SOURCES OF NITRATE LEACHED TO GROUNDWATER IN GRASSLANDS OF FERMOY, CO. CORK

Volume 1 of 2

Text, Figures and Tables.

Presented in fulfilment

of the requirements for the degree of

Doctor of Philosophy

October 1999

by Karl Richards

Department of Geology,

Trinity College Dublin.

Supervised by:

Dr. C.E. Coxon, Trinity College Dublin

Dr. M. Ryan, Teagasc Johnstown Castle.

October, 1999

To my wife and my parents

DECLARATION

This thesis has not been submitted for a degree to this or any other university and, with acknowledged exception, is entirely my own work.

I agree that this thesis may be lent in accordance with College regulations.

Karl Richards
October, 1999

ABSTRACT

Groundwater contamination with nitrate from agriculture in Ireland has mainly been attributed to specific point sources such as farmyards or to arable farming in certain areas of the country. The current study aimed to investigate the cause of high groundwater nitrate concentrations beneath an intensive dairy farm and to quantify the amount of nitrogen leaching through the unsaturated soil and Quaternary deposits. The study farm was located on a free draining sandstone soil which overlied a limestone bedrock aquifer. The results from the study farm were extrapolated to a regional level to determine if high groundwater nitrate concentrations might be expected in other areas with similar agricultural and geological/hydrogeological properties.

A detailed nitrogen budget for the dairy farm was calculated which examined numerous nitrogen sources on the farm. On a plot by plot basis extremely high rates of nitrogen application/recycling could be observed up to 805 kg N per hectare. Annual soil organic nitrogen mineralisation was equivalent to the inorganic fertiliser nitrogen input on the farm, varying from 158 to 346 kg N per hectare.

Levels of nitrate leaching through the unsaturated zone were assessed by soil solution sampling at depths of 0.5, 1 and 1.5 m and determination of inorganic soil nitrogen levels to a depth of 0.9 m. High annual farm mean nitrate concentrations of 20 to 30 mg per litre were observed leaching through the unsaturated zone. The inherently high nitrate concentrations in the soil solution were increased further by dirty water application and ploughing and re-seeding of plots. Nitrate concentrations in the soil solution were similar to observed groundwater concentrations. A significant relationship between total nitrogen applied and the quantity of inorganic soil nitrogen in autumn was observed. This relationship was not observed between soil solution nitrate concentrations and the quantity of nitrogen applied.

Groundwater nitrate concentrations more than double the EU maximum admissible concentration were observed in five boreholes on the farm. High groundwater nitrate concentrations were increased further due to the application of dirty water or the ploughing and re-seeding of a plot. When the groundwater had extremely high nitrate concentrations

a relatively fast return to similar nitrate concentrations in other boreholes was observed when the source of the high nitrate was removed. A significant relationship, over an eight year period, was observed between soil moisture deficit and groundwater nitrate concentrations in the subsequent year. A rapid travel time from soil surface to the groundwater was also observed in a Br^- tracing experiment indicating the short time taken for surface activities to affect groundwater quality.

Extrapolation of the findings on the study farm to a regional level indicated that similar high rates of nitrate leaching might be expected on other farms. Elevated nitrate concentrations were observed in a large number of groundwater supplies surveyed in the Fermoy region with 28% of supplies having nitrate concentrations greater that the maximum admissible concentration.

The occurrence of high concentrations of groundwater nitrate on the study farm and in the region indicates that the area is vulnerable to nitrate leaching. Groundwater nitrate concentrations in excess of the EU maximum admissible concentration would indicate that this area should be declared a nitrate vulnerable zone. The notion of grassland based agriculture as a non-polluting land use warrants re-examination in the light of the findings of the present study.

Acknowledgements

This project was funded by a Teagasc Walsh Fellowship with further assistance from Teagasc, Johnstown Castle and Moorepark. I would like to thank my supervisors Dr. Catherine Coxon and Dr. Michael Ryan, whose constant encouragement, guidance and continued interest made the completion of this thesis possible.

The help of Teagasc, Johnstown Castle has been invaluable and I thank Dr. John Lee for permission in allowing me to live and work in Johnstown Castle. I wish to acknowledge the help of all the staff in Teagasc, Johnstown Castle. In particular I would like to express sincere thanks to Mr. Joe Scott who worked tirelessly accommodating me and for all his help in the analysis of my countless thousands of samples. I would like to thank Michael Ryan who encouraged me and supported me throughout my academic and social life in Wexford. Special thanks to Dr. Owen Carton for his help and support throughout the study. Thanks to Aidan Fanning and Davey Noonan for their help in the laboratory and field. Thanks to Dr. William Murphy for providing soil moisture deficit data for the study area and for statistical advice. To Dr. Brian Coulter and Eddie MacDonald for GIS assistance and help. To Vinnie Staples for carrying out topographic levelling and surveying of the site. To the rest of the staff in Johnstown Castle Noel Culleton, Sean Diamond, Matt Murphy (Bushy), Denis, John, Ted, Sean, Evan, Teressa , Alan, Liam, Nick, Sam, Pat, Tommy, Eleanor and all the other staff at Johnstown castle for helping me during my stay in Wexford.

I wish to thank Teagasc, Moorepark for permitting me to study the Ballyderown Farm for this thesis. To Kevin Farrell, Eddie O'Callaghan, Mick Dolan, Jim Kiely and the other farm staff. To Anthony Brereton for access to meteorological data. And special thanks and remembrance to Patrick Feeney who carried out much of the data collection prior to and during this study until his untimely accidental death.

To Kenny Blackmore for help in producing maps and Trev for printing them.

I thank the Environmental Sciences Unit for the use of their laboratory and office facilities. Thanks to Dr. Norman Allot and Louise Scally for analysis of water samples for bromide determination.

Finally, to my wife Dorota for all her help collecting samples in the field, for analysis in the laboratory, for help computing and for all her encouragement, patience, and understanding, I am eternally grateful.

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Units, Terminology and Abbreviations

Metric units are used throughout the thesis
All water Parameters are given in mg l^{-1}

Nitrate	is expressed as nitrate-nitrogen (NO_3-N) in mg l^{-1}
l	litres
kg	kilograms
g	gram
d	day
yr	year
ha	hectare
CC	Ceramic cup soil solution sampler is referred to as
MAC	the maximum admissible concentration (for nitrate-nitrogen set by E.E.C. Directive 91/676, sets the limit at 11.3 mg l^{-1} NO_3-N)
smd	refers to soil moisture deficit
b.g.l.	refers to a depth below ground level
O.D.	refers to Ordnance Datum
A.O.D.	refers to a height above ordnance datum
Q	refers to Discharge
SC	refers to Specific Capacity
GL	refers to Guide level (for nitrate-nitrogen set by E.E.C. Directive 91/676, sets the limit at 5.6 mg l^{-1} NO_3-N)
NGQMP	refers to National groundwater monitoring programme
MRP	refers to molybdate reactive phosphate

CHAPTER 1 INTRODUCTION TO NITRATE LEACHING

1.1 Introduction to the study

1.1.1 Introduction

Nitrate contamination of groundwater in Ireland was thought to be negligible. Examination of nitrate in drinking water supplies from 1989 to 1997 by the Environmental Protection Agency (EPA) has found that less than 1 per cent of drinking water supplies have nitrate concentrations greater than MAC. However, researchers have highlighted risk areas of high rates of nitrate leaching to be arable areas such as in the South-East of the country (Daly and Daly, 1982;1984).

Arable farming systems have been believed to be the main source of nitrate leaching as the soil is normally bare during autumn and winter allowing inorganic nitrogen in the soil to leach due to the lack of plant uptake. Grassland based agriculture has been believed not to be a major source of nitrate leaching due to a number of factors. The nature of a grassland is that the soil is covered all year round which allows for uptake of inorganic nitrogen in the soil. Irish grassland systems have historically used small amounts (less than 100 kg N per hectare) of nitrogen fertilisers. Beef systems in the country still use relatively little inorganic nitrogen fertilisers whereas the dairy farming sector relies on large inputs of nitrogen.

Research during the late 1980's by the Geological Survey of Ireland (GSI) and Teagasc started to raise the issue of nitrate leaching to groundwater from intensive dairy farming as being a concern. Field data collected by Teagasc and the GSI was summarised in an MSc. thesis by McGuire (1991) which found groundwater nitrate concentrations greater than 20 mg N l^{-1} beneath an intensive dairy farm, Ballyderown, which is located in North-East Cork. The elevated groundwater nitrate concentrations were believed to be due to the farming practices which were occurring on Ballyderown.

In order to further investigate the source of the elevated groundwater nitrate concentrations beneath the farm the present study was initiated and funded by Teagasc.

1.1.2 Study Aims

The main aim of the study was to examine and account for the high groundwater nitrate concentrations, beneath Ballyderown, which were observed during the mid to late 1980's. Quantification of different parts of the nitrogen cycle on the farm could help to elucidate the source of the elevated groundwater nitrate concentrations. In order to investigate the relationship between different sources of nitrate on the farm and the hydrogeology of the aquifer/aquifers beneath the farm. The final aim of the project was to attempt to extrapolate the findings on the study farm to a wider geographic area and examine whether elevated groundwater nitrate concentrations may occur in other similar areas.

1.1.3 Thesis layout

There are nine chapters in this thesis. The first chapter introduces the concept of nitrate leaching and the occurrence of nitrate in groundwater, with a review of relevant legislation. The second chapter examines the study area and agricultural practices in a wider context. A detailed nitrogen budget is constructed in the third chapter from data collected during the study. The fourth and fifth chapters characterise the soil/Quaternary deposits and bedrock physical characteristics. The sixth chapter reviews methodologies used for quantifying nitrate leaching and nitrate leaching from grassland based dairy-farming. Detailed examination of nitrate leaching through the unsaturated soil/Quaternary deposits is presented and discussed. Chapter seven examines the occurrence of nitrate in groundwater on the study farm and identifies the source of the groundwater nitrate using other groundwater chemical and biological parameters. The detailed study is then placed in a wider content through a review of nitrate occurrence in Irish waters, by comparing inorganic soil N on the study farm to other farms in the surrounding area and by conducting a detailed groundwater sampling survey. The conclusions of the investigation, together with subject areas where further research are needed, are then presented in the final ninth chapter.

1.1.4 Specific Objectives

- 1. Detailed nitrogen budget for a study farm, e.g. chapter 3, including:
  - Soil organic N mineralisation
  - Dirty water as a N source
  - Slurry N usage

- 2. Examination of nitrate leaching through the unsaturated zone, e.g. chapter 6
  - Use of soil inorganic N as a tool for quantifying nitrate leaching
  - Use of soil solution samplers to examine nitrate leaching

- 3. Detailed examination of groundwater nitrate concentrations, e.g. chapter 7
  - Monitoring of groundwater nitrate concentrations
  - Examination of the source of elevated nitrate concentrations
  - Use of other groundwater parameters in source identification
  - Interpretation of historical groundwater nitrate concentrations

- 4. Study area site characterisation, e.g. chapters 4 and 5
  - Further geological investigation to improve the farm geological base map
  - Groundwater flow direction determination
  - Bedrock hydrogeological characterisation
  - Water budget calculation
  - Soil and Quaternary deposit characterisation

- 5. Examination of findings in a wider geographic context, e.g. chapter 8
  - Comparison of soil/Quaternary deposit nitrate concentrations
  - Evaluation of groundwater nitrate concentrations at regional/national level

1.2 Introduction to Nitrates in Groundwater

1.2.1 Introduction to nitrate leaching

On a global scale groundwater contamination by nitrate is a common occurrence. Nitrate is one of the most mobile ions in soils and losses from soil to the environment occur by two different pathways, denitrification (a gaseous loss of nitrogen from soils) and leaching, which is the removal of nitrate in solution through a soil. Nitrate in a soil is also available for plant/crop uptake which is the primary reason for agricultural application of nitrogen to soils.

Although the widespread use of nitrogen fertiliser has greatly increased the production of food, it has incurred environmental cost.

The amount of nitrate in water is expressed in one of two ways: either as the total amount of nitrate present, or as the amount of nitrogen contained in the nitrate (the latter is often referred to as nitrate-nitrogen, NO_3-N). Throughout this thesis nitrate concentration is referred to as nitrate-nitrogen (NO_3-N) unless otherwise stated.

Sources of nitrate contamination can be separated into two categories: point source pollution and non-point source or diffuse pollution. Point source pollution of groundwater in Ireland is common in small domestic water supplies and is primarily caused by septic tanks and farmyards which are often located within 100 to 200 m of a borehole. Point source pollution by septic tanks can be attributed to a number of factors such as siting close to boreholes, lack of proper soak-way systems, inadequate attenuation due to thin soils and high density of septic tanks. Point source pollution from farmyards can be caused by a number of activities which occur in the farmyard such as slurry and manure storage, silage effluent storage and dirty water storage. When these are located close to boreholes the risk of contamination is high.

Non-point source or diffuse pollution of water originates from diffuse land areas that intermittently contribute pollutants to surface water and groundwater. The primary aim of this thesis is to examine and quantify nitrate contamination of groundwater from a diffuse agricultural source.

This introductory chapter introduces nitrate as an environmental pollutant explaining briefly some of the effects of nitrate contamination of water on both the environment and human health. The nitrate directive (91/676/EEC) is introduced, which was implemented to prevent environmental degradation and potential impact on humans from the consumption of water from nitrate losses from agricultural sources. The current implementation of the nitrate directive is also reviewed. Lastly, the main aims of the study undertaken for this thesis are briefly outlined.

1.3 Environmental effects of excess nitrate

Excess nitrate losses affect the environment in two main ways. Firstly, excess nitrate in surface waters can cause eutrophication. Secondly, excess nitrate can contaminate drinking water supplies and has been thought to pose a potential threat to human health if ingested.

1.3.1 The effect of excessive nitrate concentrations in surface water

Nitrate contamination of surface water can originate from over-land flow, through flow in soils/Quaternary deposits or through groundwater input to surface water bodies. Eutrophication of surface water bodies caused by elevated nitrate concentrations only occurs where there is a plentiful supply of plant available phosphorus in the surface water. Generally rivers and lakes are limited in the availability of phosphorus for plant growth and under these conditions nitrate does not cause eutrophication. Nitrate triggered eutrophication can be observed in estuarine and marine aquatic systems where nitrogen is generally the limiting nutrient for plant growth.

Eutrophication of estuarine systems, due to the addition of nitrogen, of which nitrate is the predominant chemical form, has been reported for the Ythan estuary in eastern Scotland (SEPA, 1997) and Clonakilty bay in Southern Ireland (Cork County Council, 1998).

1.3.2 Health effect of excessive nitrate ingestion in drinking water

Human ingestion of excessive nitrate concentrations is believed to cause a number of conditions. Excessive nitrate ingestion in drinking water has been linked with methaemoglobinemia or blue baby syndrome, possible gastric cancers and other certain forms of cancer such as non-Hodgkin's lymphoma (NHL).

Methaemoglobinemia (blue baby syndrome) is known to be caused by excessive nitrate ingestion, the nitrate is converted to nitrite under certain gastric conditions, it then bonds with blood haemoglobin which is converted to methaemoglobin. Methaemoglobin cannot carry oxygen which is normally carried on exchange sites on the haemoglobin which are now filled with nitrite ions. In adults, methaemoglobin is converted back to haemoglobin by enzymes in the body restoring normal methaemoglobin levels. Newborn infants have lower levels of these enzymes and normally their blood methaemoglobin levels are 1 to 2 percent. At methaemoglobin levels above 10 per cent, symptoms of cyanosis usually appear, mucous membranes appear blue in colour and there may also be digestive and respiratory problems. Methaemoglobin levels of 50 to 70 per cent cause brain damage and death may occur (Bryson, 1984).

In the US the National Academy of Sciences concluded that available evidence on the occurrence of methaemoglobinemia in infants tends to confirm a maximum value near 10 mg l^{-1} as nitrate-nitrogen. When reviewed by the World Health Organisations European working group on health hazards from water, in 1977, a proposed limit of 50 mg l^{-1} of nitrate or 11.3 mg l^{-1} nitrate-nitrogen was set as a maximum in respect to infant methaemoglobinemia (as reported in Dudley, 1984). This level of 11.3 mg l^{-1} nitrate-nitrogen formed the basis for maximum admissible concentrations (MAC) to be set under E.E.C. water quality standards. As mentioned, the MAC limit is based on the risks associated with methaemoglobinemia in infants and not the risks of gastric or lymphatic cancers (van Maaren *et al.*, 1996).

The link between nitrate and cancer is tenuous and not fully understood, but it is thought that nitrate can act as a precursor in the formation of compounds called N-nitroso compounds in the body which are known to cause cancer in animals (Bryson, 1984). In Italy and Colombia high levels of nitrate in well water were associated with an increased risk of gastric cancer (Gilli *et al.*, 1984 and Cuello *et al.*, 1976).

In recent years elevated nitrate concentrations in drinking water were associated in the USA with an increased incidence of non-Hodgkins lymphoma (Weisenburger, 1991; van Maanen *et al.*, 1996; Ryan, 1998b; Ward *et al.*, 1996). The risk of non-Hodgkins lymphoma was observed to increase with the amount of nitrate ingested by individuals in drinking water. Dietary intake of nitrate in food was conversely found to lower the risk of contracting non-Hodgkins lymphoma which is likely to be due to vegetables and fruit (which contain the highest dietary nitrate levels). Fruit and vegetables have been linked to carcinogenic prevention.

Recently childhood diabetes was found to be strongly associated with the concentration of nitrate in drinking water in Yorkshire, U.K. (McKinney *et al.*, 1999). These observations are currently being investigated in other parts of the U.K..

Potential benefits of nitrate ingestion have been highlighted recently by researchers from the UK (Benjamin and McKnight, 1999; Duncan *et al.*, 1999; Dykhuizen *et al.*, 1996 and Li *et al.*, 1999) who observed that nitrite reduced on the tongue from nitrate released in patients saliva from their tongue, may have positive health implications. The concentration of nitrite was positively correlated with the concentrations of nitrate ingested. Under the low pH conditions found in the gastro-intestine, cytotoxic intermediates of nitrogen, such as NO, are released. These compounds, in conjunction with acidified nitrite, inhibited the activity of certain pathogenic bacteria such as *Y. enterocolitica* and *S. enteridis* (Dykhuizen *et al.*, 1996). Thus some benefits of ingesting high amounts of nitrate may be seen but it is unclear whether these are of greater importance than the other health issues already raised.

1.4 The Nitrate Directive (91/676/EEC)

1.4.1 Introduction to the Nitrate Directive

In 1980 the E.E.C. (1980) set standards for numerous chemicals in water intended for human consumption in a new directive 80/778/EEC. Limits for nitrate were set at a maximum admissible concentration (MAC) of 50 mg l^{-1} nitrate with a guide level (GL) of 25 mg l^{-1} nitrate. In the late 1980's at an E.E.C. ministerial seminar on water a number of improvements to existing legislation were identified. In 1989 the nitrate directive began life as a "Proposal for a Council Directive concerning the protection of fresh, coastal and marine waters against pollution caused by nitrate from diffuse sources" (E.E.C., 1989). The final Nitrate Directive (91/676/EEC) was concluded and signed three years later, on 12/12/91 and Member States were notified on 19/12/91.

1.4.2 Nitrate Directive aims

The objects of the directive are two fold: to reduce water pollution caused or induced by nitrates from agricultural sources and to prevent further such pollution. The directive seeks to ensure that this is carried out by requiring Member States to identify waters affected by high nitrate concentrations and water which could be affected and designating vulnerable zones around these identified waters. In vulnerable zones the Member States must draw up action programmes which contain mandatory measures concerning agricultural practices which also stipulates the maximum amount of manure which may be applied to land each year. Member States must also produce a code of good agricultural practice which is to be implemented through out member states agricultural area.

Nitrate vulnerable zones (NVZ's) are defined, by the Directive, as areas of land which drain, either directly or indirectly into either: 1. Surface freshwater or groundwater that is intended for drinking water and which would contain more than 11.3 mg l^{-1} of nitrate-nitrogen if no action were taken; or 2. Natural fresh water, estuarine or coastal water that is either already eutrophic or may become so if no action is taken.

Three main measures are enforced in NVZ's. Firstly, restrictions on the timing, rate and other conditions for the application of fertilisers. Secondly, closed periods for slurry spreading and minimum storage capacities for slurry. Thirdly, limits on the overall quantity of N per hectare of 170 kg N ha^{-1} $year^{-1}$ which may be supplied as animal manures, including that deposited by animals while grazing although, for the first four years after the introduction of the Directive, a higher level of 210 kg N ha^{-1} $year^{-1}$ is acceptable.

1.4.3 Implementation of the Nitrate Directive

All Member States, with the exception of Belgium, have produced a Code of Good Agricultural Practice, as of 30/7/97 (E.C., 1997), although only Italy and Denmark submitted Codes by the due date (20/12/93). In Ireland, the Code of Good Agricultural Practice to protect waters from pollution by nitrate was published in July 1996 by the Department of Agriculture, Food and Forestry, and the Department of the Environment. The code contains advice and recommendations on farm practices in relation to the storage of organic fertilisers, standards and specifications for the construction of storage facilities, application timings for organic and chemical fertilisers, which includes appropriate rates of application, and precautions to be taken to avoid causing water pollution.

In the designation of NVZ's (as of 30/7/97) Austria, Denmark, Germany, Luxembourg and the Netherlands all designated the whole of their territories as vulnerable. France designated 46% of the agricultural land as vulnerable, the UK designated 69 zones, Sweden designated 5 and Ireland designated no zones (E.C., 1997). No NVZ's have been designated in Belgium, Finland, Greece, Italy, Portugal or Spain. In addition the Commission are investigating the decisions made by France, Ireland, Sweden and the UK.

Action programmes submitted by Austria, Denmark, and Sweden are under review (as of 30/7/97) whereas Germany, Luxembourg have been judged not to have complied. Only these countries have implemented action programmes as of 30/7/97 (E.C., 1997).

The Commission considers the present situation to be grave, with 13 of the 15 member states subject to legal proceedings with respect to both the non-transposition and/or the incorrect application of the directive (E.C., 1997).

A report by the commission to the Council and European parliament (E.C., 1997) suggests that the MAC limit for eutrophic waters may be too high. 'The limit of 50 mg l^{-1} nitrate may not be sufficient to reduce eutrophication in estuarine conditions and therefore this is not considered to be the defined limit in the Directive, indeed it is likely to be significantly too high to reduce eutrophication.'

1.4.4 The UK situation

In the UK 68 vulnerable zones were delineated totalling approximately 600,000 hectares in March 1996 (MAFF, 1996). A further zone was delineated in 1997 at which time a total of 69 NVZ's had been delineated in the UK (E.C., 1997).

Concern about compensation of loss of income to farmers was an issue. The British government upholds the polluter pays principle and therefore no compensation of farmers in NVZ's will occur. Farm waste grants which were abolished have been reinstated in NVZ's to comply with restrictions on organic manures. This provides up to 25% towards the cost of new or improved farm waste handling and storage facilities. There is compensation for farmers within the voluntary Nitrate Sensitive Areas (NSA) scheme but this goes substantially beyond good agricultural practice required within NVZ's.

In the UK the MAFF programme for minimising potentially polluting loss of soil nutrients from agricultural land is being pursued through the voluntary NSA. In 1994 the pilot NSA scheme was replaced by a new scheme launched as part of the Agri-Environment Programme. The scheme compensates farmers in England for voluntarily changing their farming practices in ways which significantly reduce nitrate leaching. Annual payments range from £65 per hectare for restrictions on nitrogen fertilisers to £590 per hectare for the conversion of arable land to native species.

The NSA scheme offers farmers three different types of voluntary measures, involving substantial changes in farming practices, to reduce nitrate leaching from their land. These are:

- 1. Premium arable scheme (PAS) conversion of arable land to extensive grass under a number of different management prescriptions.
- 2. Premium grass scheme, the extensification of existing intensively managed grass.
- 3. Basic scheme, low nitrogen arable cropping with two options of restricted rotation and standard rotation.

The NSA scheme is voluntary and farmers may choose whether or not they wish to enter land into a range of options. Catchments of sources covered by the NSA's also fall within the areas currently designated as NVZ's. The rules in NSA's are more demanding than those to be applied within NVZ's. NSA undertakings last for 5 years and include requirements to retain environmental features on land entered into the scheme in addition to management conditions. Payments totalling £3.6 million were made in 1996-1997 on 20,000 ha of land subject to NSA undertakings (64% of the eligible land in the areas).

1.4.5 The Irish situation

In Ireland no NVZ's were identified and this was reported on 17/7/95. The Department of the Environment in Ireland is currently re-examining new water quality data which has been collected from 1995 to 1998 and they are currently establishing NVZ's within Ireland (Gallagher, Pers. Com., 1999).

In Northern Ireland, a total of three small candidate NVZ's were delineated on 16/11/98, one in Clogh Mills, Co. Down and the remaining two at Comber, Co. Down. The total area of land delineated was 1340 hectares (DOE NI and DANI, 1998). These areas have been officially designated as NVZ's in Northern Ireland (Carroll, Pers. Com., 1999).

