.4
C.12	6	4.1	0.5	4.0	3.4	4.9
C.13	6	9.5	2.5	9.9	5.0	12.3
C.14	0					
C.15	5	8.9	2.0	10.1	5.6	10.3
C.16	6	5.5	1.6	5.0	4.4	8.6
C.17	6	5.9	1.1	5.7	4.8	7.9
C.18	0					
C.19	0					
C.20	0					
O.1	5	6.4	0.3	6.5	6.0	6.6
O.2	4	5.7	0.3	5.7	5.4	6.0
O.3	5	6.4	0.6	6.4	5.6	7.2
O.4	5	8.5	0.5	8.6	7.8	9.0
O.5	5	4.3	0.2	4.2	4.0	4.5
O.6	5	3.4	0.2	3.4	3.3	3.7
O.7	5	7.5	0.4	7.4	7.1	8.1
O.8	5	5.9	0.2	5.9	5.7	6.1
O.9	5	5.3	0.3	5.3	4.9	5.6
O.10	2	8.1	0.1	8.1	8.0	8.2
O.11	5	8.3	1.4	8.3	6.8	9.8
O.12	5	6.1	0.4	6.2	5.5	6.5
O.13	5	4.7	0.4	4.5	4.4	5.3
BHO.1	5	4.1	1.0	4.3	2.3	4.9
BHO.3B	4	7.5	7.5	3.9	3.4	18.6
BHO.4	5	4.1	0.3	4.2	3.8	4.5
BHO.4A	4	4.2	0.2	4.3	3.9	4.4
BHO.5	3	4.3	1.2	4.2	3.1	5.5
BHO.6	5	3.0	0.2	2.9	2.8	3.4
BHO.7	5	5.6	0.8	5.6	4.8	6.9
BHO.8	5	3.1	0.7	3.1	2.4	3.8

Site	n	Mean	SD	Median	Min	Max
BHM.1	2	5.9	1.2	5.9	5.0	6.7
BHM.2	3	5.8	0.4	5.8	5.4	6.1
BHM.3	3	6.3	0.4	6.5	5.9	6.6
BHM.4	3	13.1	6.9	11.0	7.6	20.8
BHM.5	3	6.8	0.1	6.9	6.7	6.9
BHM.6	0					
BHM.7	3	6.1	0.2	6.1	5.9	6.3
BHM.8	3	5.6	0.2	5.7	5.4	5.8
BHM.9	3	5.3	0.3	5.1	5.1	5.6
BHM.10	1	-0.5		-0.5	-0.5	-0.5

Appendix 6B: Mean and median $\delta^{18}O\text{-}NO_3^-$ values in nitrate extracted from groundwater samples collected in the Barrow Valley (site codes with B for Ballyroe area, site codes with C for Castlemitchell, site codes with O for Oak Park, site codes with BHO for the Oak Park monitoring area) and at Moorepark Research Centre (site code with BHM). *($\delta^{18}O\text{-}NO_3^-$ is reported in ‰ against V-SMOW).*

Site	n	Mean	SD	Median	Min	Max
B.1	1	3.1		3.1	3.1	3.1
B.2	6	1.1	1.4	0.9	-0.5	3.7
B.3	6	2.2	1.0	2.0	1.1	4.0
B.4	6	2.1	0.6	2.3	1.1	2.7
B.5	6	1.9	0.9	1.6	1.3	3.6
B.6	6	2.5	1.3	2.3	0.8	4.9
B.7	6	4.4	0.6	4.3	3.9	5.5
B.8	5	2.4	1.5	2.7	-0.2	3.7
B.9	6	3.2	1.1	3.2	1.5	4.9
B.10	0					
C.1	6	2.5	0.7	2.6	1.6	3.2
C.2	6	2.6	1.6	2.5	0.0	4.3
C.3	6	1.1	1.0	1.1	-0.1	2.8
C.4	6	0.5	0.2	0.6	0.2	0.7
C.5	6	2.5	1.3	2.4	0.4	4.3
C.6	5	1.3	1.4	1.8	-1.1	2.3
C.7	6	0.6	1.6	1.0	-2.4	1.9
C.8	6	2.0	1.1	1.9	0.3	3.2
C.9	6	2.3	0.9	1.9	1.6	3.9
C.10	6	1.2	1.1	1.4	-0.7	2.6
C.11	5	5.3	3.7	4.4	2.0	10.9
C.12	6	0.9	0.3	0.9	0.5	1.5
C.13	6	4.4	1.6	4.3	2.5	7.0
C.14	0					
C.15	5	2.9	0.8	2.5	2.3	4.0
C.16	6	1.7	0.6	1.5	1.1	2.4
C.17	6	1.2	1.0	1.1	-0.1	2.8
C.18	0					
C.19	0					
C.20	0					
O.1	5	3.9	0.9	3.3	3.2	5.2
O.2	4	3.2	0.9	3.0	2.4	4.4
O.3	5	2.2	1.2	2.2	0.7	3.6
O.4	5	3.6	0.6	3.7	2.9	4.3
O.5	5	2.1	1.3	1.4	1.0	4.2
O.6	5	2.0	0.9	1.6	1.1	3.1
O.7	5	3.5	1.0	3.8	2.4	4.5
O.8	5	3.0	1.0	2.5	2.1	4.2
O.9	5	1.7	1.4	1.1	0.9	4.2
O.10	2	6.6	0.6	6.6	6.2	7.0
O.11	5	5.2	1.2	5.3	3.3	6.7
O.12	5	1.8	1.2	1.1	0.8	3.8
O.13	5	1.8	0.6	1.5	1.2	2.8
BHO.1	5	1.2	1.2	1.8	-0.2	2.3
BHO.3B	4	7.2	2.2	7.3	4.5	9.8
BHO.4	5	1.7	0.8	1.3	0.9	2.8
BHO.4A	4	1.6	0.9	1.5	0.6	2.8
BHO.5	3	0.8	0.4	1.0	0.4	1.1
BHO.6	5	0.7	0.9	0.7	-0.5	1.7
BHO.7	5	4.1	1.3	4.0	2.8	6.2
BHO.8	5	0.8	0.6	0.6	0.2	1.7