CHAPTER 2 INTRODUCTION TO THE STUDY AREA AND FARMING PRACTICES

2.1 Introduction to the Study Area Location

The area selected for this study is located in Southern Ireland in Co. Cork. The farm selected was Ballyderown which is an out farm of Teagasc, Moorepark which is located 2 km to the west of Ballyderown (Figure 2.1). The farm is operated to provide milk for research and development of milking machinery which is run by the Moorepark research centre. Figure 2.1 is drawn from the OS Discovery series 1:50000 sheets 73, 74, 80 and 81.

Ballyderown is located 5 km from Fermoy town in Northeast Cork. The farm is located in the Dungarvan valley and is surrounded by rivers on two sides, the Araglin to the east and south which feeds into the Blackwater which is also located south of the farm flowing eastwards (Figure 2.1).

2.2 Study Area Meteorology

Meteorological data are collected at Teagasc, Moorepark which is located 2 km from the study farm. The monthly variation in rainfall and air temperature can be seen in Figure 2.2 below. Annual 30 year mean rainfall at Moorepark is 981 mm. Rainfall monitored during the study period is presented in section 4.5.

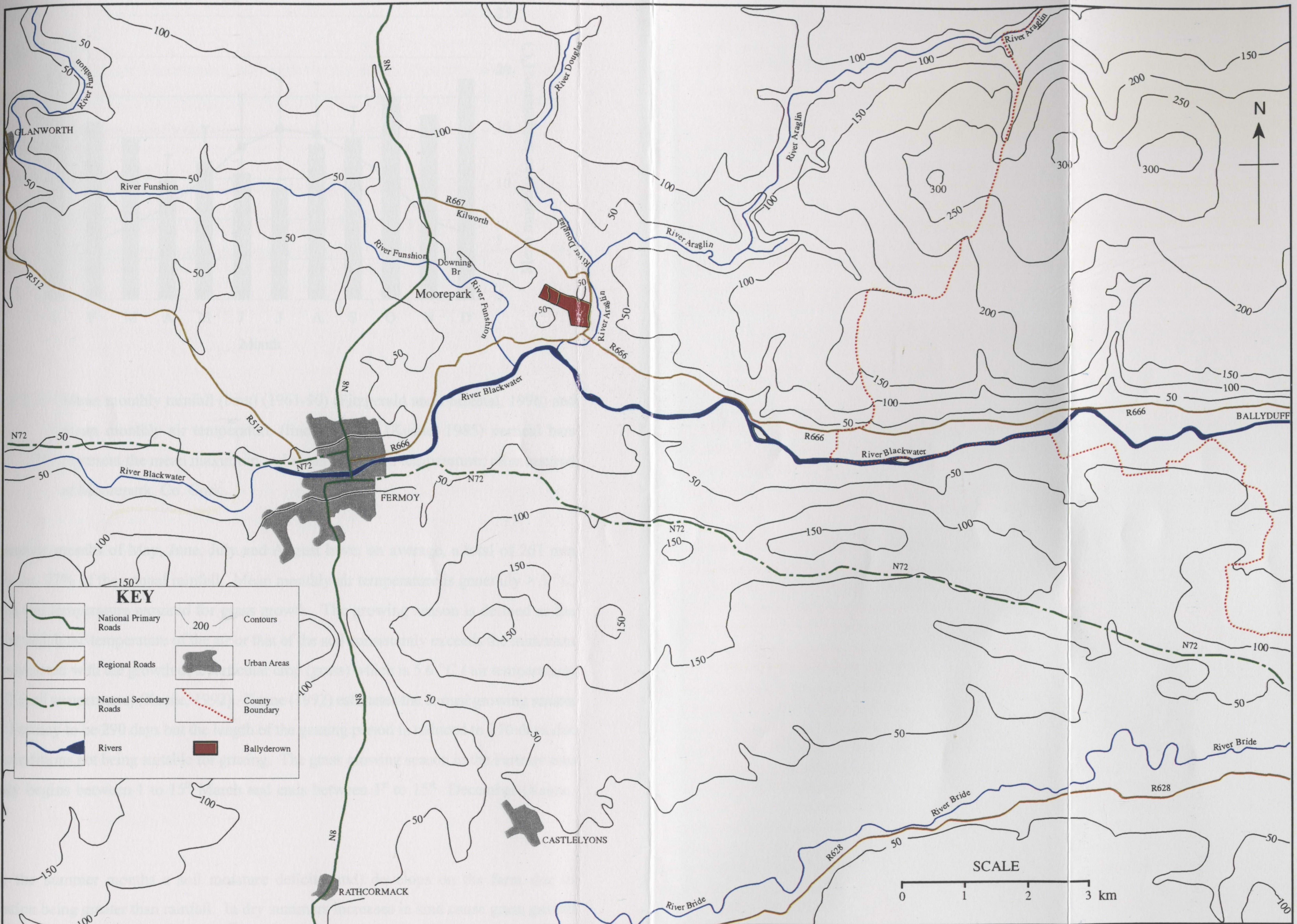


Figure 2.1 Study Area location, regional topography and surface water hydrology.

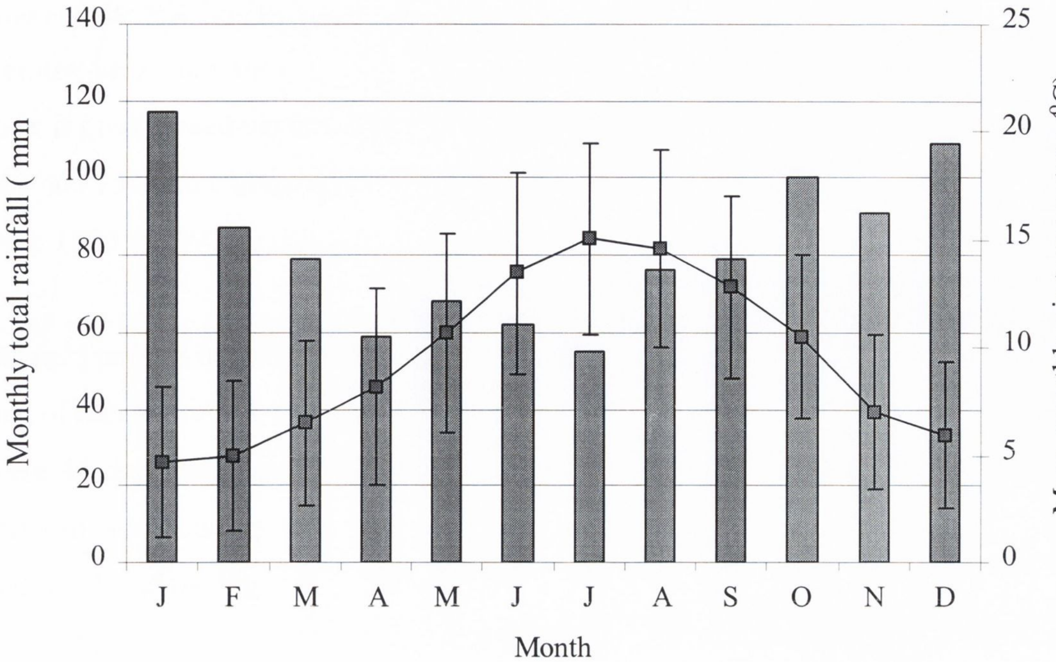


Figure 2.2 Mean monthly rainfall (bars) (1961-90) (Fitzgerald and Forrestal, 1996) and mean monthly air temperature (line) 1951-80 (Keane, 1985) vertical bars represent the mean maximum and mean minimum temperature; all measured at Moorepark, Co. Cork.

The summer months of May, June, July and August have, on average, a total of 261 mm rainfall, i.e. 27% of the annual rainfall. Mean monthly air temperature is generally > 5 °C, which is the temperature required for grass growth. The growing season is defined as the period in which the temperature of the air or that of the soil consistently exceeds the minimum value associated with the growth of a particular crop (grass) which is 5.6 °C (air temperature) and 6°C (soil temperature) (Keane, 1992). Keane (1992) estimates the annual growing season around Fermoy to be 290 days but the length of the grazing period is reduced to 270 days due to soil conditions not being suitable for grazing. The grass growing season in the Fermoy area normally begins between 1 to 15th March and ends between 1st to 15th December (Keane, 1992).

During the summer months a soil moisture deficit (smd) develops on the farm due to evaporation being greater than rainfall. In dry summers increases in smd cause grass growth restrictions which limit the utilisation of N available in the soil for plant uptake.

In Ireland a definite NW to SE trend was observed with the SE having the highest potential smd and the NW having the lowest potential smd (Connaughton, 1967). Potential smd in the Fermoy area from 1958 to 1965, for the months May to August, was 25 to 50 mm although there is great annual variation as noted in 1959 when the smd for the Fermoy area was between 100 and 150 mm Connaughton (1967). Soil moisture deficit was calculated for Moorepark, from 1980 to 1997, and is presented in section 4.5.

Drought periods have been defined as a period of 15 consecutive days on none of which ≥0.2 mm of rain fell or 1.0 mm for dry spells (Keane, 1992). During the period 1960 to 1984 there were 44 dry spells and 20 droughts observed at Kilkenny, which is the nearest synoptic meteorological station to Fermoy reported by Keane (1992). Within Ireland areas to the East and South had the highest number of occurrences during the observation period 1965 to 1984.

2.3 Geology

This section introduces the soil, quaternary deposits and bedrock geology of the general region and then specifically data previously collected by other studies of the Ballyderown farm and area. Further investigations carried out during the present study is then used to augment the available data on the farm and these are presented in chapter 4.

2.3.1 Regional Geology

The bedrock geology of north Co. Cork is dominated by Carboniferous limestone underlain by Devonian Old Red Sandstone and Silurian shale. The topography of the area strongly reflects the geology with Carboniferous limestone rocks found in the low-lying land whereas Old Red Sandstone forms ridges. The area is often referred to as the Ridge and Valley Provence (Herries Davies, 1978).

2.3.2 Regional Quaternary Geology and Soils

The area is south of the Southern Irish End Moraine and was not affected by the last glacial episode which finished in the last Midlandian Cold Stage. Thus the glacial tills consist of older drift which has been extremely modified by periglacial activity. The tills, as described by Shearley (1988) are composed of angular rock fragments of mainly sandstone, siltstone and mudrocks with very few limestone clasts due to extensive weathering and decomposition. Fluvioglacial deposits are well displayed locally which consist of alternating deposits of poorly-sorted, coarse to fine gravels and cross-bedded sands.

2.3.3 Study Area Quaternary Geology and Soils

The Quaternary deposits in the area are not well documented. McGuire (1991) describes the Quaternary deposits on the farm as glacial tills and gravels with a gravel section to a depth of 4.5 m located around the farm buildings and surrounding paddocks.

The soils above the sandstone tills are acid brown earth and the soil type corresponds to the principal soil Association 13 in the Soil Map of Ireland and is associated with brown podzolics (principal Soil Association 15). These two soil associations comprise 6.6% of the total area of Ireland although they are principally found in Cork where they are a dominant soil association (Gardiner and Radford, 1980). McGuire (1991) describes the soil on the farm as having moderate structure with a friable consistency. The soil depth (A plus B horizon) varied from 0.6 m to 0.75 m. The C horizon consists of stones and gravel of mixed origin.

A more detailed soil survey carried out during this project, which includes description of trial pit profiles, textural analyses, bulk density, infiltration rates and saturated hydraulic conductivities is presented in chapter 4.

2.4 Irish land-use and farming practices

2.4.1 Introduction to Irish Agriculture

During 1997 the total agriculturally productive land area in Ireland was 4,431,600 ha; pasture was the predominant land use accounting for 3,543,300 ha, tillage and horticulture accounting for 414,300 ha and rough grazing accounting for 473,900 ha.

2.4.2 Agricultural N use

National annual inorganic fertiliser usage from 1953 to 1998 can be seen in Figure 2.3. During the 1970's P and K fertiliser use peaked and since then it has begun to decline slightly due to growing awareness of fertiliser over use on soils with adequate nutrient reserves. However national inorganic N fertiliser use has increased from < 100,000 tonnes in 1971 to >400,000 tonnes N in 1994. The highest annual inorganic N fertiliser use to date of 431,000 tonnes was reported for 1998. (The fertiliser year runs from October 1st to September 30th).

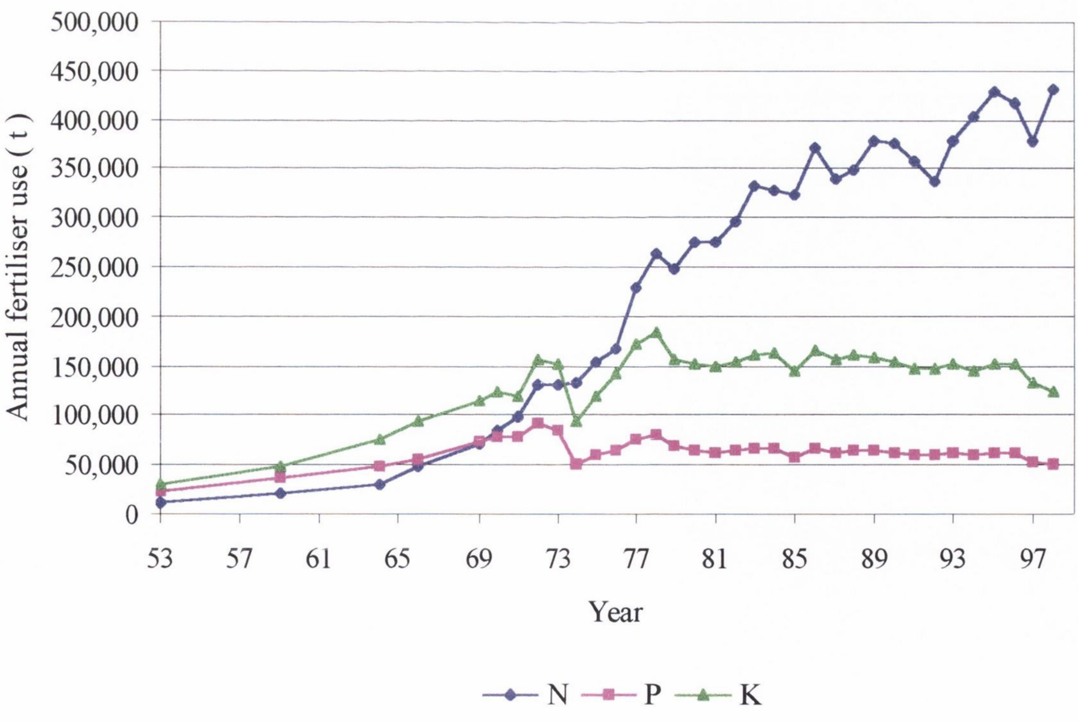


Figure 2.3 National annual use of inorganic N, P and K fertilisers between 1953 and 1998.

The current Teagasc N fertiliser recommendations for grazed grassland can be seen in Figure 2.4.

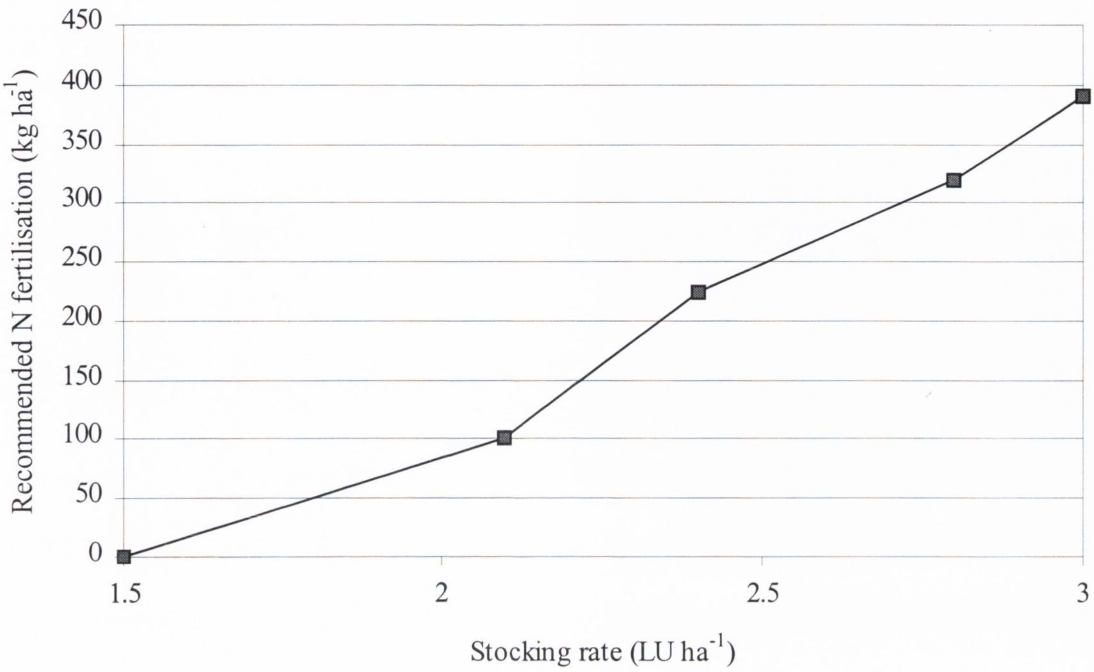


Figure 2.4 Current Teagasc recommendations for grassland grazed at different stocking rates (Gately, 1994).

The maximum advised N fertiliser rate for grazed grassland is 390 kg N ha^{-1} for 3 LU ha^{-1}, although the following additions, by Teagasc, to the fertiliser recommendations should also be considered. Grazed swards less than 3 years old should receive 25% more N than recommended. Where N use exceeds 300 kg ha^{-1} for a few years, it should be possible to cut back on late season applications due to increased soil N.

The 1995 fertiliser use survey (Murphy *et al.*, 1997) which was carried out on 1226 farms in Ireland showed a mean inorganic fertiliser N usage on grazing land of 93 kg ha^{-1} y^{-1}, with a wide variation between counties. Kildare and Cork had the highest N usage of 175 and 164 kg N ha^{-1} y^{-1} for grazed grassland. The mean annual N application rate for silage was 117 kg ha^{-1} but there were considerable inter-county differences with Kildare and Cork having the highest N fertiliser use for silage of 167 and 156 kg ha^{-1}, respectively. Leitrim and Roscommon had the lowest N fertiliser use for silage of 49 and 53 kg ha^{-1} y^{-1}, respectively.

National N fertiliser use on dairy farms was greater than on cattle rearing farms i.e. grazing land on dairy farms received 166 kg ha^{-1} y^{-1}, whereas grazing land on cattle rearing farms received only kg ha^{-1} y^{-1}. Silage produced on dairy farms received an average of 154 kg ha^{-1} y^{-1} which is considerably higher than the 88 kg ha^{-1} y^{-1} used for cattle silage. Thus on average dairy farms used considerably more N fertiliser than cattle rearing farms by 110 kg N ha^{-1} year^{-1} for grazing and 66 kg N ha^{-1} for silage.

The animal stocking rate on farms greatly influenced the N application rate which varied from 32 kg N ha^{-1} for stocking rates of 0-1 LU ha^{-1} to 179 kg N ha^{-1} for stocking rates of 2-2.5 LU ha^{-1}. Examination of the relationship between farm system and stocking rates showed that N fertiliser use increased with stocking rate (Figure 2.5). Dairy farms used the highest rates of N fertiliser of 226 kg ha^{-1} y^{-1} at a stocking rate of 1.5 to 2 LU ha^{-1}. At the higher stocking rate of 2 to 2.5 LU ha^{-1} there was a slight decline in fertiliser use to 198 kg ha^{-1} y^{-1} but this is likely to be due to the smaller sample size of farms in this category.

The higher use of inorganic N fertiliser on dairy farms and the higher stocking rates on dairy farms is important in the Cork region due to the high percentage of dairy farms in the county.

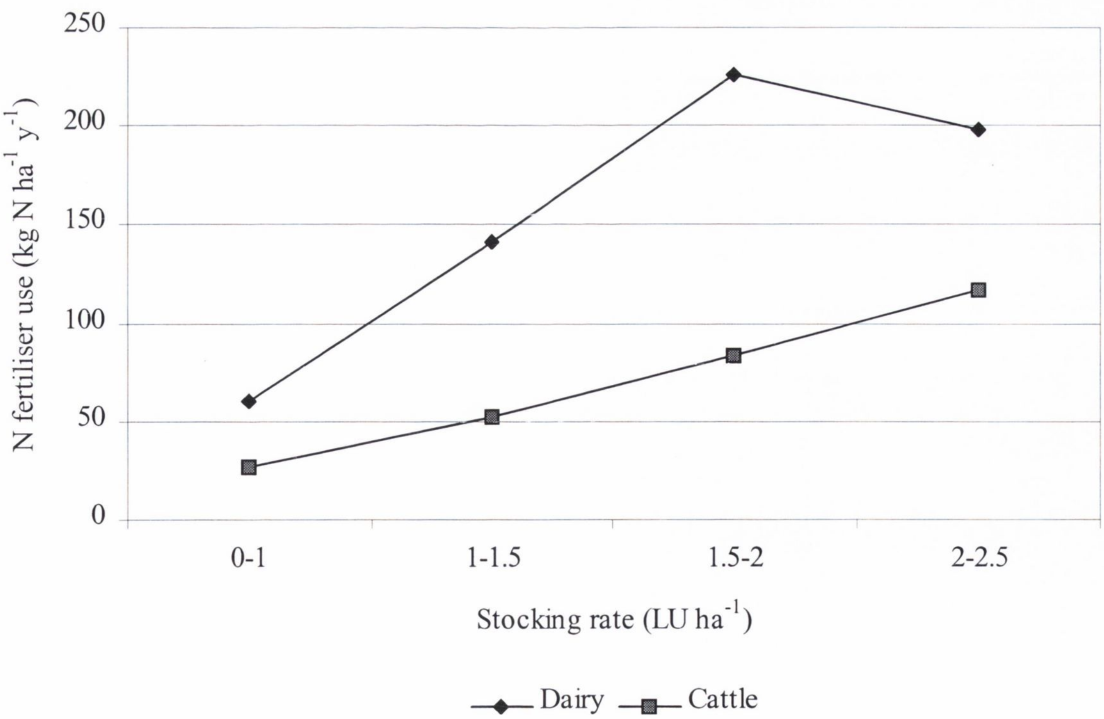


Figure 2.5 The relationship between stocking rate and N fertiliser use on dairy and cattle farms (Murphy *et al.*, 1997).

The fertiliser use survey does not detail any farms with stocking rates greater than 2.5 LU ha^{-1} due to the low number of such farms which were included in the survey. Therefore the N fertiliser use on farms with a stocking rate >2.5 LU ha^{-1} can only be estimated to be greater than the N use at a stocking rate of 2 to 2.5 LU ha^{-1}.

As dairy farming is the highest user of N fertiliser it is interesting to observe that between 1975 and 1987 the percentage of dairy farms in the country has declined from 55.9 to 23.9%, and coupled with this there was an increase in the average herd size from 11.6 to 21.8 LU (Gillmor and Walsh, 1993). The southern region of Ireland was identified as a core dairy area with 61% of dairy farms located in Counties Cork, Kerry, Limerick and Tipperary.

The increase in intensification, as a result of the Common Agricultural Policy (CAP), is associated with a significant increase in the use of off-farm inputs such as fertilisers and concentrated feedstuffs. This in turn has resulted in a trend towards greater regional specialisation and concentration of production (Gillmor and Walsh, 1993).

During the 1990's with CAP reforms there has been movement towards restrictions on output from some sectors, especially cereals and dairying with compensatory payments given to offset incomes and payments to encourage diversification into more environmentally friendly agriculture.

2.4.3 The Rural Environmental Protection Scheme

During the 1990's a Rural Environmental Protection Scheme (REPS) was implemented at a national level. The aim of REPS was to prevent pollution from agricultural related activities and to improve the general aesthetic qualities of the countryside. Under REPS a farmer is required to use all nutrients in an efficient and environmentally friendly manner. A Nutrient Management Plan (NMP) is prepared which allows the farmer to apply enough animal manures and artificial fertilisers to give a reasonable level of grass or crop production without posing a threat to water resources and the general environment. There are three 'nutrients' controlled under REPS:- nitrogen, phosphorus and lime. The N limits under REPS are the most relevant to the current study.

The maximum level of total N permitted on the grassland area of a farm is 260 kg ha^{-1} of which only 170 kg ha^{-1} may come from animal or other waste. Thus the organic N limit of 170 kg ha^{-1} limits the stocking rate on REPS dairy farms to 2 cows ha^{-1} as it is estimated that 1 cow excretes 85 kg N $year^{-1}$ (ANON, 1996). Total N is composed of N from:- the livestock present on the farm; N imported in animal manures, slurries and other wastes which are spread on the land and N from artificial fertilisers. There are also N limits for tillage farms under REPS which are variable depending on the crop type. This is not dealt with here due to having no direct relevance to the present study.

Slurry storage is also dealt with in REPS which recommends that clean water should be collected separately to manure areas of the farm yard which become soiled by livestock. Soiled areas of the farm yard should be covered with concrete and restricted in size to reduce the amount of soiled water produced. Under the REPS scheme there is no fixed storage capacity requirement for participating farms (Department of Agriculture Food and Forestry, 1996). Instead, recommendations are made on spreading times with 50% of the slurry to be spread by 1st July and the remaining 50% to be spread before 30th September. It is stated that slurry should be spread as early in the growing season as is practicable and local circumstances must be taken into consideration when applying slurry.

Currently there are 39,000 approved participants in REPS accounting for an area of 1,323,516 ha, or 30% of the country's agricultural land, with payments to farmers amounting to £310,500,000 (McLoughlin, 1998). The geographical distribution of each County under REPS can be seen in Figure 2.6 reproduced with permission from Emerson and Gillmor (1999). The North West and West have greater than 30% of the county in REPS compared to the South and Southeast which have generally 10% of the farmed land in REPS.

2.5 Ballyderown Farming practices

2.5.1 Introduction to farming practices on the study farm

The study farm is an intensive dairy farm covering 30 ha which is used for both grazing and silage harvesting; a further 12 ha are located on the low lands surrounding the Araglin and

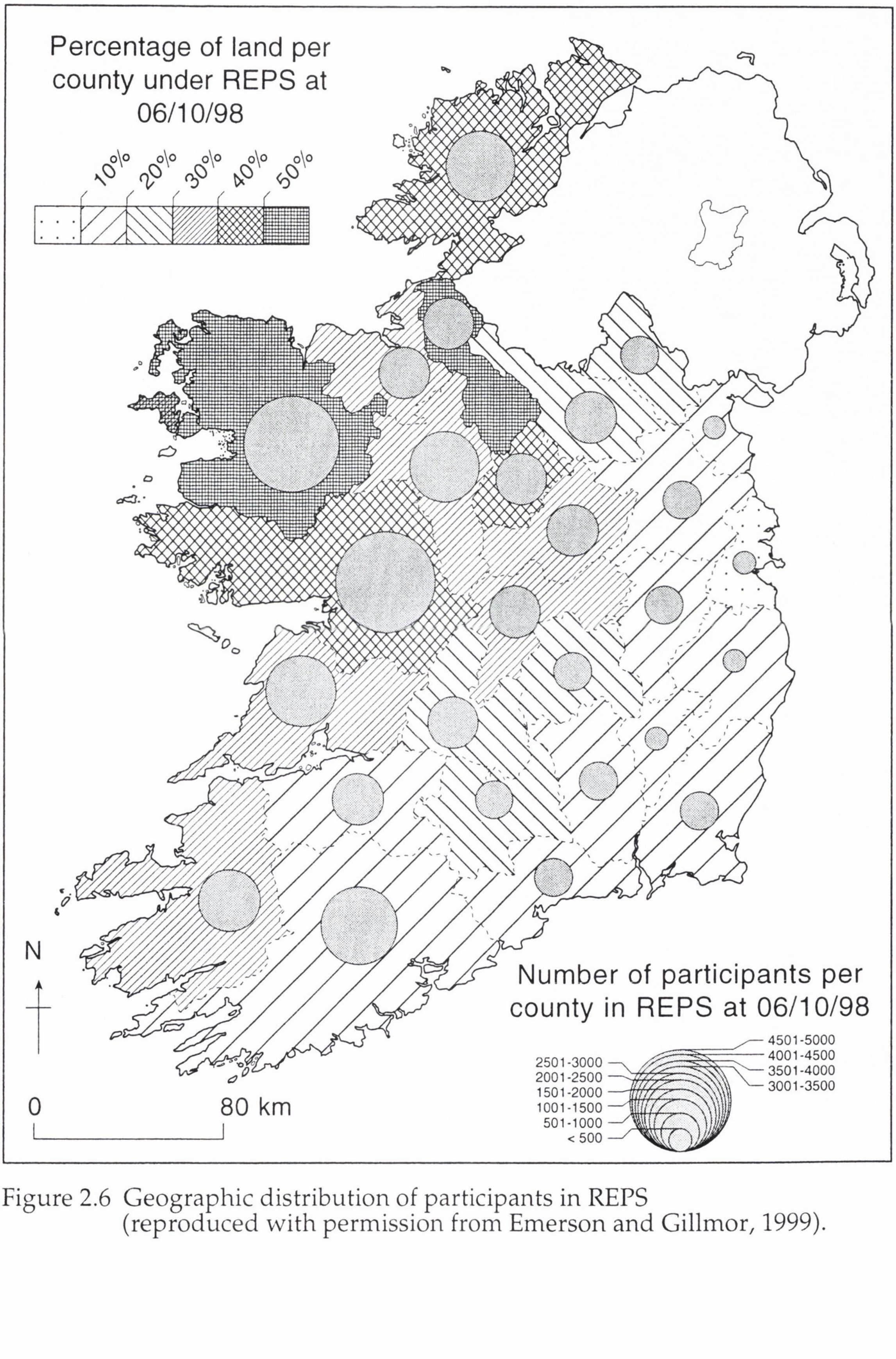


Figure 2.6 Geographic distribution of participants in REPS (reproduced with permission from Emerson and Gillmor, 1999).

Black water rivers which are predominantly used for silage harvesting although some grazing is carried out here also (Figure 2.7). The area studied for this project was the 30 ha located to the north of the farm yard, which is divided into 30 plots to facilitate the management of a 21 day rotational system (Figure 2.7). Plot areas vary from 0.4 to 1.6 hectares with a mean plot area of 1 ha (Table 2.1).

Table 2.1 Area of all plots on the study farm.

Plot No.	Plot size (ha)	Plot No.	Plot size (ha)
1	1.1	9	1.0
2	1.0	9a	1.0
2a	1.0	10	1.4
3	1.0	10a	0.4
3a	1.0	11	1.0
4	0.9	11a	1.3
4a	0.9	12	1.2
5	1.0	12a	0.8
5a	1.0	13	1.1
6	0.9	13a	1.0
6a	1.1	14	0.5
7	1.0	15	1.1
7a	1.1	15a	0.9
8	0.8	16	1.6
8a	0.9	16a	0.6

The farm is low lying with the altitudes varying between 30 and 46 m above sea level (O.D.); the northern area of the farm is topographically higher than the southern area of the farm (Figure 2.1) . To the east of the farm is a steep escarpment of ~ 15 m in height.

The dry free draining soil allows for extended grazing whereby animals can be kept out grazing the plots until late November and they are often back in the plots during February. The proportion of time the animals spend in housing is thus short (~10 weeks) compared to other areas of Ireland where animals can spend up to 20 weeks housed.

On the farm in 1997 there were 91 milking cows, 25 bulling heifers (which are cows which have not had their first calf) and 25 calves which was similar throughout the study period with slight variations due to the selling of heifers and calves each year. Historically the farm had higher stock numbers due to the renting of an extra 30 ha of land although this ceased in 1988

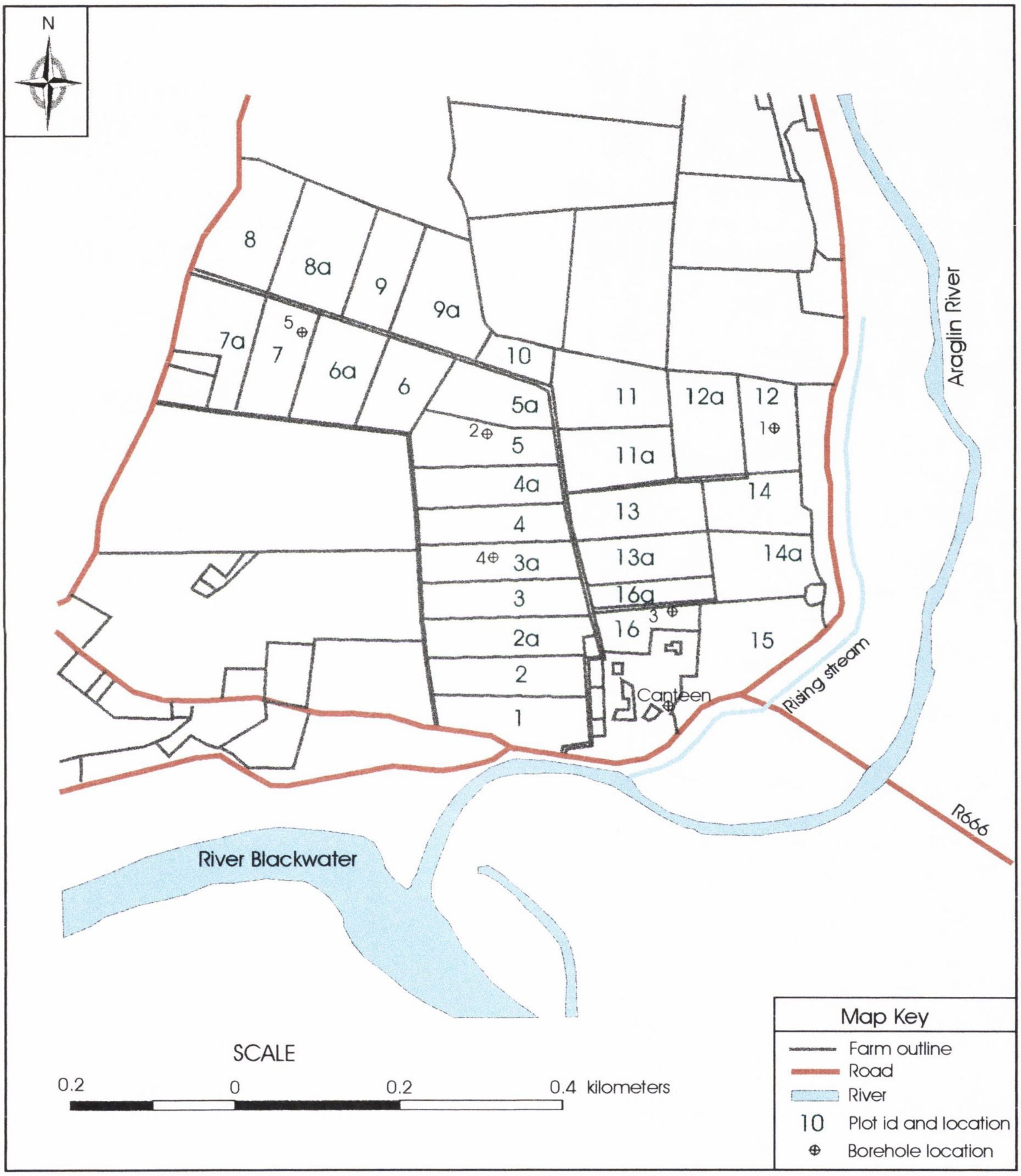


Figure 2.7 Ballyderown plot locations and identities (including borehole locations).

due to the loss of milk quota and the subsequent de-stocking of the farm to current levels. In 1986 and 1987 a total of 150 and 156 milking cows, respectively, were on the farm (McGuire, 1991).

2.5.2 Slurry

Slurry was collected in slatted tanks beneath the cow sheds in the farm yard and also collected in the traps leading into the dirty water storage tank (section 2.5.3). Dirty water originates from the farm yard and is composed of farm yard wash water, milk tank rinsings, silage pit effluent, and slurry tank over-flow.

Slurry on the farm was collected in a storage tank with a capacity of 270 m^3 beneath the slatted floor in the cow houses. All slurry was land-applied using an Abbey 5000 l tanker, with a splash plate attached.

Slurry was spread throughout the year with up to 5000 l spread per week during the winter housing period (McGuire, 1991). Slurry must be spread during the winter due to the lack of slurry storage capacity on the farm. Slurry which is spread during the winter is skimmed off the surface of the slurry tanks with no agitation due to the animals being housed.

Table 2.2 Quantity of slurry produced for a 12 week winter housing period.

Animal quantity and type	Slurry volume (m^3 $week^{-1}$)	Animal housing duration (weeks)	Slurry volume produced (m^3)
91 milking cows	0.315	12	344
25 bulling heifers	0.250	12	75

The total slurry produced for a 12 week winter housing period is 419 m^3 (Table 2.2) which is 150% of the slurry storage capacity on the farm of 270 m^3. This is a serious lack of storage capacity necessitating land spreading of slurry during the winter housing period. Mounsey *et al.* (1998) in a survey of 12 dairy farms observed mean slurry storage capacity of 996 m^3 (varying from 409 to 1727 m^3).

2.5.3 Dirty Water

Dirty water was historically applied to the land by direct pumping using a pump fitted with an automatic timer which pumped water to a stationary rain gun. The radius of the irrigation zone is <10 m and the rain gun must be moved periodically. The rain gun was not moved regularly leading to localised nutrient over-application and soil damage (McGuire, 1991). During the early 1990s the rain gun was replaced with a dirty water 3-way system and self propelled irrigator (Plate 2.1).

The dirty water 3-way system consists of a 3-chambered settlement tank (3 way system) through which dirty water passes before entering the dirty water storage tank. Larger particles of organic matter suspended in the dirty water settle to the bottom of the tanks to prevent the pump and irrigator becoming blocked. Dirty water from the storage tank is pumped via a small bore pipe line which distributes the dirty water to a self-propelled travelling irrigator which land-applies the liquid.

The dirty water irrigator is comprised of a rotating boom mounted on a wheeled carriage and connected to a dirty water hydrant by a flexible pipe (Plate 2.1). The reaction force of the dirty water leaving nozzles at each end of the boom causes the boom to rotate.

This turns a specially shaped cam which operates a ratchet and pawl mechanism and drives a drum to winch in a steel cable attached to a fence post at the other end of the plot. The irrigator is winched along until most of the cable is wound back onto the drum. The irrigator must then be turned around and the steel cable attached to a fence post at the other end of the plot.

Irrigation of dirty water is automated with a float in the storage tank triggering irrigation when the storage tank is filled to a certain level. Dirty water irrigation normally occurs twice a day after the cows are milked due to large amounts of water being used to clean the milking parlour and milking equipment. During wet periods rainfall enters the dirty water system via farm yard runoff; a separate system collects and removes water from the farm building roofs. Land application of dirty water can occur during periods when the soil is unsuitable due to water logging or frozen top soil.

As for slurry on the farm, the limited storage capacity for dirty water means that dirty water is land-applied during periods when crop uptake of nutrients contained in the effluent is limited or absent.

Land application of dirty water can be carried out on all plots except 10, 16 and 16a due to the absence of the dirty water piping system in these plots (see Figure 2.7). There is no fixed management system of the land application of dirty water on the farm. Generally dirty water is irrigated in a certain plot for a period of time, which can last up to a number of months, before being moved to another plot. When the irrigator is moved to another plot it is often moved a short distance from the last irrigation plot. During the period of dirty water spreading the irrigator must be turned around within a plot once it reaches the other side of the plot. Although this is generally carried out soon after the irrigator reaches the other side of the plot sometimes the irrigator may remain in one specific area for a number of days before being turned around. Thus areas at the ends of plots receiving dirty water may receive a very high dirty water application rate. During the winter period the irrigator was generally kept within sight of the farm yard often in plots 3, 3a, 4, 4a and 13. Dirty water use during the study is presented in section 3.5.

2.5.4 Ploughing of Grassland

Ballyderown was sown with perennial rye grass during the 1960's. During recent years on the farm the grassland has been re-seeded with ryegrass due to decreases in the proportion of ryegrass in the sward. Gradual re-seeding began in 1990 and was completed in 1997 (Table 2.3).

Table 2.3 Ploughing and grassland re-seeding of plots at Ballyderown during the 1990s.

Year of re-seeding	Month of re-seeding	Plots re-seeded
1990	September	6
1991	September	10, 10a
1993	September	12, 12a, 13, 13a, 15, 15a
1994		
1995	January	7, 7a
1995	September	4, 4a, 5, 5a
1996	September	2, 2a, 3, 3a, 6, 6a
1997	September	8, 8a, 9, 9a

All ploughing and re-seeding was carried out in September of each year, except in 1995 when plots 7 and 7a were re-seeded in January after calves and heifers were held in these plots from October to the beginning of January due to an outbreak of Tuberculosis in the herd (plot locations can be seen in Figure 2.7).

CHAPTER 3 FARM NITROGEN BUDGET

3.1 Introduction

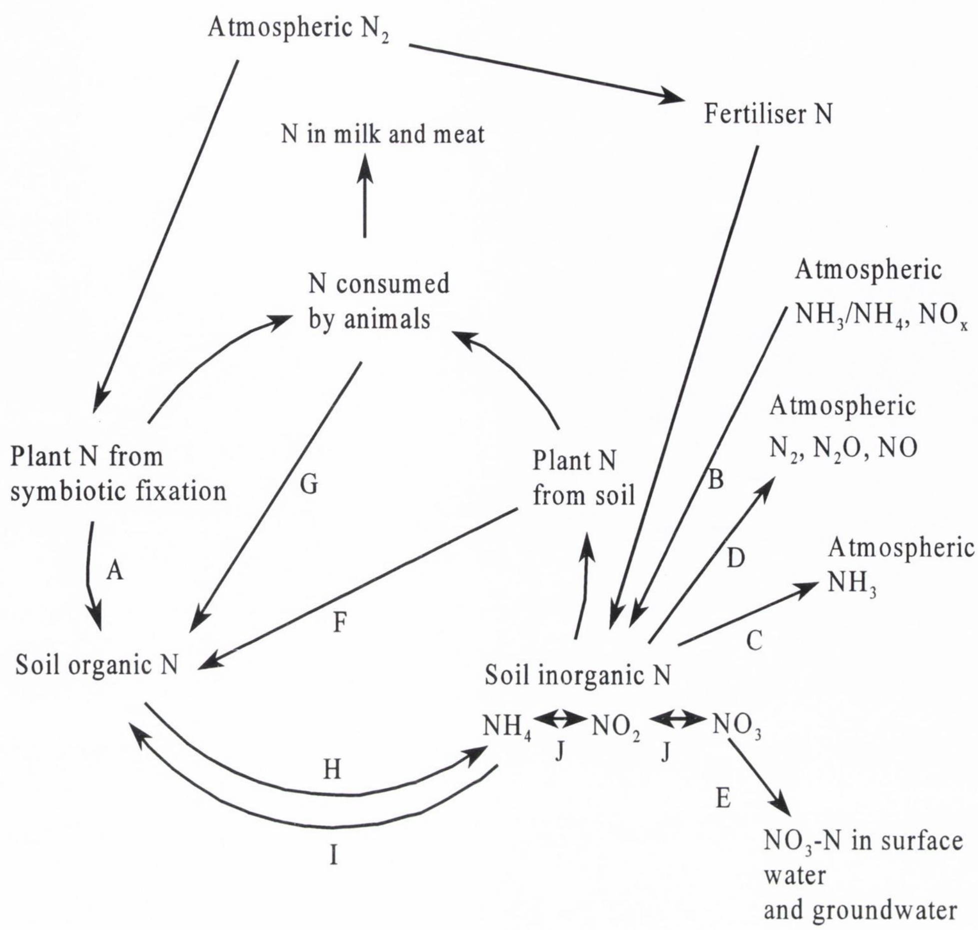
This chapter deals with nitrogen (N) inputs and recycling on the study farm, to provide the reader with a greater understanding of the source or sources of nitrate which can lead to excessive levels of nitrate occurring in drinking water. Section 3.2 introduces the grassland N cycling relating to dairy farms, 3.3 details the use of artificial fertiliser on the farm; 3.4 quantifies slurry N inputs; 3.5 describes dirty water use on the farm; 3.6 quantifies N cycling in the form of soil organic N mineralisation; 3.7 quantifies both atmospheric N deposition and concentrate feed inputs; 3.8 estimates N exportation from the farm system; 3.9 quantifies total N inputs and recycling on the farm; 3.10 details N balance for the farm.

3.2 The grassland nitrogen cycle

The grassland N cycle consist of a large number of biological and chemical transformations (Figure 3.1) which, to date, are poorly defined due to the complex nature of the factors controlling those processes (Jarvis, 1993; Whitehead, 1995). During N cycling there is no clear cut sequence of transformations but a number of options exist, which option is dominant depends on the physical, chemical and biological conditions present. For example, nitrate occurring in the soil has a number of possible transformations possible such as plant uptake, denitrification, leaching, and immobilisation in the soil microbial biomass or the more stable soil organic N fraction.

The N cycle can be divided into 3 sub-cycles,

- 1. Atmospheric sub-cycle which inputs N into the N cycle in the form of N fixation via biological and industrial fixation (to form N fertilisers), and deposition of NH_3/NH_4 and NO_x as wet and dry deposition.
- 2. The N inputs from the atmosphere are then cycled within the second sub-cycle which is the circulating of N between the soil, plants and animals.
- 3. Microbial biomass which determines the rates of mineralisation of soil organic N and immobilisation of soil inorganic N to organic N forms.



A	Fixation by legumes
B	Wet and dry deposition
C	Ammonia volatilisation
D	Denitrification
E	Nitrate leaching
F	Decay of plant tissue
G	Dung and urine deposition, manure application
H	Mineralisation
I	Immobilisation
J	Nitrification

Figure 3.1 Principal N transformations in grassland (Redrawn from Whitehead, 1995)

The most dominant form of N in the N cycle is the soil organic N fraction which frequently contains between 5 and 15 t N ha^{-1} in a grassland plot (Ball and Ryden, 1984) and 2 to 6 t N ha^{-1} in an arable plot (Powlson, 1993). The inorganic soil N is present in soil at levels generally <100 kg N ha^{-1} (Powlson , 1993).

Concentrations of 500 kg inorganic soil N ha^{-1} have been reported, when the soil has been affected by urine excretion from ruminants (Whitehead, 1995). There is tremendous heterogeneity in soil N arising from excretal returns from animals deposited in small discrete patches which is a most important feature of N cycling in grazed grassland.

An N balance for the study farm was calculated using the parameters in table 3.1 below, which were quantified on the farm.

Table 3.1 N budget parameters quantified at Ballyderown.

N Inputs	**N Outputs**
Artificial fertiliser	Milk
Slurry and dirty water	Meat
Atmospheric N deposition	

3.3 Artificial N Fertiliser Use on the Farm

3.3.1 Introduction to Artificial N Fertiliser use on the study farm

The provision of the required grass feed supply on the study farm requires the input of artificial N fertilisers due to the unreliability of symbiotic N fixation, soil organic matter mineralisation and atmospheric deposition of N compounds.

Artificial fertiliser N is manufactured industrially by mixing atmospheric N_2 with hydrogen and then passing the mixture over an iron catalyst at a high temperature and pressure to form ammonia (NH_3), as in equation 1 (Whitehead, 1995).

Equation 1

$$N_2 + 3H_2 \xrightarrow[\text{400-540 °C; 80-270 atm}]{\text{Fe Catalyst}} 2\,NH_3$$

The ammonia is then converted to one of the main forms of fertiliser used today *i.e.* ammonium nitrate, urea or ammonium phosphate.

The practice of rotational grazing, which is currently carried out, in preference to continuously grazing, on modern intensive dairy farms, allows the regular application of fertiliser between grazing cycles.

3.3.2 Artificial N fertiliser Methodology

Artificial fertiliser records were kept, detailing the type and timing of fertiliser application to each plot on the farm. The quantity of N applied was calculated from the %N content in the fertiliser, supplied by the fertiliser manufacturers, multiplied by the weight of N applied per hectare. Fertiliser application to plot 3 can be seen in Plate 3.1, looking from plot 3a towards the river Blackwater to the south.

3.3.3 Artificial Fertiliser Results and Discussion

Using detailed records of fertiliser applications to each plot on the farm it was possible to calculate a budget for artificial N applications for the years 1992 to 1996 inclusive (Table 3.2)(see Figure 2.7 for plot locations). There were four different main sources of artificial N fertiliser used on the farm; Urea (46% N), Super Calcium Ammonium Nitrate (S CAN) or CAN (27.5% N), Super NET (27.5% N) and Sulphate of Ammonia (21% N). Which fertiliser type was more dominant in a given year depended on availability from the manufacturers. Generally Urea was used in early spring with the other types used later in the grazing season.

Table 3.2 Artificial N applications to all borehole plots, the mean application rate of all plots on farm (farm mean), and the mean application to the borehole plots over 5 years (5 year mean), expressed as kg N ha^{-1}.

Plot No. (Borehole No.)	Year 1992	1993	1994	1995	1996	5 year mean
12 (1)	344	193	244	245	338	273
5 (2)	309	210	336	296	270	284
16 (3)	241	287	160	219	259	233
3a (4)	320	176	262	330	302	278
7 (5)	275	275	278	136	270	247
Farm mean	315	246	253	269	293	275

Average annual N application of approximately 277 kg ha^{-1} were applied to all borehole plots except plot 16. This value was the same as the farm mean for the 5 years. Average N application of 233 kg ha^{-1} was applied to plot 16 which was grazed by calves rather than cows. Calves have a lower annual grass requirement than cows.

There was between year variation in the N applications to the borehole plots within the range 136 to 344 kg ha^{-1}.

3.4 Slurry Nitrogen use on the study farm

3.4.1 Introduction to slurry N

This section quantifies the contribution from applied slurry to the N input on the survey farm. The recycling of stored organic manures (slurry) is an important component of nutrient management on farms. However, little or no account is taken of the contribution from applied slurry on farms due to variable crop responses (Smith *et al.*, 1985). Quantifying precisely the contribution of slurry N is difficult as losses to the atmosphere occur. Equally, quantifying the contribution of the N in the excreta to the grazing and silage areas creates problems on grassland farms.