Site	n	Mean	SD	Median	Min	Max
BHM.1	2	4.3	2.2	4.3	2.7	5.8
BHM.2	3	4.2	1.5	4.0	2.9	5.8
BHM.3	3	2.5	1.5	2.7	0.9	3.9
BHM.4	3	7.3	5.4	7.1	2.1	12.8
BHM.5	3	1.6	1.4	1.4	0.4	3.1
BHM.6	0					
BHM.7	3	3.3	1.5	3.5	1.7	4.7
BHM.8	3	2.8	1.4	3.0	1.3	4.1
BHM.9	3	2.5	2.1	3.0	0.2	4.3
BHM.10	1	5.5		5.5	5.5	5.5

Appendix 7: OSI grid coordinates (northing and easting) of the Barrow Valley groundwater sampling sites.

site	Area	Northing (x)	Easting (y)
C.1	Castlemitchell	265 333	192 454
C.2	Castlemitchell	264 976	192 702
C.3	Castlemitchell	263 855	193 389
C.4	Castlemitchell	264 275	193 376
C.5	Castlemitchell	263 655	193 342
C.6	Castlemitchell	266 613	194 680
C.7	Castlemitchell	266 218	194 847
C.8	Castlemitchell	266 186	194 847
C.9	Castlemitchell	264 975	195 021
C.10	Castlemitchell	263 522	195 279
C.11	Castlemitchell	266 698	195 324
C.12	Castlemitchell	266 220	195 243
C.13	Castlemitchell	263 001	194 841
C.14	Castlemitchell	264 369	195 137
C.15	Castlemitchell	266 727	194 653
C.16	Castlemitchell	263 697	193 389
C.17	Castlemitchell	263 760	194 370
C.18	Castlemitchell	263 825	195 645
C.19	Castlemitchell	263 724	194 261
C.20	Castlemitchell	265 804	193 486
B.1	Ballyroe	270 755	191 018
B.2	Ballyroe	270 302	191 642
B.3	Ballyroe	270 653	189 349
B.4	Ballyroe	270 610	188 623
B.5	Ballyroe	271 837	191 016
B.6	Ballyroe	271 636	190 459
B.7	Ballyroe	271 339	189 916
B.8	Ballyroe	271 697	188 944
B.9	Ballyroe	270 805	188 259
B.10	Ballyroe	274 173	189 579
O.1	Oak Park	273 342	178 617
O.2	Oak Park	273 937	179 044
O.3	Oak Park	273 789	178 620
O.4	Oak Park	273 448	178 484
O.5	Oak Park	274 517	179 833
O.6	Oak Park	274 311	179 425
O.7	Oak Park	273 393	178 439
O.8	Oak Park	272 576	181 115
O.9	Oak Park	273 438	181 388
O.10	Oak Park	272 110	181 134
O.11	Oak Park	273 319	179 906
O.12	Oak Park	273 933	181 053
O.13	Oak Park	274 465	179 695
BHO.1	Oak Park RC	272 739	178 956
BHO.3B	Oak Park RC	272 679	179 398
BHO.4	Oak Park RC	272 587	179 111
BHO.4A	Oak Park RC	272 586	179 112
BHO.5	Oak Park RC	272 791	179 243
BHO.6	Oak Park RC	272 911	178 994
BHO.7	Oak Park RC	272 387	179 525
BHO.8	Oak Park RC	272 415	178 808