3.4.2 Slurry N Literature Review

Excretion of non-utilised dietary N, which varies from 75 to 80% of the ingested N for dairy cows, occurs in faeces and urine, with the proportion devolved to each pathway depending mainly on the concentration of N in the diet. The amount of ingested N excreted in urine increases proportionately with dietary N concentration whereas the amount of N excreted in faeces remains relatively constant (van der Meer, 1983). A grazing cow excretes between 80 and 115 kg N ha^{-1} $year^{-1}$ as urine and 45 kg N ha^{-1} $year^{-1}$ as faeces (Salette, 1996). Van der Meer (1983) estimated between 56 and 145 kg N in urine and 40 kg N as faeces with the differences in urine excretion due to different herbage N contents

N Excretion in Urine

The typical concentration of total N in urine varies widely with dietary N intake but generally ranges between 2 and 20 g N l^{-1}. For a spring-calving cow, fed entirely on grass, fertilised at a rate of 300 kg N ha^{-1} $year^{-1}$, urine N excretion was estimated to be 350 g day^{-1} in early May, decreasing to ~230 g day^{-1} in September (Kemp *et al.*, 1979). Urea accounts for between 60 and 90% of the urine total N content, but when the diet is high in N, the proportion is generally greater than 80% urinary N as urea (Lantinga *et al.*, 1987). Cows normally urinate between 8 and 12 times per day with urine volumes typically varying between 1.5 and 3.5 l per urination, the larger volumes being excreted by larger breeds of cattle (Holmes, 1989).

N Excretion in Faeces

The production of faeces varies with the amount and digestibility of the feed ingested, typically ranging from ~2.5 to 5.0 kg DM day^{-1} for a dairy cow (Holmes, 1989; Haynes and Williams, 1993). The daily output of faecal N typically varies between 100 and 150 g N cow^{-1} day^{-1} for a 500 kg dairy cow (Whitehead, 1995). Most of the N in faeces is in an insoluble form, *i.e.* 45-65% is in amino form, 5% occurs in nucleic acids and 3% as ammonia (National Research Council, 1985). The frequency of defaecation by cattle generally ranges between 7 and 15 times daily (Lantinga *et al.*, 1987).

Storage and utilisation of stored excreted N

When livestock are housed over winter, their excreta are normally collected and stored as slurry or farm yard manure. Slurries consist of dung and urine whereas farmyard manures have dung with a variable urine content and bedding materials.

Stored animal manures are usually utilized by land-spreading to crops and grassland which can take up the available nutrients for growth. Slurries are often regarded as a disposal problem rather than a resource by farmers and often farmers spread slurries during periods of little grass growth such as in autumn and winter (Smith and Chambers 1993).

The N content of slurry mainly varies due to cow diet and to dilution of the slurry by rainwater entering the storage tank (Archer 1988).The amount of inorganic N in slurry is ~50% of the total N content (Whitehead 1995) but the NH_4-N content of slurry is variable depending on the amount of ammonia volatilised during storage.

Land-spreading of Slurry

The timing of slurry application is crucial in determining the utilisation of slurry N. The recommended application times for slurry in Ireland are spring (February/March), after 1st cut silage (late May/early June)and after 2nd cut silage (late July/early August) (Carton and Harnett, 1990).

Between 0 and 50% of applied slurry N can be recovered in the crop, depending on the amount of ammonia volatilisation which occurs after slurry spreading; of the remaining organic N in the applied slurries it is estimated that 50% is mineralised during the first year after slurry spreading (Carton and Harnett, 1990). Ammonia volatilisation and nitrate leaching are two main processes that reduce the efficiency of slurry as a N fertiliser. When slurry is applied during warm, windy periods NH_3 volatilisation is the dominant form of N loss, with up to 60% of NH_4-N applied being lost within 24 hours of slurry application under Irish conditions (Carton *et al.*, 1994; Richards, 1998).

3.4.3 Slurry N methodology

Field sampling

Detailed records were kept of slurry spreading, location and the quantity of slurry spread on plots. Slurry samples were taken by removing a 5 l bucket of slurry from the back of the slurry tanker, which was well mixed and a 500 ml sub-sample was taken for return to the laboratory for analyses.

The samples were kept at 4 °C until analyses for Kjeldahl N, P, K and Na was carried out. The total load of slurry N was then calculated from the quantity of slurry applied and the concentration of N in the slurry.

Laboratory analyses

A 5 g slurry sample was weighed into a Kjeldahl flask to which 2 lithium sulphate tablets, 2 glass beads, 10 ml H_2SO_4 and 6 ml H_2O_2 were added. The sample was then digested for 2.5 hours over a hot gas flame. Sample splashes on the sides of the flask were washed into the acid solution by gently swirling the mixture. When cool, the sample was diluted to 100 ml and filtered through a Whatman No. 2 filter paper into a 50 ml beaker. The filtrate was then analysed by a Teagasc technician for N and P on a Chemlab continuous flow auto-analyser; K and Na were analysed on a Varian atomic absorption spectrophotometer.

Slurry samples from both the slatted houses and the settlement tanks (3-way system) for dirty water were collected during 1994- 1995 and January to February 1996. A mean slurry total N concentration for the 3 years was used to calculate the slurry total N inputs from June to December 1993.

The slurry N concentrations during the monitoring period were analysed as total Kjeldahl N (TN), which is the inorganic N concentration (Available N, AN) plus organic N concentration. Only the slurry AN is available for plant uptake and NO_3-N leaching. Thus to express N inputs on the basis of total N could be misleading as the mineralisation of the slurry organic matter occurs slowly over time.

An estimate of available N was calculated as the inorganic NH_4-N concentration in the slurry minus 15% to account for ammonia loss from the applied slurry (Pain *et al.*, 1998). A more realistic estimate of the contribution of slurry N to the field crop can thus be achieved. The organic N in the slurry contributes to mineralisation of organic soil N.

3.4.4 Slurry Nitrogen Results and Discussion

Total Slurry Nitrogen Levels

Slurry from the slatted houses contained a mean TN concentration of 3 kg N m^{-3} whereas the 3-way system slurry contained 1 kg N m^3 (Table 3.3). The lower mean TN concentration of the 3 way system slurry is probably due to the source of the slurry being more dilute and the likely removal of water soluble NH_4-N in the form of dirty water. The mean slurry TN content of 3 kg N m^{-3} for the slatted housing is similar to the reported mean of 3.6 kg N m^3 for dairy slurry in Ireland (Dept of the Environment and Dept of Agriculture, Food and Forestry, 1996).

Table 3.3 Mean ($\bar{x}$) slurry total N content (kg m^{-3}), with the standard deviation (STD) and the total number of samples (n) analysed from both slatted house and 3-way system.

	Slatted house slurry			Slurry from 3 way system		
Year	$\bar{x}$	STD	n	$\bar{x}$	STD	n
1994	2.2	0.8	31	0.8	0.4	4
1995	3.2	1.3	41	1.2	1	20
1996	3.6	0.5	15			
Mean	3	0.6	3	1		2

Loadings of slurry TN for each plot were calculated (Table 3.4) For the duration of the monitoring period plots 1, 14 and 16 received no slurry.

Table 3.4 Slurry TN applications for each of 4 years to plots on the farm (kg ha^{-1}), see Figure 2.7 for plot locations.

Plot	1993	1994	1995	1996	Plot	1993	1994	1995	1996
1					9	41	116	125	105
2	80		112		9A		222		
2A	104	164			10		192		65
3	89		112		10A		206		87
3A	89				11		126	73	63
4	15	15	232		11A	20	83	19	107
4A			45		12	89	80		87
5	104		134		12A	45	52		88
5A	89		39		13	152	59	118	
6		71	173		13A	76	130	145	
6A		71	102		14				
7		25	329		15	119	56		
7A	31	62			15A	104	131	27	
8		155	75	109	16				
8A		100	61	109	16A		7		

The annual slurry TN load on the farm for the years 1994 and 1995, were 2123 and 1819 kg, the annual quantities applied in 1993 and 1996 were not calculated due to the lack of information. There was considerable between plot variation in the quantities of slurry TN applied ranging from a low of 7 to a high of 329 kg ha^{-1}, the very low loads (<20 kg N ha^{-1}) were slurry from the 3-way system which had a lower TN content.

During most of the monitoring period slurry was spread evenly over each plot, but at certain times this was not the case. Frequently between December 1994 and March 1995 slurry was dumped in plots as the plot conditions were not trafficable (Plate 3.2). The load of slurry TN spread in this manner cannot be accurately calculated due to the unknown area of soil affected by this practice.

Slurry Available N (AN)

A more realistic level of the quantity of slurry N which may have been available for plant uptake or nitrate leaching is the net input of inorganic NH_4-N (AN) to the soil which is considerably less than the slurry NH_4-N concentration. Large quantities of inorganic N are lost from slurry through NH_3 volatilisation. Carton *et al.* (1994) reported losses of 60% of applied slurry NH_4-N by volatilisation under Irish conditions when slurry was applied using a vacuum tanker fitted with a splashplate. This was the method of slurry spreading used on the survey farm.

The timing of slurry spreading on the farm is shown in Table 3.5. The majority of slurry was applied outside the main growing season.

Table 3.5 Seasonal load of slurry N applied from 1993 to 1995, kg total N ha^{-1}.

Year	January to March	April to September	October to December
1993		573	656
1994	783	569	780
1995	1080	746	540

Approximately 50% of the slurry TN is in the AN form (Carton and Harnett, 1990). MAFF (1994) indicate that between 60 and 0% of the AN applied in slurry during the periods April-September and October-March, respectively, are lost in volatilisation.
Therefore estimates of AN applied to the plots were made using the data which is summarised in Tables 3.4 and 3.5 and presented as part of section 3.9 in Tables 3.16 to 3.18.

3.5 Dirty Water N Loading

3.5.1 Introduction

Dirty water or soiled water is generated in large quantities on most modern dairy farms. Land spreading is the most effective management option. The use of dirty water on the study farm was introduced in section 2.5.3.

This section quantifies the amount of N applied to plots which received dirty water applications. As for slurry N, the dirty water N applications are separated into total Kjeldahl N (TN) and available N (AN) applied to plots.

3.5.2 Dirty water Literature Review

"Dirty water"or "soiled water" are commonly accepted descriptions for dilute effluents consisting of water contaminated with livestock faeces, urine, silage effluent, milk bulk tank rinsings or leachate from stored manures (McDowall and Thomas, 1961; Ryan, 1990; ADAS *et al.*, 1994).

A number of papers have reported the chemical composition of dirty water from dairy farming (ADAS *et al.*, 1994; Ryan, 1990). However, accurate nutrient loadings to soil from applied dirty water have not been reported.

Most of the inorganic N in dirty water is in the NH_4-N form with low NO_3-N concentrations reported (ADAS *et al.*, 1994; Ryan, 1990). Seasonal changes in dirty water nutrient composition have been observed, with higher concentrations in summer than in winter. Observed NH_4-N (AN) concentrations were in the range 43 to 126 mg l^{-1} in winter and summer, respectively, in Ireland (Ryan, 1990) and 94 to 586 mg l^{-1} for winter and summer in the U.K. (ADAS *et al.*, 1994). Ryan (1990) also observed TN concentrations ranging from 88 to 225 mg l^{-1} in winter and summer, respectively.

3.5.3 Dirty water Methodology

Field Sampling Methodology

From January to June 1994 weekly grab samples of dirty water were taken from the Roto Rainer irrigator at the end of its spreading cycle by placing a 0.5 l plastic bottle below the outlet nozzle (Plates 3.3). The sample was then placed in a cool box for transport to the laboratory.

From June 1994 until February 1996, daily samples of dirty water were taken from the dirty water storage tank by removing 5 l of dirty water in a bucket and then taking a 0.5 l sub-sample. Samples were stored at 4°C prior to analysis.

A timer was attached to the dirty water pump to record the total amount of time the pump was active, this was noted and re-zeroed daily. The running time of the pump was then related to the volume of dirty water irrigated. The irrigation volume was calculated by timing the filling of 210 l barrels with dirty water in each plot which received dirty water, this was replicated 6 times in each plot.

A budget of total N and NH_4-N then could be calculated by multiplying:

Kjeldahl N(mg l^{-1}) * quantity of dirty water (l) = load of N applied (mg)

Analytical Methodology

A 50 ml sample of dirty water was measured into a Kjeldahl flask and analysed using the same methodology as slurry TN section 3.4.3.

Inorganic NO_3-N, NH_4-N and Cl were determined on samples which were collected on the day of transport to the laboratory and on the previous day. The methodology for analysing these parameters is explained in Chapter 6.

Similar to slurry, ammonia volatilisation following application may reduce the quantity of AN applied by dirty water, as discussed for applied slurry. Pain *et al.* (1998) estimated 15% of NH_4-N in dirty water was volatilised when applied to grass during summer periods. This value was used to adjust AN applied in the current study when dirty water was applied from April to October, as presented in Tables 3.16 to 3.18

3.5.4 Dirty water Results and Discussion

Dirty water TN variation during any day was from 1.2 to 35 mg N l^{-1} with a coefficient of variation (C.V.) between 0.7% to 23.5% of the mean total N concentration (Table 3.6). On average, daily dirty water total N varied by 6.4% of the mean N concentration during the day.

Table 3.6 Dirty water TN daily variation.

Date	Mean (mg l^{-1})	Standard deviation (mg l^{-1})	C.V.(%)	No. Samples
23/02/94	99	3	3	5
15/03/94	89	2	2.2	4
23/03/94	65	1	1.5	4
06/04/94	135	5	3.7	3
04/05/94	194	10	5.2	6
11/05/94	149	35	23.5	3
23/05/94	259	2	0.7	4
31/05/94	224	27	12	6

Due to the low variation of dirty water total N during any one day it was decided to take one sample per day and to use this as a representative sample for that day. Therefore one sample day^{-1} was taken for calculating the dirty water TN and occasional NH_4-N^+ loads applied.

Dirty water TN composition

A summary of the total N concentrations for 556 daily dirty water samples collected from 17/6/94 to 27/2/96 can be see in Table 3.7.

Table 3.7 Range in dirty water TN concentrations observed during monitoring (17/6/94 to 27/2/96).

	TN (mg l^{-1})
Maximum	1360
Minimum	8
Mean	188
Standard Error (±)	6.7

The composition of total N followed the same pattern as the inorganic nutrients, the highest concentrations were observed during the summer and the lowest during the winter. The highest concentration, 1360 mg l^{-1}, on 25/6/95 and the lowest concentration, 8 mg l^{-1}, on 19/12/95 was observed. Dirty water TN concentrations monitored from 17/6/94 to 22/2/96 is presented in Appendix A2.

Annual variation of monthly loads of TN and AN applied in dirty water on the farm can be seen in Figure 3.2. Peak total N applied in dirty water occurred in June 1994 and May 1995. There was a marked increase in the monthly load of N between April and May 1995.

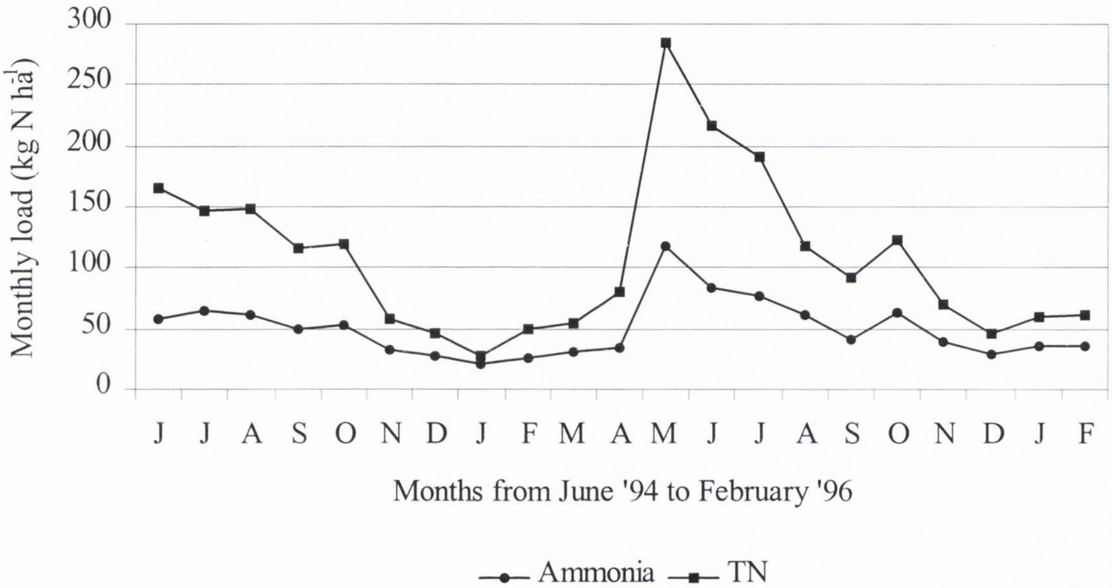


Figure 3.2 Sum monthly total N and inorganic NH_4-N loads for dirty water for the monitoring period, from June 1994 until February 1996.

A dirty water annual budget of N applications on the farm (30 ha) for 1995 amounted to 1349 kg total N and 623 kg inorganic NH_4-N. The measured total N application of 1349 kg was similar to a calculated amount for Ballyderown of 1180 kg N for the years 1986 and 1987 (McGuire, 1990). Slight differences were observed between 1994 and 1995 for the period June to December.

There were temporal trends in the N load (Figure 3.2), winter months generally had a sum monthly load of total N of $\leq$ 100 kg ha^{-1}, whereas summer monthly loads ranged from 117 to 285 kg total N ha^{-1}. During 1995, approximately 60, 25 and 15% of the dirty water TN load was applied in the inclusive periods May to August, September to December and January to April, respectively.

There are a number of factors which could cause increases in dirty water N loads during the summer months. Silage effluent is also released in late May to early June from freshly ensiled silage, which would also increase the load of N in dirty water at this time. Also a second factor for the seasonal increases in dirty water N loads could be that the cows are near their peak milk production in early June (Brereton *et al.*, 1995) and they spend more time in the milking shed. Thus it is likely that a greater number of excretions occur at milking. As herbage N contents increase during the summer there is also an increase in the concentration of N excreted.

Thus if dirty water is contributing to NO_3-N pollution of ground water, careful management of spreading must be concentrated in summer months when the total N load is the highest and total N concentrations can reach 1360 mg l^{-1}. In summer months the contribution of the N load from dirty water must be considered.

Inorganic nutrient composition of dirty water

Throughout the monitoring period NO_3-N concentrations were low. The maximum was 11 mg l^{-1}, the minimum was 0 and the mean concentration was 0.9 mg l^{-1} with a standard deviation of 2 mg l^{-1} (Appendix A.1). The highest NO_3-N concentrations were observed during the winter but in general the concentration was below the detection limit of the analytical equipment.

Inorganic N was primarily observed to be NH_4-N. The maximum concentration observed was 285 mg l^{-1} and the minimum was 1.3 mg l^{-1}; the average NH_4-N concentration observed was 86 mg l^{-1} with a standard deviation of 66 mg l^{-1}. Highest observed concentrations occurred during the summer with the lowest concentrations in the winter (Figure 3.2).

There was an insufficient number of samples analysed for inorganic N to calculate an AN budget. However a significant relationship was found between total N and inorganic N in the dirty water based on the available data.

A highly significant relationship ($P<0.0001$) was found between NH_4-N and total N (Figure 3.3). i.e., NH_4-N in the dirty water = 20.46 + (0.34 * total N concentration) $R^2=0.56$.

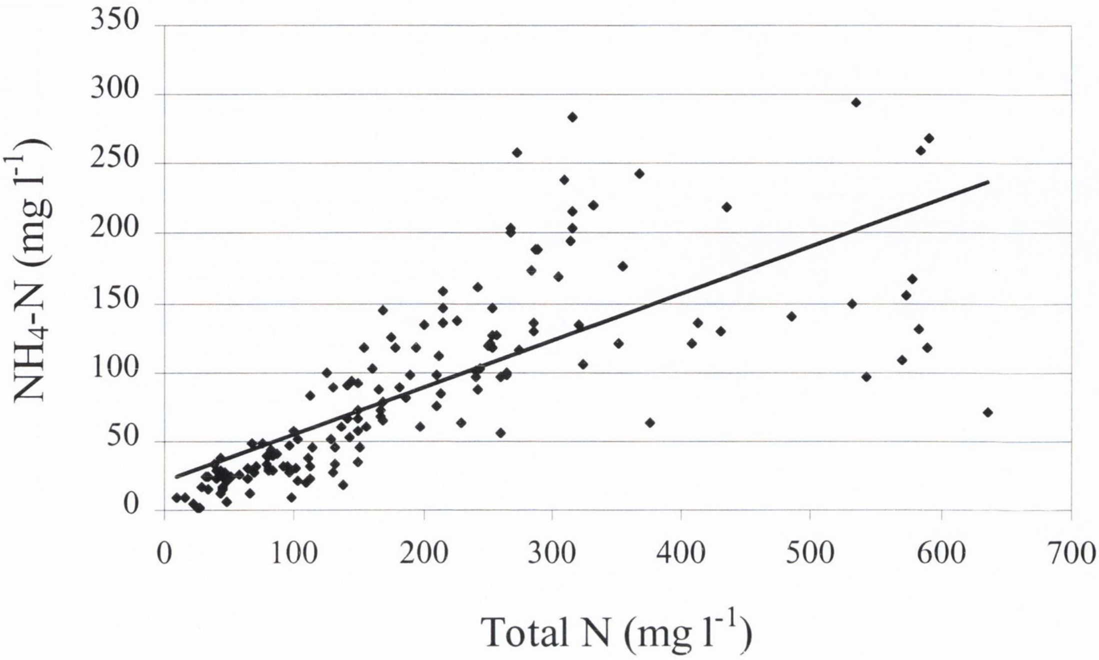


Figure 3.3 The relationship in dirty water between TN and inorganic NH_4-N.

It is clear that at higher total N concentrations the relationship between NH_4-N and total N is not as good at lower total N concentrations (Figure 3.3). Separate regression analysis for summer and winter did not yield better predictive relationships. Therefore the relationship in Figure 3.3 was used to calculate missing inorganic NH_4-N concentrations.

Load of nutrients from dirty water to plots

The nutrient applications to plots receiving dirty water are summarised in Table 3.8.

Average monthly dirty water nutrient loads were used to calculate the quantity of nutrients applied to plots 4 and 4a in late 1993 and early 1994 (See Figure 2.7 for plot locations), as there were only grab sample dirty water concentrations available during this period.

Table 3.8 Nutrient loadings from dirty water application to plots, 1994-1996.

Plot	Start of Irrigation	Duration of Irrigation (days)	Load of nutrients applied (kg) NH_4-N[†]	Total N	P	K	Na	Volume of water applied (l)
4[‡]	02/12/93	68	57	89	16	173	43	
4a[‡]	03/02/94	128	226	504	99	851	152	
5	10/06/94	87	177	444	81	758	91	1254049
5a	05/09/94	24	42	98	14	118	23	431270
6	29/09/94	72	100	199	31	273	58	1604035
3a	10/12/94	122	105	186	38	276	80	2657348
6a	11/04/95	59	171	422	84	734	95	1515968
6	09/06/95	83	189	437	65	569	94	1403908
6a	31/08/95	126	175	334	48	378	131	2918609
3	12/02/96	58	71	121	18	192	58	1718036

[†] Calculated NH_4-N (mg l^{-1}) = 0.34 * Total N (mg l^{-1}) + 20.46
[‡] Mean monthly loads used to calculate applied nutrient load.

Long periods of dirty water irrigation occurred in certain plots, as can be seen in June and December 1994, with dirty water irrigation occurring for 87 and 122 days, respectively. It is possible however to observe that long periods of irrigation during the winter applied less nutrients than long periods during the summer. An irrigation of 122 days during the winter (December 1994 to April 1995) applied only 186 kg total N whereas a period of 87 days during the summer (June to September 1994) applied 444 kg total N. During the summer of 1995, 437 kg N were applied to plot 6 during 83 days of dirty water irrigation, which is very similar to the same period in 1994 during which 444 kg N were applied to plot 5.

The practice of irrigating dirty water on small areas of land which was observed in plot 4a in 1994 can lead to large loads of N being applied. During the summer and winter of 1995 this practice of spreading dirty water on small areas was imposed on plots 6 and 6a, where ceramic cups had been installed to ascertain the effect on nitrate leaching to groundwater; this point is returned to in section 6.3.3.

From the relationship between total N and NH_4-N in Figure 3.3 it was possible to calculate loads of NH_4-N applied to plots receiving dirty water (Table 3.8); the NH_4-N load applied in 1995 was 623 kg applied to a total land area of three ha.

3.6 Soil Organic N Mineralisation

3.6.1 Introduction

Mineralisation of soil N is a process whereby organic forms of soil N are converted to inorganic forms due to ammonification by the soil biomass (Whitehead, 1995). This section estimates the contribution which net mineralisation makes to the overall N cycling in plots 5, 16, 3a and 7 using a new N mineralisation methodology (see Figure 2.7 for plot locations).

3.6.2 Literature Review

Numerous methods are used by workers to estimate mineralisation of organic soil N. Early methods of measurement of field mineralisation involved incubation of sieved field soils (Westermann and Crothers, 1980). More recent studies have shown that the rate of mineralisation predicted from incubations of sieved soil samples overestimated the actual rate because soil disruption increased microbial accessibility to microsites with mineralisable N (Sierra, 1992; Hook and Burke, 1995; Raison *et al.*, 1987).

Qian and Schoenau (1995) used the buried anion exchange membrane technique (AEM) for measuring N mineralisation in field soils. They found N mineralisation measured by AEM to be highly correlated with plant uptake and they also found that there was higher N mineralisation at the base of slopes where organic N contents were highest.

Hook and Burke (1995) evaluated a number of field mineralisation methods and they concluded that short incubations of 15 to 30 days were best to prevent artificially high rates of net mineralisation caused by soil disturbance.

Very few studies of *in situ* undisturbed soil N mineralisation are reported in the literature. One method (Raison *et al.*, 1987; Sierra, 1996) takes two undisturbed soil cores; one is returned to the laboratory for extraction of the initial N level and the second is incubated in a plastic cylinder in the field. The difference in N content between the initial and final core is the amount of N mineralised during the incubation period.

The implicit hypothesis is that the initial mineral N content and the amount of mineralisable N in the two cores does differ significantly. Sierra (1996) found that samples taken immediately adjacent to each other were similar in their N content and rate of N mineralisation. When covered cores are left in the field it is possible, where high nitrification rates are present, that denitrification could reduce the net mineralisation rate significantly (Olff *et al.*, 1994).

Hatch *et al.* (1991) proposed an *in situ* field incubation of soil cores in a sealed container in the presence of acetylene (C_2H_2) to inhibit nitrification and which would thereby minimise loss of N through denitrification and leaching.

Measured mineralisation rates

Hatch *et al.* (1990, 1991) observed rates of N mineralisation in grass swards ranging from 0.02 to 1.9 kg N ha^{-1} day^{-1} with peak values occurring due to re-wetting of dry soil after dry weather. Annual rates of 310 kg N ha^{-1} for 180 days, from March to October, were reported for a grass sward receiving 420 kg N ha^{-1} $year^{-1}$ (Hatch *et al.*, 1991). Gill *et al* (1995) reported net N mineralisation rates of between 135 and 376 kg N ha^{-1} $year^{-1}$ for intensively managed grasslands in the U.K. In Ireland Travers *et al.* (1997) reported high annual N mineralisation rates for a beef farm in Co. Meath of between 782 and 872 kg N ha^{-1} $year^{-1}$.

Springob and Mohnke (1995) measured N mineralisation in a sandy arable soil, which was formerly grassland, during winter and spring. They reported between 6 and 40 kg N ha^{-1} mineralised between mid December and early March; mineralisation rates were closely correlated with soil organic C and N contents. They also found that in 5 out of 7 plots measured, mineralisation alone could cause NO_3-N pollution of groundwater, especially in areas with low rainfall.

Factors which influence the rate of N mineralisation include soil temperature, soil moisture, concentrations of soil organic N and C and fractions of C (Bakken, 1995; Gill *et al.*, 1995; Sierra, 1996; Hassink, 1994).

There are numerous reports that the greatest soil N concentrations and mineralisation rates occur during re-wetting of dry soils (Wong and Nortcliff, 1995; Sparling *et al.*, 1995) and that gross N mineralisation declines again as the soil dries (Sparling *et al.*, 1995).

3.6.3 Methodology

Field sampling

Soil organic N mineralisation was determined using the method described by Hatch *et al.* (1990, 1991). Soil was sampled using a soil corer, 10 cm deep and 3 cm wide. Two soil cores were taken close together, one was placed in a polythene bag for return to the laboratory and the other core was placed in an adapted 75 cm^3 Kilner jar for incubation in the field. A total of four cores were incubated in each plot. The four soil cores were bulked into two groups and placed in Kilner jars, the respective replicate samples being stored in labelled polythene bags for return to the laboratory.

The cores were sampled randomly in each plot but samples were not taken near dung patches to avoid bias. Each pair of cores was placed in a Kilner jar which was modified with a rubber septum to allow head gas samples to be taken. Ten cm^3 of head gas were removed and C_2H_2 was added to the Kilner jars, which were incubated in the field for one week.

Field soil samples (pre and post incubation) were chilled and returned to the laboratory, where inorganic N determination was carried out within 24 hours of sampling. Sampling began on 28/3/95 and continued until 14/3/96. On some occasions samples were incubated for more than 7 days due to unavoidable practical difficulties.

Laboratory Methodology

Head gas chemistry

On return to the laboratory head gas samples were analysed for CO_2 and N_2O concentrations before mineral N analyses. Determination of N_2O was carried out by a Teagasc technician using gas chromatography methods. A sample of air was removed from the jar using a 10 ml disposable syringe. Nitrous oxide was determined via the electron capture technique using a PYE - Unicam GCV gas chromatograph having Argon as a carrier gas through a 3 m column using porapak Q as the stationary phase.

Determination of head-gas CO_2 concentrations was carried out by gas chromatography using a Perkin-Elmer Sigma 3B gas chromatograph with a thermal conductivity detector, a drying column (100 mm) packed with magnesium perchlorate and a 750 mm separating column packed with porapak Q (80-100 mesh) at 70ºC. Samples (1 ml) were taken from the headspace of the Kilner jar with a gas tight syringe and injected into the gas chromatograph. A standard gas (99% N_2 and 1%CO_2) was analysed with the head-gas samples, to calculate %CO_2 head-gas concentrations.

Soil N determination

Soil samples were extracted in duplicate shaking a random 20 g sample of sieved (2 mm) soil in 100 ml 2M KCl for one hour on a rotary shaker. The samples were then filtered through Whatman No. 2 filter paper into disposable plastic beakers which were sealed using a screw cap top.

The samples were then stored at 4 °C before analyses by a Teagasc technician on a Chemlab continuous flow auto analyser for NO_3-N and NH_4-N. Soil moisture content was calculated gravimetrically by weighing 20 g of soil on to pre-weighed petri dishes and drying the sample in an oven at 104 °C for 24 hours. The sample was allowed to cool in a desiccator and weighed when cool. The soil moisture results were expressed as g H_2O 100 g^{-1} dry soil.

Net N mineralisation was calculated by subtracting the pre-incubation inorganic N concentrations from the post incubation inorganic N concentrations and expressed as g N ha^{-1} day^{-1}.

3.6.4 Results and Discussion

Head Gas Chemistry

The head gas of the incubation jars was analysed for CO_2, which was used to indirectly measure the O_2 status of the jar atmosphere by quantifying the CO_2 increase; N_2O analysis was used to measure the amount of nitrate-N which was denitrified during the incubation. The O_2 status of the jar atmosphere was important as Parker and Tiedje (1984) found a rapid increase in the rate of denitrification below an O_2 concentration of 6%.

On two dates the O_2 concentration was found to have decreased below 6%, i.e., on 11/5/95 in borehole plots 2 and 3, and on 27/7/95 in borehole plots 4 and 5. Mean CO_2 concentrations in the head gas varied between 5 and 6% over the entire monitoring period and thus head gas O_2 concentrations were ~ 15%.

Denitrification during the incubation period occurred but the rates were low throughout the monitoring period with the exception of plot 5 which had a maximum rate of 2.1 kg N ha^{-1} day^{-1} denitrified which occurred on 11/04/95 (Table 3.9).

Table 3.9 Denitrification summary for the four borehole plots, as measured during the mineralisation monitoring period (g N ha^{-1} day^{-1}) (28/3/95-14/3/96).

	Plot No. (Borehole Plot)			
	5 (2)	16 (3)	3a (4)	7 (5)
Mean Rate	136	25	3	2
Maximum Rate	2107	558	4	30
Minimum Rate	5	3	7	5
Standard Deviation (±)	379	130	9	6

Daily rate of N mineralisation

Mean daily N mineralisation rates in four plots 5, 16, 3a and 7, which contained boreholes 2 to 5, varied from a low of 0.5 kg N ha^{-1} day^{-1} in the plot 16 to a high of 1.1 kg N ha^{-1} day^{-1} in plot 3a (Table 3.10). The mean rate of N mineralisation for the four plots was 0.7 ± 1.0 kg

N ha^{-1} day^{-1}. During the monitoring period there were large deviations from the mean rate of N mineralisation for each plot; the deviation ranged from 1.6 to 2.3 kg N ha^{-1} day^{-1} for plots 16 and 3a, respectively.

Table 3.10 Daily N mineralisation rates in borehole plots (kg N ha^{-1} day^{-1}) (28/3/95-14/3/96).

	Plot No. (Borehole No.)				4 Plot
	5 (2)	16 (3)	3a (4)	7 (5)	Mean
Maximum Rate	11	4.9	7.1	7.6	---
Minimum Rate	-1.7	-4.4	-7.4	-5.9	---
Mean Rate	0.8	0.5	1.1	0.6	0.7
Standard Deviation (±)	1.8	1.6	2.3	2.1	1.0
Median	0.5	0.5	0.7	0.4	---

Plot 5 had the highest daily N mineralisation rate of 11 kg N ha^{-1} day^{-1} and this large amount of N mineralisation could be attributed to the preparation of this plot for ploughing and re-seeding by application of the herbicide glyphosate (Round-Up) to the plot.

The highest N mineralisation rates measured during the monitoring period occurred in the month of September, 1995. It is likely that the re-wetting of the soil after the summer drought caused this surge in mineralisation. During August 1995 there were 3 rainfall events which amounted to <7 mm rainfall whereas in September there were 14 rainfall events amounting to 32 mm of rainfall. Soil moisture content increased from 7 to >30 mm water 100 g^{-1} dry soil. This frequent re-wetting of the top soil during September caused large fluxes between net N mineralisation and net N immobilisation. Immobilisation is the process whereby inorganic N is converted into organic forms of N, the reverse of mineralisation.

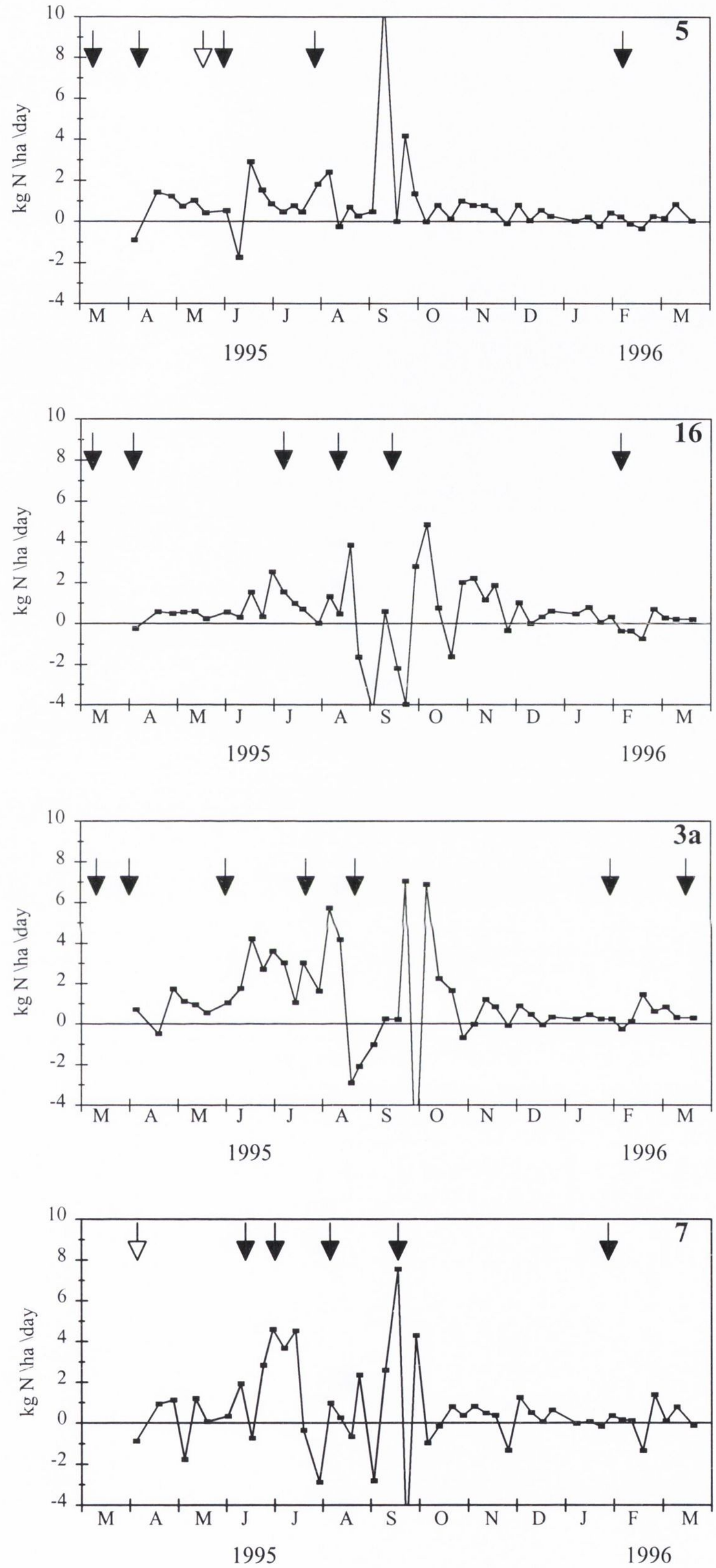


Figure 3.4 Daily soil N mineralisation rates, kg N ha^{-1} day^{-1}. Solid arrows are inorganic fertilisation events the hollow arrow is a slurry application event. Numbers in the top right refer to plots.

The variation in N mineralisation rates for the four plots can be seen in Figure 3.4. The peak mineralisation rate in plot 5 was observed in September. From December 1995 to March 1996 the mineralisation rates were less than 0.5 kg N ha^{-1} day^{-1}. There were only two net N loss events during the monitoring in this plot, the first was in March 1995 at the start of monitoring and this occurred in conjunction with denitrification rates of 2 kg N ha^{-1} day^{-1}. The second loss of N during incubation was in early June 1995 which again corresponded to high rates of denitrification ~0.2 kg N ha^{-1} day^{-1}.

The maximum observed mineralisation rates for plot 16, which contains borehole 3, were during August 1995 and in late September/early October (Figure 3.4). Net losses of up to 4 kg N ha^{-1} day^{-1} occurred during incubations in September. On only one sampling date in September 1995 was the head gas analysed for N_2O and thus it is not possible to state that this was due to denitrification but this would be a likely cause of N loss during incubation. During late October/early November there were high rates of mineralisation i.e. up to 2 kg N ha^{-1} day^{-1}, whereas during December 1995 and January 1996 the rate of mineralisation was low, ~0.3 kg N ha^{-1} day^{-1}.

In plot 3a during August there was a peak mineralisation rate of 6 kg N ha^{-1} day^{-1} (Figure 3.4). In June and July 1995 mineralisation increased a week or two after fertiliser application to the plot. Azam *et al.* (1994) also observed higher rates of mineralisation and immobilisation with inorganic N addition, which they termed an added N interaction. In late August/early September there was net N loss during incubation and there were no denitrification measurements made during this period.

Plot 7, which contains borehole 5, had peak mineralisation in late September/early October (Figure 3.4). An earlier peak of ~4 kg N ha^{-1} day^{-1} occurred in June, after 2 applications of fertiliser. Again there appears to be evidence of priming of the soil by fertiliser addition. It is also interesting to note that fertiliser was applied to this plot at a time of high mineralisation in autumn.

In plots 16, 3a and 7 (which contain boreholes 3, 4 and 5, respectively) September was the month which had the highest rates of net N immobilisation of 4, 7.4 and 5.9 kg N ha^{-1} day^{-1}, respectively. Plots 3a and 7 had the highest immobilisation rates measured; the highest rate of N immobilisation in plot 16 occurred at the end of August 1995.

Late September/early October, which was the period with the highest N mineralisation rates also had the highest pre-incubation soil inorganic N levels (Section 6.4.3, Figure 6.6), which supports the finding of high N mineralisation rates. This period was a time of soil re-wetting (Figure 3.5) and thus any nitrate is at risk of being leached below the root zone. This risk is exacerbated by the late application of inorganic N fertiliser to plots 16 and 7 in September, a period which had the highest pre-incubation inorganic soil N levels and the highest mineralisation rates.

Increases in gravimetric soil moisture can be observed during late July to early August (~day 210) and during September (day 240 to 270). Increased mineralisation was observed during late July to early August in plots 5, 3a and 16. Peak mineralisation rates were observed during September/October which also corresponded to a period of soil re-wetting (Figure 3.5).

Net N mineralisation

The total net N mineralised on the Ballyderown farm during the monitoring period April 1995 to March 1996 was 276, 158, 346 and 191 kg N ha^{-1} for plots 5, 16, 3a and 7, respectively (Table 3.11). The mean total N mineralised for the 4 plots, during the monitoring period, was 243 ± 74 kg N ha^{-1}.

Table 3.11 Net N mineralised for each plot (kg N ha^{-1}) and the average for the four plots, with the total N mineralised for the periods April to September 1995 and October 1995 to March 1996 inclusive.

	Plot				Farm
	5	16	3a	7	Average
Total N mineralised	276	158	346	191	243
N mineralised 04/95 to 09/95	224	88	262	156	183
N mineralised 10/95 to 03/96	52	70	84	35	60

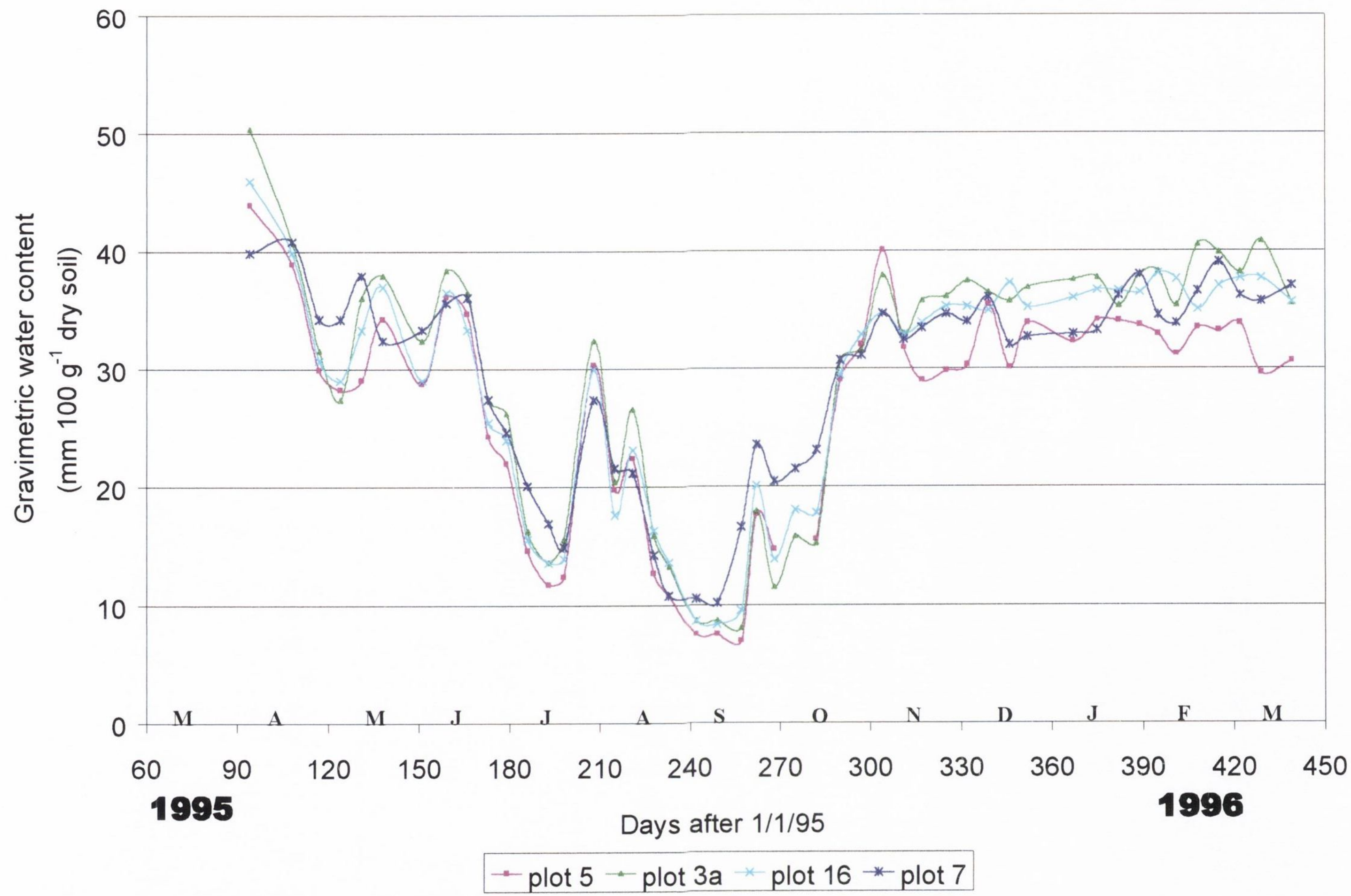


Figure 3.5 Gravimetric soil moisture contents of incubated soil samples (g H_2O g dry soil^{-1}).

Mineralisation of N predominantly occurred between April and September 1995, inclusive which on average for the four plots accounted for 75% of the total N mineralised during the year (Table 3.11). The values for winter mineralisation were considerably lower than reported values of up to 102 kg N ha^{-1} mineralised from November to February (Gill *et al.*, 1995). In plot 16 there was almost the same net N mineralisation for the periods April to September 1995 and October 1995 to March 1996, but these levels were the lowest of the four plots.

Peak observed mineralisation rates in September/October during this study support the findings by Jamieson *et al.* (1998) who also observed peak mineralisation rates in autumn/winter on a calcareous semi-natural grassland. Jamieson *et al.* (1998) also observed that soil moisture played a critical role in N mineralisation; enhanced summer rainfall significantly reduced N mineralisation rates in autumn whereas summer drought increased autumn mineralisation rates. In Ireland, Herlihy (1979) also observed peak mineralisation rates during the periods of April to May and August to October. Herlihy (1979) also observed that when soil was moisture was allowed to vary N mineralisation rates were higher than when the soil moisture was kept constant although varying soil moisture did not affect the timing of the mineralisation peak.

Ryan *et al.* (1998) although not directly measuring rates of mineralisation observed two peaks in soil inorganic N concentrations which occurred during a denitrification study in S.E. Ireland. The peaks occurred at the end of May and August 1996. Increased inorganic soil N concentrations were observed from 0 to 30 cm below the soil surface thus indicating possible mineralisation of N at deeper depths than sampled in the present study.

The estimated mineralisation rates measured during 1995 are similar to but slightly lower than rates estimated using the same methodology in the U.K. (Hatch *et al.,* 1991; Gill *et al*., 1995). The maximum N mineralisation rates of 4 to 11 kg N ha^{-1} day^{-1}, measured in the present study, were considerably higher than the maximum of 3.19 kg N ha^{-1} day^{-1} reported by Gill *et al.* (1995) but lower than peak daily rates of 4 kg N ha^{-1} day^{-1} reported by Hatch *et al*. (1991). The mean observed mineralisation rate of 0.5 to 1.1 kg N ha^{-1} day^{-1} are similar to mean rates of 0.36 to 1.03 kg N ha^{-1} day^{-1} observed by Gill *et. al.* (1995).

The estimated N mineralisation rates measured in this study are slightly lower than values reported for a beef farming system in Co. Meath (Travers *et al.*,1997). These workers observed N mineralisation in the range 391 to 436 kg N ha^{-1} $year^{-1}$ for a number of different beef systems in Ireland. The slightly higher rates of mineralisation estimated by Travers *et al.* (1997) are likely to be due to different methodologies used to estimate mineralisation.

3.7 *Other N inputs*

3.7.1 Introduction

The remaining two other N inputs which were included in the N balance for the farm are atmospheric deposition of N compounds and the amount of N which was imported on to the farm in the form of purchased concentrate feedstuffs.

3.7.2 Literature Review

Atmospheric N deposition

Atmospheric deposition of N occurs in two forms i.e. wet deposition which deposits NH_4^+ and NO_3^-, and dry deposition which deposits NO_3^- , NH_3, NO_2^- and HNO_3. Atmospheric deposition of N has been included in N balances for many years (Russell and Richards, 1919). In the UK, rates of atmospheric deposition of N have been reported between 35 and 40 kg N ha^{-1} $year^{-1}$ on arable land in the south and east of England (Goulding, 1990). The amount of N deposited from the atmosphere depends on the surface area of the crop and thus Goulding (1990) suggests that lower rates of atmospheric N will be deposited on grassland.

Jordan (1997) suggests that high concentrations of NH_4-N and NO_3-N in bulk rainfall is predominantly due to intensive livestock density in small areas. Jordan also notes that although some small areas have high atmospheric N deposition rates due to local intensive livestock production, mean annual N deposition rates for Ireland range from 2.3 to 3.9 kg NH_4-N ha^{-1} $year^{-1}$ and from 2.3 to 3.2 kg NO_3-N ha^{-1} $year^{-1}$. The highest NO_3-N deposition rate in Ireland, of 12.4 kg NO_3-N ha^{-1} $year^{-1}$, was observed at Dublin airport and was primarily attributed to NO_x emission from cars in the Dublin city.

Concentrate Feeds

The function of grass growth on dairy farms is to provide feed for cows for both grazing during the grass growing season and for silage feed during the winter housing period. Nutritional requirements of cows on intensive farm systems are also supplemented through the use of concentrated feeds, which are generally composed of cereals but can contain protein-rich supplements. In the UK, grass supplies ~60% of the feed requirements of dairy cows with the remaining 40% being provided by concentrated feeds (Lazenby, 1981).

In Ireland the use of concentrated feeds in dairy farming has increased from 578 t in 1980 to 1019 t in 1994 and currently farmers use an average of 0.5 t concentrated feed per dairy cow (Brereton *et al.*, 1995). A spring calving dairy cow typically ingests 5475 kg DM $year^{-1}$, thus in Ireland concentrate feed stuffs provide 9% of the annual feed requirements, which is considerably lower that the 40% which has been reported for the U.K..

Utilisation of dietary N in the cow is inefficient ranging from 20 to 25% of the ingested N for dairy cows with the remaining N excreted in the faeces and urine. Interestingly, lactating animals have a higher utilisation of ingested N than growing animals (Holmes, 1970). One of the roles of feeding concentrated feeds to cows is to increase the utilisation of ingested herbage N by providing energy for microbial utilisation of amino acids and ammoniacal N in the rumen. This then increases the quantities of amino acid N for absorption in the small intestine, which would otherwise be lost from the herbage in the rumen by absorption into the blood and excreted in the form of urea (van Vuuren and Meijs, 1987).

3.7.3 Methodology

Atmospheric N deposition

Atmospheric N input was determined by collecting rainfall samples and analysing the inorganic chemical composition of the sample. A plastic rain-gauge was placed within the fenced borehole area at borehole 4, within plot 3a, and when possible, a rainfall sample was taken on the day of groundwater sampling. The sample was returned to the laboratory for determination of NH_4-N, NO_3-N, MRP, K, Na and Cl concentrations as previously outlined. The rain-gauge and collection cylinder were rinsed with de-ionised water after a sample was removed.

Nutrient loads were determined by calculating the rainfall between sampling periods using meteorological data for the area.

Nutrient load in (kg ha^{-1}) = rainfall (m^3 ha^{-1}) * nutrient conc.(kg l^{-1}/1000)

Concentrate feed

Concentrate feed was fed to the animals over the duration of the experiment. The animals received the feed when they were being milked. The feed was manufactured from grain cereals and molasses. Samples of the feed were taken from the bulk storage silo and from the Kjeldahl N content and from the quantity of concentrate fed, it was possible to calculate the load of N imported in the concentrate feed.

The feed sample was returned to the laboratory where it was ground using a Christy and Norris 13 cm hammer mill which had a four bladed cross, spinning at 13000 rpm.
The sample was then passed through a 1 mm mesh and was stored in a plastic container. A 0.5 g of the ground sample was weighed into a 50 ml Kjeldahl flask, and digested by the methodology used for slurry and dirty water, section 3.4.3.

3.7.4 Results and Discussion

Rainfall Chemistry

The rate of atmospheric N deposition was determined by chemical analyses of rainfall samples collected in plot 3a, which contains borehole 4. On some sampling dates small insects were found in the rain gauge sample collection cylinder. A total deposition of 25 kg N ha^{-1} $year^{-1}$ was observed during 1995, of which 5 kg N ha^{-1} $year^{-1}$ was in the NO_3-N form and 20 kg N ha^{-1} $year^{-1}$ was in the NH_4-N form (Table 3.12).

Table 3.12 Nutrient loadings from atmospheric deposition in rainwater during 1995 (kg ha^{-1} $year^{-1}$).

NO_3-N	NH_4-N	Total inorganic N	Sample Size (n)
5	20	25	30

The seasonal distribution of atmospheric N deposition can be seen in Figure 3.6. The highest N deposition rates occurred during autumn and early winter.

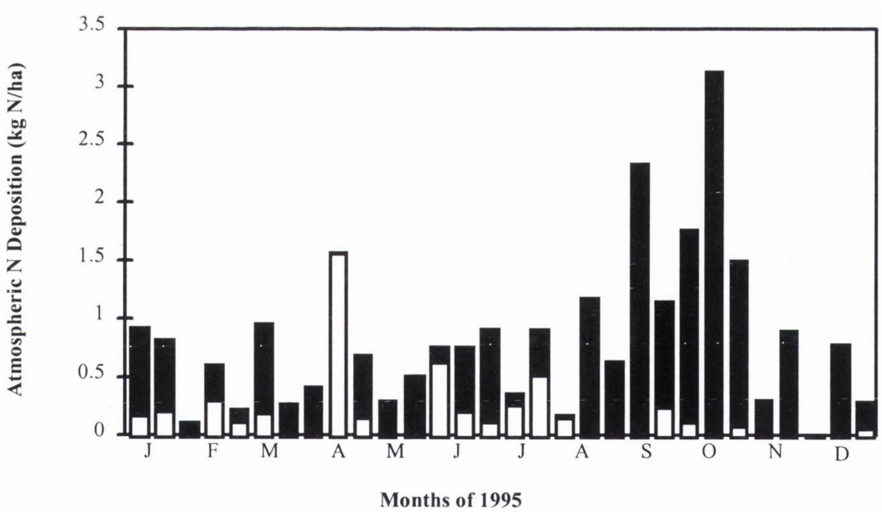


Figure 3.6 Rainfall N load in 1995 (kg N ha^{-1}) measured at borehole 4. Hollow bar is the load of NO_3-N and the solid bar is the load of NH_4-N.

The overall N deposition of 25 kg N ha^{-1} $year^{-1}$ is higher than an assumed rate of 10 kg N ha^{-1} $year^{-1}$ (Sherwood and Tunney, 1991) and higher than the average N deposition in a forest in

Co. Cork of ~13 kg N ha^{-1} year^{-1} as NO_3-N, NH_4-N and NH_3-N in rainwater (Farrell *et al.*, 1996). The annual atmospheric N deposition rate of 25 kg N ha^{-1} year^{-1} measured on the study farm is the same as used by Jarvis (1993) in South West England, whereas Goulding (1990) estimated 40 kg N ha^{-1} deposited to arable land in southern and eastern England.

A possible reason for the higher than previously reported atmospheric N deposition load on the study farm in 1995 could be that there are a number of NH_3 sources surrounding the study farm, which includes two intensive piggery units. Numerous workers have reported deposition of volatilised N within a short distance from the area of NH_3 volatilisation (Hill *et al.,* 1997; Ross *et al.,* 1997; Sommer and Jensen, 1991). Jordan (1997) also reported some high rates of atmospheric N deposition (6 to 20 kg N ha^{-1}) related to intensively managed grassland areas around Banbridge in Northern Ireland.

Concentrate Feed

Annual total input of N to the study farm from imported concentrate feed-stuffs can be seen in Table 3.13. The highest importation of concentrate feed was 167.1 t in 1995 and this was due to feeding of concentrate during the summer of 1995 because of restriction of grass growth due to drought.

Table 3.13 The total amount of concentrated feed imported and the amount of N in the feed.

Year	Concentrated Feed (kg)	N Imported (kg)
1993	103700	2593
1994	122100	3053
1995	167100	4178

The average concentrated feed N content was 2.5% and this was used to calculate the load of N imported in concentrate feed which ranged from 2593 kg N in 1993 to 4178 kg N in 1995.

3.8 Exportation of N from the farm system

3.8.1 Introduction

The total N export in the form of milk and meat which leaves the farm, as calculated in this section, was used to calculate the net N balance on the farm. This section quantifies the export of N from the farm in the form of milk and meat.

3.8.2 Literature review

The proportion of N converted into the end products of milk and meat varies between 20 and 25% of the ingested N (Holmes, 1989, Jarvis, 1993). The utilisation of ingested N is highest when the ratio of available N and available energy is optimal for the specific milk yield or live weight gain required (McDonald *et al.*, 1995).

Dairy cattle consuming a herbage diet, which receive no concentrate feed, would generally have a maximum milk production of 20-25 kg day^{-1}, which is limited partly by available energy and partly by the amount of amino acid N available for utilisation in the small intestine (Whitehead, 1995).

Van Vuuren and Meijs (1987) estimated that when a cow ingested 626 g N day^{-1} (based on 3.9 %N in the diet) 107 g N day^{-1} was removed in the milk, 361 g N day^{-1} excreted as urine and 158 g N day^{-1} excreted in the faeces. Thus only 17% of the ingested N was removed in milk produced by a dairy cow. The excretion of non-utilised dietary N has already been dealt with in section 3.4.2.

3.8.3 Methodology

N Exportation in Milk

Annual removal of milk from the farm was calculated from receipts obtained at the local creamery. The amount of N exported in the milk was calculated by converting the kg milk exported to kg crude protein(C.P.) produced by using a mean % C.P. value of 3.4% which was measured as part of a separate project examining milking machines on the farm. The same value of %CP in milk was reported by McDonald *et al.* (1995) as the average %C.P. of milk. The load of N removed from the farm was then calculated by using a factor of 156.8 g N (kg CP)$^{-1}$ (McDonald *et al.*, 1995).

N Exportation in Meat

From the number of animals leaving the farm it was possible to estimate the amount of N leaving the farm in the form of meat. The weight of animals (as livestock units, LU) leaving the farm was estimated by using conversion factors for the age of the animal (Murphy, 1978).

The N load leaving the farm was then estimated by using an assumed meat N content of 12 kg N t^{-1} of meat (Sherwood and Tunney, 1991) with 1 LU equivalent to a 550 kg animal.

3.8.4 Results and Discussion

Removal of N in milk from the farm ranged from 2165 to 2359 kg N year^{-1} (Table 3.14).

Table 3.14 Load of milk, calculated crude protein and N removed from the farm in milk, 1993 to 1995.

Year	Milk Load (l)	Crude Protein (kg)	N Removed (kg)	N Removed (kg ha^{-1})
1993	442480	15044	2359	79
1994	406067	13806	2165	72
1995	423969	14415	2259	75

Between 72 and 79 kg N ha^{-1} was removed from the farm in the form of milk exported to the creamery in the years 1993 to 1995, inclusive.

The load of N leaving the farm in meat can be seen in Table 3.15. No estimate has been made of N assimilated as live-weight gain for animals which remained on the farm.

Table 3.15 Number of animals sold, and the amount of N leaving the farm in meat for 1993 to 1995.

Animal Type	1993	1994	1995
Cow	19	32	28
Steer 0-6‡	45		
Steer 6-12		5	39
Steer 18-24			30
Heifer 0-6	27		
Heifer 6-12			9
Heifer 18-24	1	3	18
LU Sold†	34.1	36.1	80.8
kg N removed*	225	238	533

‡ Age of the animal in months.
†Use conversion factors from Murphy (1978).
* 12 kg N t^{-1} meat(Sherwood and Tunney, 1991).

Very little of the N on the farm left in the form of meat. The greater number of animals sold and the correspondingly high N removal in 1995 was due to steers from 1994 being sold in 1995 due to Tuberculosis in the herd in 1994. For the years 1993, 1994 and 1995 a total of 8, 8, and 18 kg N ha^{-1} was removed from the farm as meat.

It is possible to see in tables 3.14 and 3.15 that the majority of N was removed from the farm in the form of milk.

3.9 Total N inputs

3.9.1 Introduction

This section quantifies on an individual plot basis the total N inputs and an estimate of plant available N, which includes N recycling in the form of slurry N, dirty water N and mineralised N. The total quantity of N which is applied to or recycled in plots annually is important, as the excess N (not utilised by plants) is then available for environmental loss.

The calculated total and available N loads will then be used to determine the relationship between applied N load and nitrate leaching in chapter 6.

3.9.2 Methodology

The data used to calculate total and available N inputs to the individual plots on the farm are artificial fertiliser input (section 3.3), slurry N input (section 3.4), dirty water N input (section 3.5), net soil organic N mineralised (section 3.6), and atmospheric deposition (section 3.7). The total N budget for the plots is likely to be an overestimate since as previously discussed, a significant proportion of the total Kjeldahl N in slurry and dirty water is in organic form and thus would rely upon mineralisation to make the N available for plant uptake. Thus a second N input for each plot was calculated based on the N available for plant uptake and allowing for NH_3 volatilisation in the field. The available N input is likely to be the more accurate quantity of N applied to each plot which is available for plant uptake and environmental loss. All calculations are based on a calendar year rather than a hydrological year.

Total N applied (TN)	= 100% of N load applied
Available N applied (AN)	= 50% of the total N when slurry when applied between October and March inclusive or 20% of the total N when applied between April and September inclusive (see 3.4.4) (Pain *et al.*, 1998).

For N mineralisation there was only one full year of data (1995) and this has been used for calculating the N input budgets for other years. This is a gross simplification as mineralisation is affected by many environmental factors which varied between each year of the study. The year 1995 had a very hot and dry summer; this could have inhibited mineralisation during the summer and the large increase in mineralisation in September could have been due to re-wetting after the drought. Thus the year 1995 was not the best year to use for an average N mineralisation rate. So although the mineralisation rates were extrapolated from 1995 to the other years of the project as no other data were available, this limitation must be borne in mind when interpreting the budget results.

3.9.3 Results and Discussion

The total amount of N inputs from artificial fertiliser, organic fertilisers and net soil N mineralisation for the plots which contain boreholes have been summarised for 1993, 1994, 1995 tables (3.16, 3.17, and 3.18, respectively), see Figure 2.7 for plot locations.

Table 3.16 The 1993 N budget accounting for artificial fertiliser, slurry, dirty water and soil N mineralisation (kg ha^{-1}).

	Plot No. (Borehole No.)				
Nitrogen Source	12 (1)	5 (2)	16 (3)	3a (4)	7 (5)
Artificial Fertiliser N	193	210	287	176	275
Slurry total N	89	104	---	89	---
Dirty water total N	---	---	---	---	---
Atmospheric N Deposition	25	25	25	25	25
Total N application	**307**	**339**	**312**	**290**	**300**
Slurry NH_4-N - volatilisation	18	52	---	45	---
Dirty water NH_4-N - volatilisation	---	---	---	---	---
Available N	**236**	**287**	**312**	**246**	**300**

During 1993, plots 12, 5 and 3a which contained boreholes 1, 2 and 4, respectively, received organic fertiliser in the form of slurry N. Whereas plots 16 and 7 which contained boreholes 3 and 5, respectively, received only artificial fertiliser (Table 3.16). Thus the total N budget for the borehole plots is influenced mainly by the load of artificial fertiliser.

Plot 5, which contained borehole 2, received the highest N load of 339 kg N ha^{-1} in 1993 with plot 3a receiving the lowest total N load of 290 kg N ha^{-1}.

All slurry N was applied to plots 5 and 3a during the October to March period and thus the available N is calculated as 50% of the total N applied. Whereas plot 12 had the slurry applied during the period April to September, when ammonia volatilisation may have been significant.

Table 3.17 The 1994 N budget accounting for artificial fertiliser, slurry, dirty water and soil N mineralisation (kg N ha^{-1}).

	Plot No. (Borehole No.)				
Nitrogen Source	12 (1)	5 (2)	16 (3)	3a (4)	7 (5)
Artificial Fertiliser N	244	336	160	262	278
Slurry total N	80	---	---	---	25
Dirty water total N	---	444	---	26	---
Atmospheric N deposition	25	25	25	25	25
Total N application	**349**	**805**	**185**	**313**	**328**
Slurry NH_4-N - volatilisation	10	---	---	---	9
Dirty water NH_4 -N - volatilisation	---	150	---	16	---
Available N	**279**	**511**	**185**	**303**	**312**

Only three plots received organic N applications during the year 1994 (Table 3.17). Plot 5 which contained borehole 2 had the largest total N input of 805 kg N ha^{-1} which was mainly attributable to a high applied N load from dirty water, the available N was calculated to be 511 kg N ha^{-1}, which is significantly lower than the total N application for the plot.

The total N loads, in 1994, for plots which contained boreholes, varied from 185 to 805 kg N ha^{-1}, whereas estimated available N varied from 185 to 511 kg N ha^{-1}.

Table 3.18 The 1995 N budget accounting for artificial fertiliser, slurry, dirty water and soil N mineralisation (kg N ha^{-1}).

	Borehole Plot				
Nitrogen Source	12 (1)	5 (2)	16 (3)	3a (4)	7 (5)
Artificial Fertiliser N	245	296	219	330	136
Slurry total N	---	134	---	---	329
Dirty water total N	---	---	---	160	---
Atmospheric N Deposition	25	25	25	25	25
Total N application	**270**	**455**	**244**	**515**	**490**
Slurry NH_4-N - volatilisation	---	43	---	---	119
Dirty water NH_4-N - volatilisation	---	---	---	89	---
Available N	**270**	**364**	**244**	**444**	**280**

The year 1995 (Table 3.18) had the best data resolution due to the large number of slurry and dirty water samples which were collected in that year. Thus the N budget for 1995 was the best estimate of the N load applied to the farm in any year.

Total N loadings in 1995 ranged from 244 to 515 kg N ha^{-1} and estimated available N loads varied from 244 to 444 kg N ha^{-1} (Table 3.18). The difference between total N load and available N load was small for most borehole plots due to only three plots receiving organic fertiliser. For plot 7 there was a difference in the total N and the available N load of 210 kg of N which significantly reduced the total N load from 490 to an estimated available N load of 280 kg N.

For the years 1993 to 1995, total N loadings to plots containing boreholes ranged from 343 to 1081 kg N ha^{-1}, the average application of total N for the 5 plots was 528, 809, 405, 720, and 564 kg N ha^{-1} for the plots which contained boreholes 1 to 5, respectively. Estimated available N average loadings for 1993 to 1995 were 502, 672, 405, 677, and 488 kg N ha^{-1}, for the plots which contained boreholes 1 to 5, respectively.

A summary of total and available N loads applied to all plots throughout the study is shown in Table 3.19. The N loads applied to each individual plot are in Appendix A.3.

Table 3.19 Summary of total N and estimated available N applied to all plots on Ballyderown (kg N ha^{-1} $year^{-1}$).

	Load of total N applied (kg ha^{-1})			Load available N applied (kg ha^{-1})		
	1993	1994	1995	1993	1994	1995
Maximum load	339	805	515	312	511	444
Minimum Load	290	185	244	236	185	244
Mean Load	310	396	395	276	318	320
Standard Error(±)	8	106	57	15	53	37

The mean total N loads varied from a low of 310 kg N ha^{-1} in 1993 to a high of 395 kg N ha^{-1} which was applied in 1995. The low mean N application in 1993 is an underestimate of the total N applied as no allowance was made for cattle slurry which was applied from January to May 1993 due to the lack of slurry quantity data for these months. The mean total N load applied each year was similar.

It is realised that the amount of N returned to each plot in the form of excretion by grazing animals, as faecal N or urinary N, has not been included in this calculation due to the lack of information on the number of cow grazing days each plot received and also the quantity of N which was excreted in the field. The inclusion of excreted N by grazing animals would increase the N input to plots which were grazed each year and would also give a more realistic idea of the total amount of N available for plant uptake and environmental loss. Although the Rural Environmental Protection Scheme (REPS) uses total N excretion load of ~85 kg N LU^{-1} $year^{-1}$ (section 2.4.3), the time the cows spent in each plot is unknown thus making it difficult to estimate excretal return of N to each plot (Bell, 1996).

3.10 Nitrogen balance for Ballyderown

3.10.1 Introduction

This section estimates an overall farm gate N budget, quantifying the N inputs which cross the farm boundary such as fertiliser, concentrate feed stuffs and atmospheric deposition which are termed N inputs. The outputs from the farm system are products which leave the farm in end product such as milk and meat.

3.10.2 N Balance Literature Review

Nitrogen balances are carried out for different ecosystems to estimate the efficiency of the system through the calculation of total inputs to and total outputs from the system. Schleef and Klienhanss (1997) outline N balances on a European scale. There are two different nutrient balances which can be carried out, i.e., the farm gate balance and the surface balance. The farm gate balance delineates the system boundary as the farm gate. The N content of all material entering the farm is measured as input (purchase of feedstuffs, living animals, mineral fertiliser and organic manure) and output of the system is measured as all N leaving the farm in product (sales of living animals, animal products, crop products and organic manure). Whereas in the surface-balance approach the soil surface is regarded as the boundary of the system. Input elements are N from fertiliser and from livestock manure. Outputs are characterised by the N content of the harvested material. Both approaches take into account N deposition from the atmosphere, fixation of molecular N by legumes and N losses to the atmosphere through NH_3 volatilisation and denitrification. Usually a constant stock of soil N is assumed by both approaches.

Schleef and Kleinhanns (1997) estimated an average N surplus for Ireland of 47 kg N ha^{-1}, with the highest estimated surpluses in Europe of 489 kg N ha^{-1} for the Noord-Brabant area of The Netherlands and 358 kg N ha^{-1} for the Antwerpen area of Belgium, which are attributed to high stock densities.

For example a N balance on a 30 ha dairy farm in the Netherlands had a total farm input of 15.6 t of N $year^{-1}$ and an output of 3.3 t of N $year^{-1}$, with a surplus of 407 kg N ha^{-1} $year^{-1}$ for the year 1994/95.

In the Netherlands there is growing interest in implementing a minerals accounting system with a registration of mineral input used on a farm in fertilisers and animal feeds (MLNV, 1995).

Jarvis (1993) carried out a N balance for a model farm in the SW England. In this study an annual N input of 25.6 t N was observed with only 20% of the N input transferred to end product of protein or milk. A further 46% of the total N input or 165 kg N ha^{-1} was estimated to have been lost to the environment and 34% or 112 kg N ha^{-1} was unaccounted for.

Brouwer *et al.* (1997) using data from the farm accountancy data network (FADN), estimated the average N supply by organic manures for Ireland at 93 kg N ha^{-1} $year^{-1}$, with 8% of farms having organic N inputs in excess of 170 kg N ha^{-1} $year^{-1}$, as stipulated in the Nitrates Directive (C.E.C., 1991). Sherwood and Tunney (1991) estimated a N input for Ireland of 684,000 t N for 1988; they estimated that 112,000 t N (16%) was removed in end product. With soil immobilisation assumed to be 12%, a total of 72% of the N inputs was available for loss to the environment. In Northern Ireland (Watson *et al.*, 1992) showed large imbalances in N input versus N output with between 60 and 240 kg N ha^{-1} $year^{-1}$ available for loss to the environment.

3.10.3 Methodology

All data used for this N balance have been obtained from earlier sections in this chapter. The N inputs used for the balance are all N inputs which cross the farm boundary, thus no attention is paid to recycling of N on the farm such as soil organic N mineralisation.

The following N inputs are used; fertiliser (section 3.3), concentrate feed importation and atmospheric N deposition (section 3.7.) N exportation from the farm in milk and meat is quantified in (section 3.8); animal liveweight gain is not included in the N balance as this N remains on the farm.

3.10.4 Results and Discussion

An overall farm gate N budget was calculated for Ballyderown (Table 3.20). The atmospheric deposition was calculated at 25 kg N ha^{-1} as measured in 1995 and this was then extrapolated to the 30 ha of the study farm.

Table 3.20 Farm Gate N budget for the whole farm as kg N and as kg N ha^{-1} $year^{-1}$.

	N loading kg N 30 ha^{-1}			N loading kg N ha^{-1}		
	1993	1994	1995	1993	1994	1995
Inputs						
Fertiliser	7373	7585	8077	246	253	269
Concentrated feed	2593	3053	4178	86	102	139
Atmospheric Deposition	750	750	750	25	25	25
Outputs						
Milk	2359	2165	2259	79	72	75
Meat	225	238	533	7.5	8	18
Balance	8132	8985	10213	271	300	340

The farm gate N budget in Table 3.20 shows that there was between 80 and 93 kg N ha^{-1} removed from the farm in milk and meat. The net excess N input (input-output) on the farm ranged from 271 to 340 kg N ha^{-1} in 1993 and 1995, respectively. This is similar to estimates of between 291 and 334 kg N ha^{-1} surpluses for 42 dairy farms in Belgium (Verbruggen *et al.*, 1996). When inputs are compared to outputs 24, 21 and 21% of the N input to the farm for 1993, 1994 and 1995, respectively, was removed in end product. This is very close to an estimate by Sherwood and Tunney (1991) of 16% of N inputs removed in end product from farms in Ireland.

Of the remaining N, some of this is assimilated in protein in animals on the farm, some is stored in silage, and some N is immobilised in the soil. A large amount of the N is also available for environmental loss to water as NO_3-N and to the air as NH_3-N. Some may be lost as N_2O or N_2 through denitrification processes.

CHAPTER 4 PHYSICAL PROPERTIES OF THE SOIL AND QUATERNARY DEPOSITS

4.1 Introduction

This chapter describes site-specific soil and quaternary deposits properties at Ballyderown, as measured during the course of the study. The chapter builds on the preliminary data which were introduced in chapter 2. The physical properties that were measured during the course of the study are important for extrapolating the general findings of the project to other sites.

These are soil profile descriptions of the soil and quaternary deposits, textural analysis (particle size analysis), soil bulk density, soil infiltration rates and sub-soil permeabilities and soil moisture characteristics. Also included are a water balance calculated for the farm during the study period and a tracing experiment measuring movement of Br^- down the soil profile.

4.2 Soil and Quaternary Deposit Descriptions

4.2.1 Introduction

McGuire (1991) presented preliminary data on plots 12, 5 and 16, containing boreholes 1, 2 and 3 respectively (see Figure 2.7 for plot and borehole locations), which are reported in section 2.3. No detailed County level soil map exists for Cork and thus the General Soil Map of Ireland (Gardiner and Radford, 1980) is the only soil map available for describing the soils on the farm. The soils on the farm were described as thin, varying from 75 cm in plot 12 to 60 cm in plots 5 and 16, sandy loam, acid brown earths corresponding to the principal soil of association 13, in the General Soil Map of Ireland (Gardiner and Radford, 1980), (Maguire, 1991). Due to the limited nature of Maguire's (1991) investigation of the field site, a more detailed investigation was warranted for this study. Particle size analysis was used to determine the texture of different soil horizons which were identified during the soil profile descriptions.

4.2.2 Methodology

Soil Profile Descriptions

Trial pits were dug close to the five boreholes during January 1996 to a depth of 1.5 m using a mechanical digger. The soils were then described and soil samples were taken for textural analysis and bulk density measurements. The colour was described from wet soil using the Munsell colour chart (USDA, 1975). The soil profile was described using standard methods as outlined by Hodgson (1976).

Textural Analysis (Particle Size Analyses)

Soil samples were taken from the units described in the soil and quaternary deposit from the trial pits. These samples were returned to the laboratory where they were dried, dissaggregated and passed through a 2 mm sieve. Each sample was stored at 4°C to await particle size analysis. Particle size was measured using the micro-pipette method as described by Burt *et al.* (1993) and Miller and Miller (1987) and is described in Appendix B.1.

4.2.3 Soil Profile Results

The soil profile descriptions of plots containing boreholes are presented below. To summarise, the soils at each borehole site were very similar (Plates 4.1 to 4.5), differing only slightly in the textural analyses, structure and depth.

Plot 12 (Borehole 1) Plate 4.1

Horizon	Depth (cm)	
A	0-30	Dark brown (7.5YR 3/2); sandy loam with few large stones; fine granular structure; friable; abundant roots.
B	30-60	Strong brown (7.5YR 4/6); sandy loam abundant small to medium rounded pebbles with occasional limestone pebbles; single grain structure; friable; very few roots.
C	60-90	Very dark greyish brown (2.5Y 3/2); sandy silt loam; single grain structure; friable; no roots.

Plot 5 (Borehole 2) Plate 4.2

Horizon	Depth (cm)	
A1	0-15	Dark reddish brown(5YR3/2); sandy loam; abundant stones 2-5cm sub rounded; fine granular structure; loose; layer of partially decomposed organic matter at 15 cm; abundant roots.
A2	15-34	Dark reddish brown (5YR3/2); sandy loam abundant sub-rounded stones 2-5 cm diameter; medium granular structure; friable; few fine roots.
BA	34-46	Strong brown (7.5YR4/6); sandy loam; abundant small sub-rounded pebbles; vertical infilling (5YR3/2) of A horizon material in the top 10 cm of B; single grain structure; friable; few fine roots.
B2	46-60	Yellowish red (5YR4/6); sandy loam; abundant large stones; single grain C; friable; very few roots.
C	60-130	Reddish brown (5YR4/3); sandy silt loam; few large stones; sub-angular blocky structure; firm brittle consistence; no roots.

Plot 16 (Borehole 3) Plate 4.3

Horizon	Depth (cm)	
A1	0-10	Dark brown (7.5YR3/2); sandy loam; very few small stones; fine granular structure; friable; abundant roots.
A2	10-24	Dark brown (7.5YR3/2); sandy silt loam; common small to medium stones; medium granular structure; friable; few fine to medium worm channels; many roots.
B	24-73	Strong brown (7.5YR4/6);sandy silt loam; common large stones 5-10 cm; vertical infilling (7.5YR3/2) of A horizon material in top 10 cm of B; single grain structure; friable; few fine to medium worm channels; few roots decreasing with depth to 45 cm.
C1	73-123	Reddish brown (5YR4/4); sandy silt loam; common well rounded medium stones; massive structure; slightly firm in situ; no roots.
C2	124-160	Reddish brown (5YR4/4); sandy silt loam; few small quartz stones; massive structure; slightly firm; discontinuous wavy manganese pan; no roots.

Plot 3a (Borehole 4) Plate 4.4

Horizon	Depth (cm)	
A1	0-10	Dark brown (7.5YR3/2); sandy silt loam; few small stones; medium granular structure; friable; abundant roots.
A2	10-30	Dark brown (7.5YR3); sandy loam; abundant well rounded small stones; medium granular structure; friable; many roots.
B1	30-75	Brown (7.5YR4/4); sandy loam; abundant small stones 1-2 cm; single grain structure; friable; few roots.
B2	75-106	Reddish brown (5YR4/4); sandy loam; few very large sandstone stones; single grain structure; friable; discontinuous wavy manganese pan; few fine to medium worm channels; no fine roots.
C	>106	Dark reddish brown (5YR 2.5/2); sandy loam; abundant small stones; single grain structure; friable; no fine roots; dock roots present at 1.2 m.

Plot 7 (Borehole 5) Plate 4.5

Horizon	Depth (cm)	Description
A1	0-12	Dark brown (7.5YR3); sandy silt loam; very few small stones; medium granular structure; friable; dark red mottles along root channels; abundant roots.
A2	12-30	Dark reddish brown(5YR3/2); sandy silt loam; abundant small quartz stones; sub-angular blocky structure; firm; many roots.
B1	30-50	Brown colour(7.5YR4/4); sandy silt loam; few small stones; medium sub-angular blocky; firm; no roots .
B2	50-70	Brown matrix (7.5YR5/4) grey prism faces; clay loam; prismatic structure; firm; no roots.
C1	70-96	Brown (7.5YR5/4); loamy sand; common small pebbles and few large stones; massive structure; moderately firm; no roots.
C2	90-140	Reddish brown matrix (5YR4/4) grey prism faces; sandy silt loam; prismatic structure; moderately firm; no roots.

The soil profiles in plots 12, 5 and 16 were similar in textural classification, with a sandy loam overlying a sandy silt loam soil, although in plot 16 the sandy loam layer occurred from 0 to 10 cm whereas at the other two plots the sandy loam layer occurred from 0 to 60 cm. Plots 3a and 7 had sandy silt loam overlying either sandy loam in plot 3a and differing layers which varied from clay loam to loamy sand in plot 7. The soil particle size analysis can be seen in Appendix B.2.

In general the soil was friable and massive although plots 5 and 7 had angular to sub-angular blocky structure in some soil layers deeper down the soil profile. In plot 5 the C horizon had angular blocky structure and it also had a firm brittle consistence; this layer is termed a fragipan.

The common rooting depth seen in the soil profiles was between 0 and 20 cm, although occasionally roots were seen at deeper depths, such as in plot 3a where roots could be seen at greater than 100 cm deep.

The shallowest depth to bedrock (soil+quaternary deposits) for plots containing boreholes was 90 cm in plot 12 whereas at the other borehole sites the bedrock was not found at the 150 cm depth (the maximum depth of the mechanical digger). During late 1993 eight trials pits using a JCB and one soil auger using the geological survey drilling rig were carried out to determine depth to bedrock. A depth to bedrock map was constructed using information from trial pits dug during this study together with previous studies on the farm and with the expert knowledge of the farm staff (Figure 4.1). In general the depth to bedrock on the farm was thin.

The depth to bedrock varied over the farm area. Plots to the east of the farm roadway had the thinnest depth to bedrock which was generally less than 1 metre, farm staff reported that the grass died in these areas during dry summers. To the west of the roadway the depth to bedrock was greater than two metres which was the full extent of the JCB. A soil auger carried out using the geological survey drilling rig did not reach bedrock when drilling stopped at six metres.

4.3. Bulk Density

4.3.1 Introduction

Bulk density (B_d) is defined as the mass of a unit of dry soil (Brady, 1990) and it reflects soil structure and packing. Bulk density was measured using a modified core method described by Blake and Harge (1986). Soil bulk density influences the movement of water through a soil profile (Dils, 1997). Soil bulk density tends to increase with the degree of compaction and tends to increase with depth in the soil profile because of increasing overburden and decreasing disturbance.

Typical soil bulk densities range from 1.12 g cm^{-3} for a wet clay to 1.9 g cm^{-3} for a heavily compacted sandy loam soil. Typical sandy subsoil has a bulk density of about 1.6 g cm^{-3} (Marshall *et al.*, 1996). The main purpose of measuring soil bulk densities was to use the results to convert soil inorganic N measurements (sections 3.6, 6.2 and 8.2) from mg N kg^{-1} dry soil to kg N ha^{-1}.

4.3.2 Bulk Density Methodology

Samples for bulk density measurements were prepared using a modification of the cylinder method described by Blake and Harge (1986). A steel cylinder (internal diameter 2.4 cm and length 5 cm) was pushed into the soil at the required depth in the trial pit (Plate 4.6) and then the soil sample obtained was placed in a labelled plastic bag for return to the laboratory for

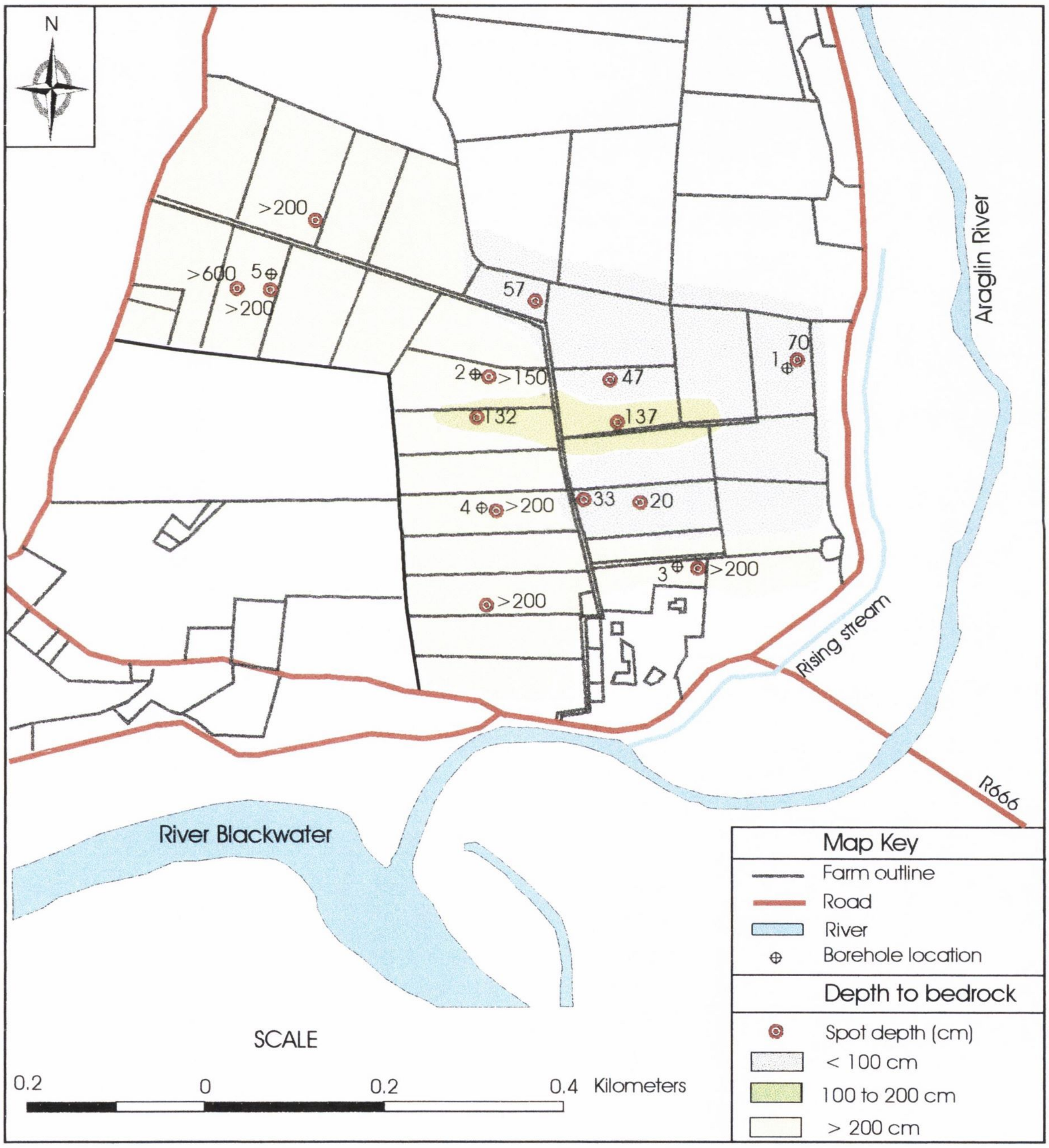


Figure 4.1 Depth to bedrock (cm) on Ballyderown Farm.

mass determination. Six replicate samples were taken at each depth and aggregated into 3 groups. Bulk density determinations were carried out at 5 cm depths from the soil surface to a depth of 1 m, where bedrock permitted.

On return to the laboratory the soil in each cylinder was emptied into a clean, dry, pre-weighed petri dish. The sample was weighed for determination of the soil wet weight. The soil sample was then dried for 24 hours at 104°C after which the sample was cooled in a desiccator and then weighed for dry weight determination.

$$\text{Bulk Density} = \frac{\text{Soil dry weight}}{\text{Cylinder volume}}$$

Stone content

The stones from each sample were then removed by wet sieving through a 2 mm sieve, the clean stones were then placed on a clean dry pre-weighed petri dish and dried for 24 hours at 104°C. The petri dish was allowed to cool in a desiccator and weighed for stone dry weight determination.

The volume of stones from each cylinder was determined by pouring the stones into a 100 cm^{-3} graduated cylinder containing 50 cm^{-3} water, the volume of the stones being measured as the volume of water displaced in the graduated cylinder. Where stone volume was >50 cm^{-3}, a 200 cc graduated cylinder was used.

$$\text{Corrected Bulk Density (g cm}^{-3}\text{)} = \frac{\text{soil dry weight of cylinder (soil dry weight - stone dry weight)}}{\text{Cylinder volume - stone volume in cylinder}}$$

4.3.3 Bulk Density Results

The results of the soil bulk density measurements carried out for the five plots which contained boreholes, plots 12, 5, 16, 3a and 7, are shown in Figure 4.2.

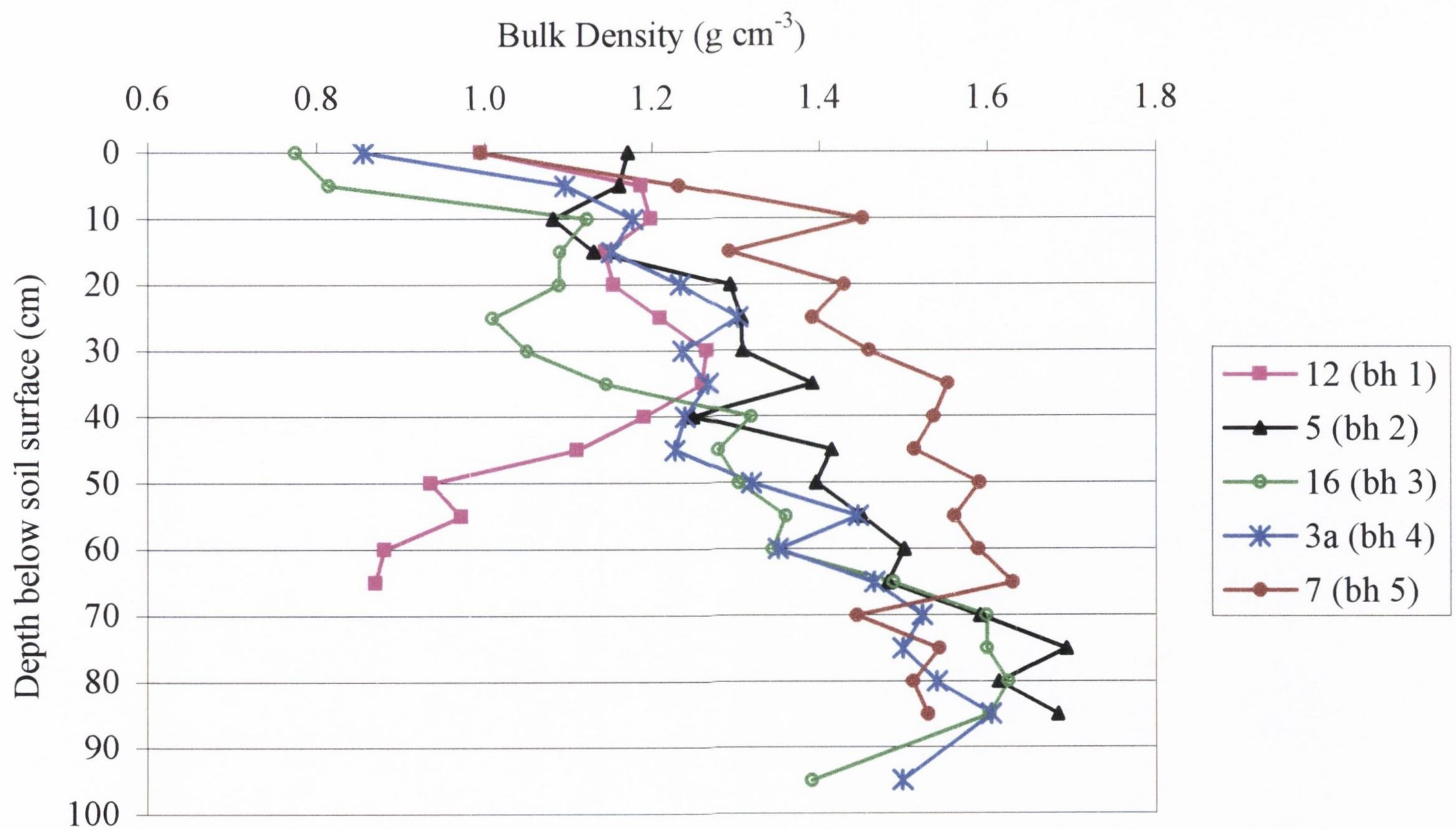


Figure 4.2 Soil Bulk Density profiles as measured in plots 12, 5, 16, 3a, and 7. The depth below soil surface e.g., 0 cm refers to the sampling depth 0 to 5cm.

Plots 5, 16, 3a and 7, which contain boreholes 2, 3, 4, and 5, respectively, have similar soil bulk density profiles which gradually increase with soil depth. With the exception of plot 12 maximum bulk densities of 1.53 to 1.68 g cm^{-3} were observed between 75 and 90 cm below the soil surface. The increasing soil bulk density measured in plots 5 and 7 are also reflected in the soil profile descriptions which refer to the soil being moderately firm or brittle. The bulk density between 90 and 100 cm decreases in plots 3a and 16.

The soil bulk density profile measured in plot 12, which contains borehole 1, differs from the other four plots; maximum bulk density of 1.27 g cm^{-3} was observed at a depth of 30 to 40 cm. The bulk density then decreases to a low of 0.87 g cm^{-3} at the 65 to 70 cm depth. Thus, the soil loses cohesion with increasing depth down the soil profile, which is reflected in the soil profile descriptions that noted the soil at this depth is friable.

From the soil bulk density profiles it is possible to infer that the permeability of the soil in plots 5, 16, 3a and 7 decreases with depth due to increasing soil bulk density, whereas in plot 12 permeability is likely to increase with depth due to decreasing bulk density.

4.4 Soil Permeability Characteristics

4.4.1 Introduction

Infiltration capacity represents the ability of a soil to accept incoming water rather than lose it as surface runoff (Youngs, 1991). During a rainfall event the soil moisture content increases and the rate of infiltration exponentially decreases, eventually reaching a constant value referred to as the infiltration capacity of the soil. Physical characteristics of the soil including texture, structure and porosity determine the infiltration capacity. For example, cracks and fissures create preferential flow paths that increase the infiltration capacity, whereas soil surface compaction or formation of a surface crust by rainfall impact or the washing of fine particles into surface pores may limit the infiltration capacity.

4.4.2 Methodology

Soil Infiltration Capacity Methodology

Soil infiltration rate were measured at three borehole sites using the double-ring infiltrometer method (Youngs, 1991) in March and April 1995 (Plate 4.7). Representative locations in plots 12, 16 and 3a, which contained boreholes 1, 3 and 4 (see Figure 2.7), were chosen and the infiltrometers were installed in triplicate. The inner and outer ring diameters were 30 ±2 cm and 55 ±2 cm, respectively. Each ring was inserted 10 cm into the soil by tamping on a wooden plank placed over the ring.

Water barrels (50 l) were filled with water and placed beside the three infiltrometers. First, the outer ring was filled with water followed by filling of the inner ring and the stop-watch was started. This process was repeated for the other two infiltrometers. A ruler was then used to measure the drop in depth of the water level from the top of the inside cylinder at a clearly marked point every minute for the first 20 minutes and then every 5 minutes until steady state was achieved (Plate 4.7). When the water level in the rings was low they were refilled to the top of the inner ring and the height achieved was recorded.

Quaternary Deposit Permeability Methodology

The inversed auger-hole method was used to determine the permeability of the quaternary deposit at a known depth below the soil surface (Ritzema, 1994). The method is based on the principle:- that if one bores a hole into the soil and fills this with water until the soil below and around the hole is practically saturated, the infiltration rate (v) will be constant and K is the saturated hydraulic conductivity of the wetted soil.

The total infiltration, Q will then be equal to v*A (where A is the surface area of infiltration i.e. the surface area of the cylindrical hole.).

With v = K, Q=K*A.

The infiltration capacity and the inversed auger-hole methods were used to evaluate rates of soil water movement through the soil.

A Dutch auger was used to drill a hole to a depth of 60 cm into the soil profile. Water was then poured into the hole and left to infiltrate; this was repeated again so that the soil was saturated over a considerable distance. A float device was then placed in the hole, the standing water height was measured on the measuring tape and the stop-watch was started. (Plate 4.8) The rate of infiltration was monitored by measuring the water height every minute for the first 10 minutes and then measuring every two minutes for the next 10 minutes. After 20 minutes the height was measured at five minutes intervals. When the float was near to the base of the auger hole the inverted auger was removed and water was poured into the hole and the process was repeated. Triplicate permeability values were measured in plots 12, 16 and 3a.

The theory of the inversed auger-hole method is described in full by Ritzema (1994). Saturated hydraulic conductivity (K) was calculated using Equation 1.

$$K = 1.15r \frac{\log(h_o + \frac{1}{2}r) - \log(h_t + \frac{1}{2}r)}{t - t_o} \qquad \text{Equation 1}$$

Where t_o = start time (s)

t = time after start (s)

h_o = standing water height at t_o (cm)

h_t = standing water height at t (cm)

r = radius of auger-hole

4.4.3 Results

Soil Infiltration Capacity

Temporal variation of soil infiltration rate is presented in Figure 4.3. Plot 3a exhibits the characteristic relationship of soil infiltration rate decreasing with time, the infiltration rate decreased from a high rate of 135 mm $hour^{-1}$ to a steady rate of 51 mm $hour^{-1}$. The decrease of the soil infiltration rate with time can not be seen as clearly in plots 12 and 16 although in plot 16 the infiltration rates shown in this diagram are from day two of monitoring due to a steady rate of infiltration not being reached on the first day.

The changes of infiltration rate in plot 16 between the first day of measurement and the second day can be seen in Figure 4.4. It is possible to see that the infiltration rate was not steady at the end of day 1 and thus the infiltration rates were continued on day two until a steady infiltration rate was achieved.

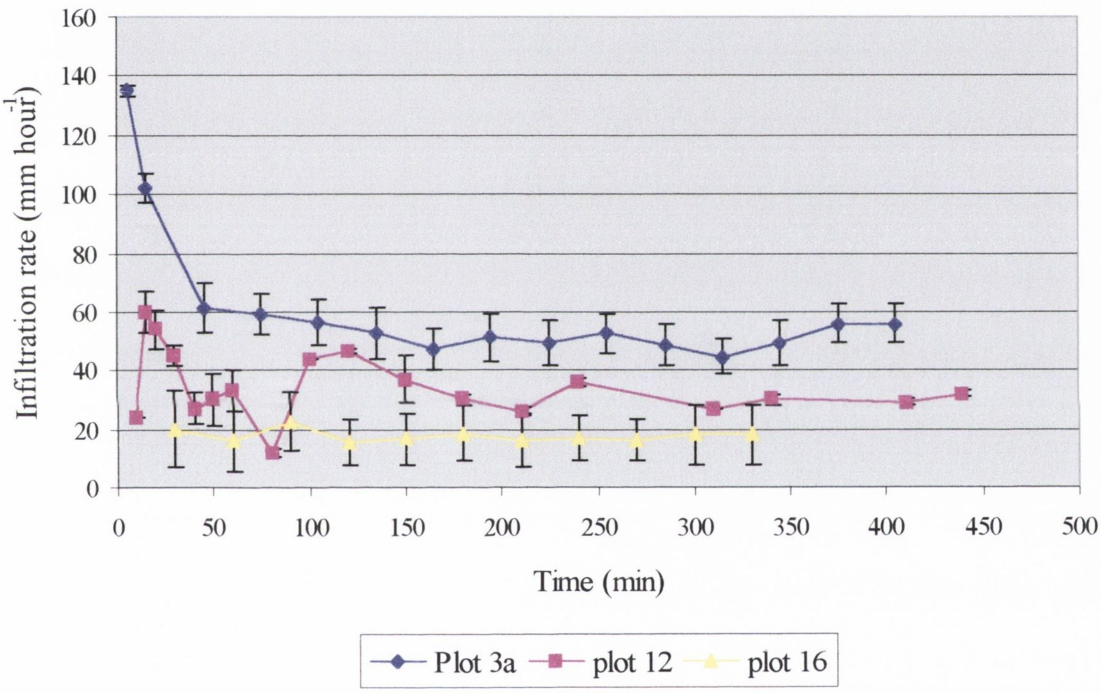


Figure 4.3 Mean infiltration rates (mm $hour^{-1}$) measured in plots 3a, 12 and 16 (vertical bars represent 1 standard error).

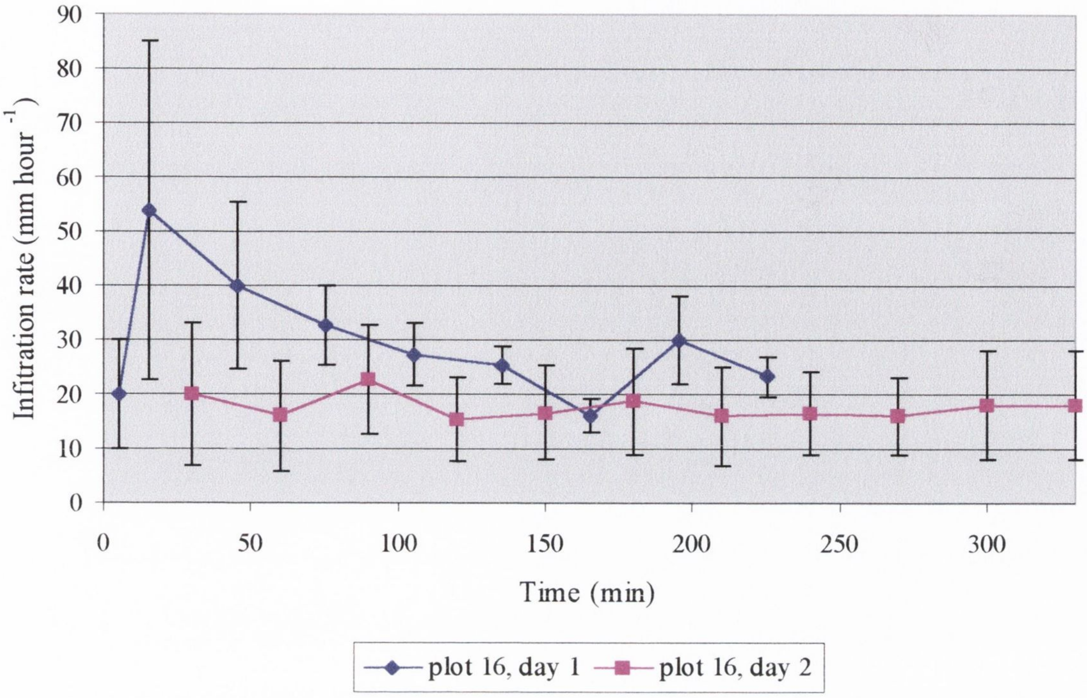


Figure 4.4 Changes of infiltration capacity between two successive measurement days (vertical bars represent 1 standard error).

The mean soil infiltration capacities of plots 12, 16, and 3a are given in Table 4.1.

Table 4.1 Mean soil infiltration capacities of plots 12, 16, 3a and farm mean.

Plot No (Borehole No.)	Infiltration Capacity ($mm\ hr^{-1}$) Mean	Range	S.E. of mean	n
12 (1)	31	29 - 32	1	3
16 (3)	17	7 - 54	9	3
3a (4)	51	24 - 68	7	3
Farm Mean	33	7 - 68	7	9

Infiltration capacities ranged from 7 to 68 mm $hour^{-1}$ in the three plots. Mean soil steady state infiltration capacities measured in three plots ranged from 17 mm $hour^{-1}$ in plot 16, to 51 mm $hour^{-1}$ in plot 3a, or from 0.41 to 1.22 m day^{-1}.

Quaternary Deposit Hydraulic Conductivity

The results of the measured hydraulic conductivity (K) are presented in Table 4.2.

Table 4.2 Observed quaternary deposit hydraulic conductivity (measured at 0.6 m b.g.l.).

	Quaternary deposit K (m day^{-1})			
Plot No. (Borehole No.)	Mean	Range	S.E. of mean	n
12 (1)	0.044	0.039 - 0.052	0.004	3
16 (3)	0.042	0.034 - 0.051	0.005	3
3a (4)	0.036	0.014 - 0.049	0.011	3

Mean K rates measured ranged between 0.036 and 0.044 m day^{-1} in the fields measured. Plot 3a, which contains borehole 4, had the lowest mean K value of 0.036 m day^{-1} which was due to one of the three replications having an extremely low K value of 0.014 m day^{-1}, whereas plots 12 and 16 had lower variability with standard errors of 0.004 and 0.005 m day^{-1}, respectively.

4.4.4 Discussion

Diamond and Shanley (1998) reported mean infiltration capacities, of four different soil types, which ranged from 22 to 72 mm $hour^{-1}$ for repeat measurements carried out in summer and winter, respectively, on the same soil. The time of the year of infiltration capacity measurement is important as summer has higher capacities than winter and the measurements carried out during this study were taken during summer. Lower soil infiltration capacities were reported by Mulqueen (1991), with capacities ranging from 2.1 to 22.9 mm $hour^{-1}$ for a loam and sandy loam soil, respectively. The infiltration capacities measured in Ballyderown were in the same range as those reported by Diamond and Shanley (1984) and those of Mulqueen (1991).

The measured infiltration capacities are generally greater than a mean rainfall intensity of 16.5 mm $hour^{-1}$, which has a return period of five years in the study area (Rohan, 1986; Logue, 1971). The Irish Meteorological Service has measured rainfall intensities at Cork Airport varying from 11.2 mm hour^{-1} for a one year return period to 16.5 mm hour^{-1} for a five year return period to the highest intensity of 28.7 mm hour^{-1}, which had a 50 year return period. Comparison of mean soil infiltration capacities and rainfall intensities, overland flow would be unlikely on any plot at rainfall intensities of <16.5 mm hour^{-1}, which had a return period of 5 years. Even at the 50 year return period rainfall intensity of 28.7 mm hour^{-1}, overland flow on the parts of the plots measured would be unlikely, as maximum infiltration capacities in all plots were >28.7 mm hour^{-1}. Due to the high infiltration capacities observed runoff is thought to be unlikely and is not accounted for in the water budget.

Similar K values were reported by Diamond (1984) ranging from 0.04 to 0.13 m day^{-1} for a till parent material in east County Waterford, which is very close to the Ballyderown farm in East Cork. Diamond (1984) also reported high soil K values for alluvial soils, which ranged from 0.34 to 2.3 m day^{-1}.

Soil permeability values measured using the inversed auger-hole technique were considerably lower than the soil infiltration rates measured using the double ring infiltrometer. The mean K value measured in plot 12 was 0.044 m day^{-1} whereas the infiltration rate was 0.744 m day^{-1}. A possible reason for the lower K rates would be the increased bulk density at 60 to 70 cm below the soil surface in plots 16 and 3a. The amount of head applied in each method was also different accounting for some of the difference in rates between methods. Time also could be a determinant in that the soil infiltration capacities were measured during April 1995 whereas the subsoil permeability values were measured during June 1995. Diamond (1998) found significantly different soil infiltration capacities when he compared summer and winter measurements taken on the same site; the difference was as much as 1.2 m day^{-1}.

4.5 Temporal variation of Soil Moisture

4.5.1 Introduction

The movement of water through the soil profile is crucial to understanding the movement of nitrate from the soil surface to the groundwater, as water is the transport agent of nitrate through soils. Through the study of changes in soil water content and effective rainfall it is possible to observe water movements (and infer nitrate movement) during periods when soil solution samples were not taken.

Soil moisture variation was measured using the neutron probe. Soil water movement also was estimated on the farm by modelling the quantity and temporal variation of effective rainfall (actual rainfall - evapotranspiration) during the study period. Using these two methods it was possible to observe periods when nitrate movement was likely to have occurred.

4.5.2 Water Budget Calculation and Method

The amount of rainfall which is available for leaching through soil is termed effective rainfall, and is the difference between actual rainfall and evapotranspiration. Potential evapotranspiration (E_p) can be calculated using the Penman formula as described in Shaw (1994) and MAFF (1967). Potential evapotranspiration can be modelled from standard meteorological measurements which are routinely carried out at synoptic stations throughout Ireland.

During the summer a soil moisture deficit (smd) develops when evapotranspiration is greater than effective rainfall. When smd increases above 30 mm, grass growth is restricted, which causes a reduction in evapotranspiration: thus E_p is overestimated during dry periods. Aslyng (1965) proposed evapotranspiration restriction from a soil moisture deficit $\geq$30 mm, with evapotranspiration decreasing linearly to a value of 120 mm. A soil moisture deficit of 75 mm would therefore decrease evapotranspiration by 50 per cent.

A farm scale water budget was calculated using meteorological data from a climatic station located at Teagasc, Moorepark, which was 1.5 km from the study area (Figure 2.1). Daily meteorological data were used to calculate potential evapotranspiration (E_p), soil moisture deficit (smd), grass growth and actual evapotranspiration (E_a). The water budget was used to calculate the onset of leaching (when soil moisture deficit was zero) and to calculate the quantity of effective rainfall which was recharging the aquifer being studied.

Soil moisture deficit was calculated using a model developed in Johnstown Castle for calculating grass growth (Brereton *et al.*, 1987; Brereton and Keane, 1982). Soil moisture deficit is calculated as the difference between rainfall and evapotranspiration. Potential evapotranspiration (E_p) was modified using the Aslyng scale (Aslyng, 1965) to calculate actual evapotranspiration (E_a).

Effective rainfall was then calculated by subtracting estimated weekly actual evapotranspiration from measured weekly rainfall. When rainfall was less than actual evapotranspiration effective rainfall was expressed as zero.

4.5.3 Water Budget Calculation Results

The annual water budgets calculated for the farm are given in Table 4.3.

Table 4.3 Annual water budgets (mm) for Ballyderown from 1993 to 1995 (1st Jan. to 31st Dec.).

	Year		
	1993	1994	1995
Potential Evapotranspiration (E_p)	509	556	625
Actual Transpiration (E_a)	489	518	411
Total Rainfall	1062	1159	1061
Total Effective Rainfall	573	641	408

The annual rainfall in the years 1993 to 1995 was similar, with 1994 having ~ 100 mm more total rainfall that 1993 and 1995. However when the total effective rainfall is compared for each year, 1995 had the lowest amount of 408 mm whereas 1994 had the largest effective rainfall amount of 641 mm.

Detailed weekly water budgets (total rainfall, E_a, effective rainfall and soil moisture deficit) from 1/1/93 until 28/4/96 can be seen in Appendix C.1 to C.4.

During 1993, soil re-wetting after the summer dry period occurred from 7/9/93 to 13/9/93 with the sum weekly effective rainfall of 48 mm (Appendix C.1). The soil moisture deficit reached zero during 21 to 27/9/93. Thus it is hypothesised that leaching began at about week 39, probably between week 37 and week 39 (Appendix C.1). The smd peaked in week 36 at 67 mm and then decreased rapidly after that date. During the period 13/9/93 to 17/10/93 151 mm of effective rainfall occurred. There was then a dry period for three weeks with effective rainfall occurring again after this.

In 1994 the soil moisture deficit decreased to zero from 10/9/94 to 16/9/94 week 37(Appendices C.2, D). Effective rainfall started during the week 3/9/94 to 9/9/94 therefore it is hypothesised that leaching began in early September. There was a total of 1159 mm of rainfall during the year and there was 826 mm of effective rainfall recharging the aquifer (Table 4.3). Of the total rainfall, 425 mm fell between January and June, 48 mm fell between June and the end of August and 353 mm fell from September to December.

During 1995, the soil moisture deficit was above 30 mm from week 23-29/4/95 until week 22-29/10/95 but there were occasional effective rainfall events during this period (Appendix C.3). The soil moisture deficit reached zero during 30/10/95 to 06/11/95, week no. 43. Effective rainfall began on 9/9/95 but during 16-21/10/95 there was nearly 60 mm. Thus leaching began during the period 15/10/95 to 6/11/95, which was mid October to early November.

Leaching began a month later in 1995 compared to the leaching patterns of the two previous years. This was in part due to the summer drought which affected grass growth from late-April until October, a 26 week duration. In 1994 the soil moisture deficit was greater than 30 mm for 12 weeks and in 1993 the soil moisture deficit was above 30 mm for 9 weeks.

4.5.4 Soil Moisture Measurement Techniques and Methodology

Numerous methods have been developed to measure soil moisture such as tensiometry, time-domain reflectometry, electrical resistivity, gamma ray attenuation and neutron probe measurements.

The neutron probe moisture meter is widely used in agriculture, hydrology and soil engineering. This method was developed during the late 1940's and is based on the principle that hydrogen (H) a dominant source of which is the water ion (H_2O) which slows down fast neutrons, because the mass of the neutron and proton are closely similar (Marshall *et al.*, 1996). The neutron probe consists of a source of fast neutrons (^{241}Am mixed with Be) and close to the source a detector of slow neutrons. The detector is not shielded from the source as it is only sensitive to thermal neutrons.

The probe is lowered down an access tube during which time a concentration distribution of slow neutrons is established immediately in the soil surrounding the probe. The neutrons also populate the area of the access tube where the detector measures the density of slow neutrons. The mass of slow neutrons is proportional to the volumetric soil water concentration. A water content of the soil profile can then be obtained by lowering the probe to successively greater depths, at increments of about 0.3 m.

Water potential, as measured by tensiometry, is based on the principle that as the water potential of the soil around the tensiometer decreases relative to that of the water in the tensiometer cup, water moves out of the tensiometer through the pores in the tensiometer cup and into the soil. The pressure of the water in the tensiometer cup is increased which is measured by a gauge. If the soil surrounding the tensiometer receives water the reverse of the mechanism described above occurs and the pressure in the tensiometer increases (Cassell and Klute, 1986).

Volumetric soil moisture was measured at the study site by the neutron moisture meter (503 DR Hydroprobe, Soil Moisture Inc., California, USA) and soil moisture potential was measured using jet filled tensiometers. Volumetric soil moisture was measured using the neutron probe by lowering the probe down 1.5 m aluminium access tubes located in plots 5, 16, 3a, and 7. These access tubes were installed using a screw auger to drill a 5 cm diameter hole. The neutron probe access tube was pushed down the hole and capped with a rubber bung. Volumetric soil moisture measurements were carried out weekly on Ballyderown farm from 21/3/95 until 4/3/96. Neutron probe readings were measured at 25, 50, 75, 100 and 140 cm below the soil surface.

Soil moisture was measured as counts per unit time, which is the basic reading carried out by the neutron probe. A calibration curve could not be calculated due to the lack of actual soil moisture measurements but counts per unit time can be used indirectly to observe changes in soil moisture at different depths below the soil surface.

Regression analyses were carried out between neutron probe measurements at different depths down the soil profile and estimated smd to ascertain the relationship between observed volumetric soil moisture and estimated smd. Thus, the commencement of leaching as indicated by estimated smd returning to zero could be extrapolated to each year of the study.

Jet-filled tensiometers (model 2725, Soil Moisture Equipment Corp., Santa Barbara, CA, USA) with vacuum dial gauges were also installed in plots 5, 16, 3a, and 7 at 0.5 m, 1.0 m, and 1.5 m depths. A hole was augered to the required depth using a hand auger (5 cm diameter) and sieved soil was mixed into a slurry into which the tensiometer was inserted into the bottom of the hole. Soil was backfilled around the tensiometer as described by Cassell and Klute (1986). The tensiometers were then filled with water, de-areated and allowed to equilibrate in the soil before readings were taken.

Tensiometers were read weekly and the water was replaced in the tensiometer when needed. Readings of soil matric suction began on 15/9/94 and continued until 27/1/96.

4.5.5 Soil Moisture Measurement Results

Temporal variation of volumetric soil moisture in plot 16, as measured by the neutron probe, can be seen in Figure 4.5 which shows the changes in soil moisture at 25, 50, 75, 100 and 140 cm b.g.l.. Temporal variation of soil moisture content, as measured by the neutron probe in plots 3a and 7 are presented in Appendix E. These variations follow almost the identical pattern of soil moisture variation as presented in Figure 4.5 and it was considered repetitive to include them in the main text.

Soil moisture content as indicated by the neutron probe method decreased, at the 25 cm

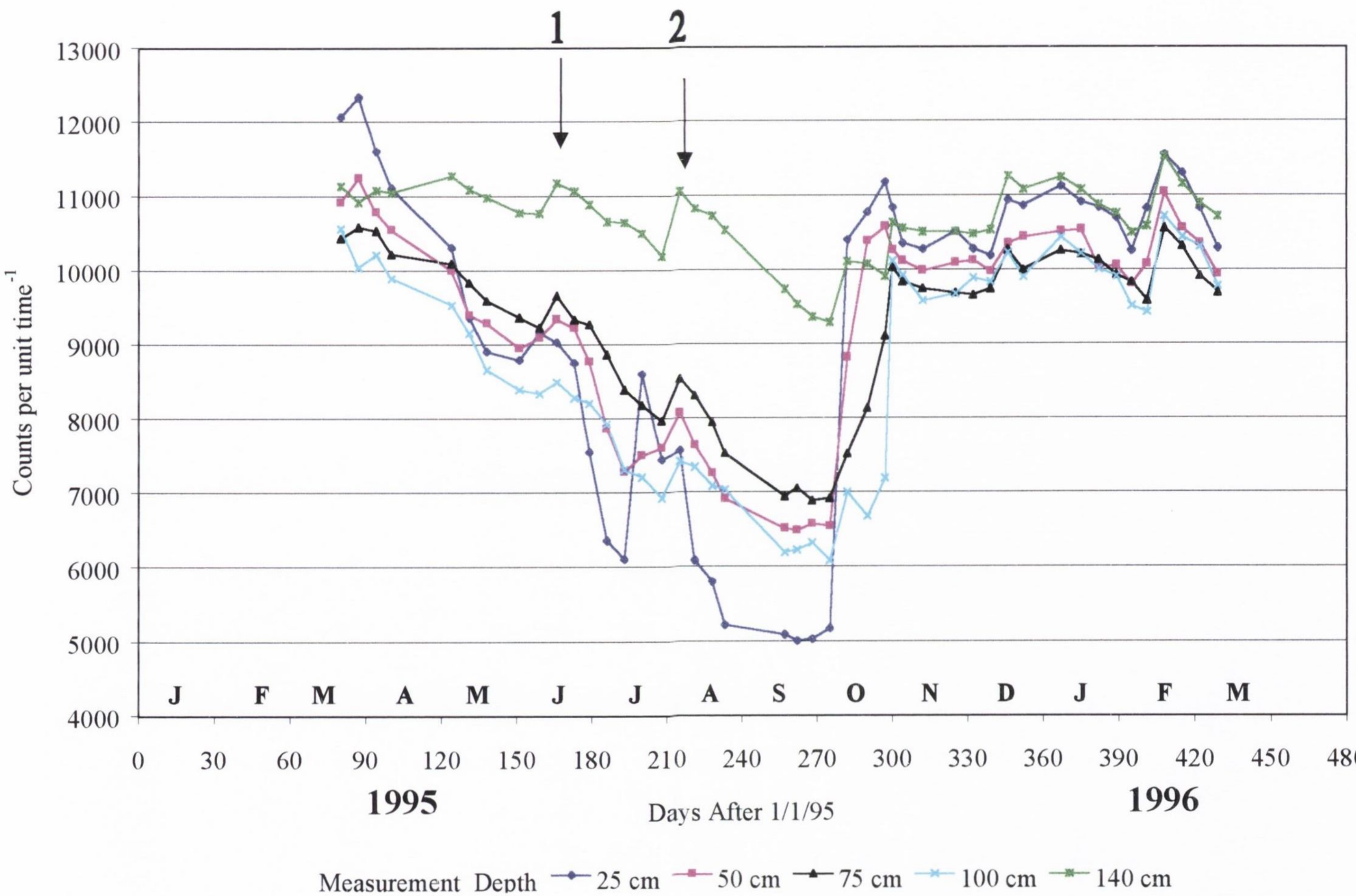


Figure 4.5 Temporal variation of soil moisture as measured using the neutron probe method in plot 16 (see text for explanation of arrows 1 and 2).

measurement depth, from 4/4/95 until 9/10/95. Although it is possible to observe slight increases in soil moisture during the summer of 1995 at all measurement depths, the most visible examples are highlighted by the arrows in Figure 4.5 which occur at the 140 cm measurement depth. The soil moisture measured at the 140 cm depth increased between 15 and 22/6/95 (arrow 1) and also on 3/8/95 (arrow 2), this indicates that there was subsurface flow from the soil surface down to the 140 cm depth during the summer. The movement of soil solution at these times would also indicate a potential for nitrate leaching if NO_3-N was available in the soil.

The soil matric suction measured in plot 16 is presented in Figure 4.6. The soil matric suction temporal variation in plots 3a and 7 are plotted in Appendix F and showed similar trends. When the tensiometers were installed at the start of September 1994 the soil had already returned to field capacity as shown by the low matric suction levels at the start of monitoring. After the winter of 1994/95 the soil matric suction began to increase on 12/4/95 peaking at 74 centibars at the 50 cm depth on 9/8/95 after which the soil suction decreased to 58 centibars. The decrease observed after 9/8/95 (arrow 3) at the 50 cm depth, was not observed at the deeper depths of 100 and 150 cm. At the deeper depths peak suction was observed at 100 cm on 19/9/95 and on 9/10/95 at the 150 cm depth.

A highly significant ($P<0.001$) association existed between soil matric suction, as measured by tensiometers and soil moisture, as measured by the neutron probe. The relationship between soil moisture measured by the neutron probe method and soil matric suction can be seen for plot 16 at the 50 cm depth in Figure 4.7.

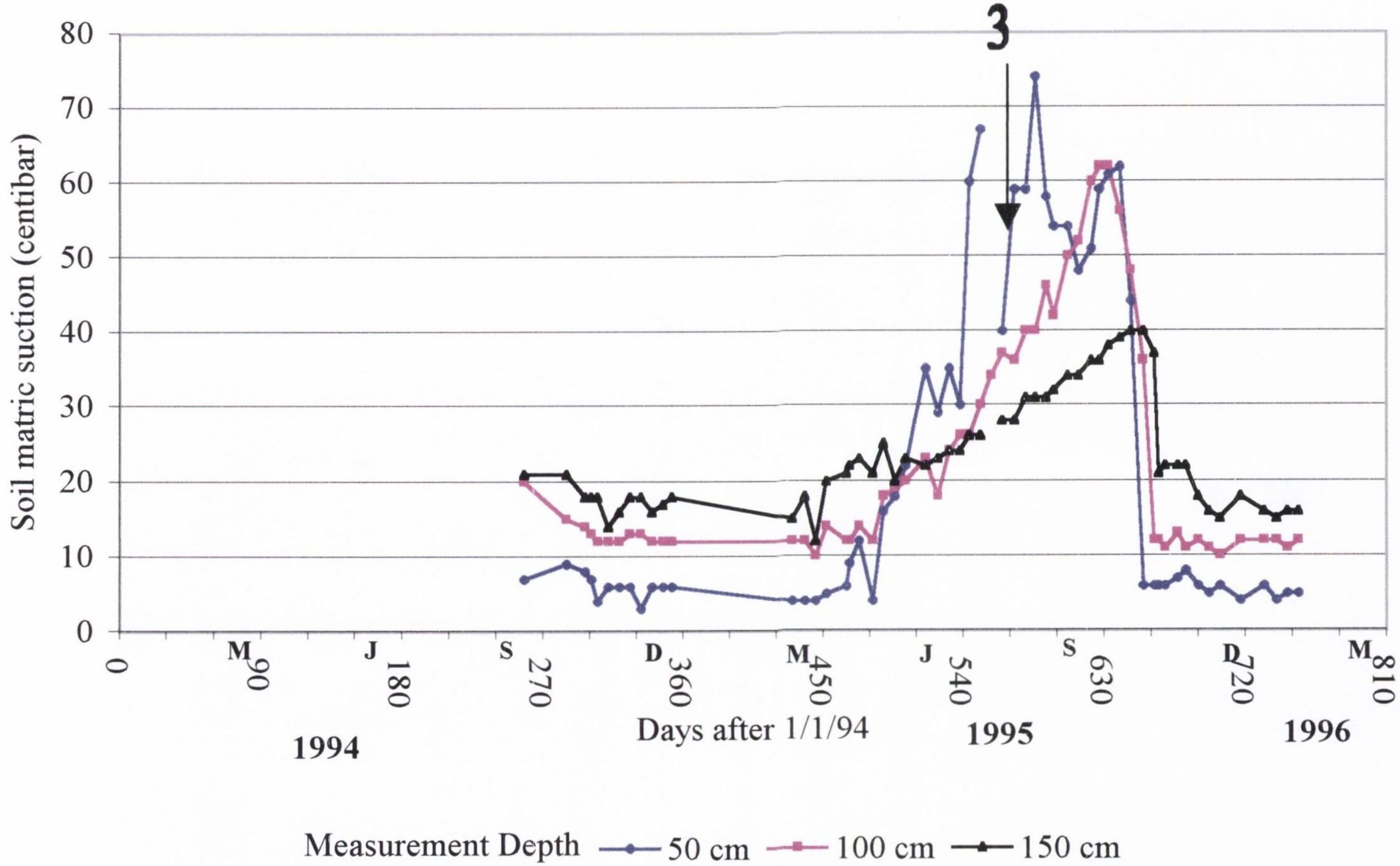


Figure 4.6 Soil matric suction measured at depths of 50, 100 and 150 cm below the soil surface in plot 16 (see text for explanation of arrow 3).

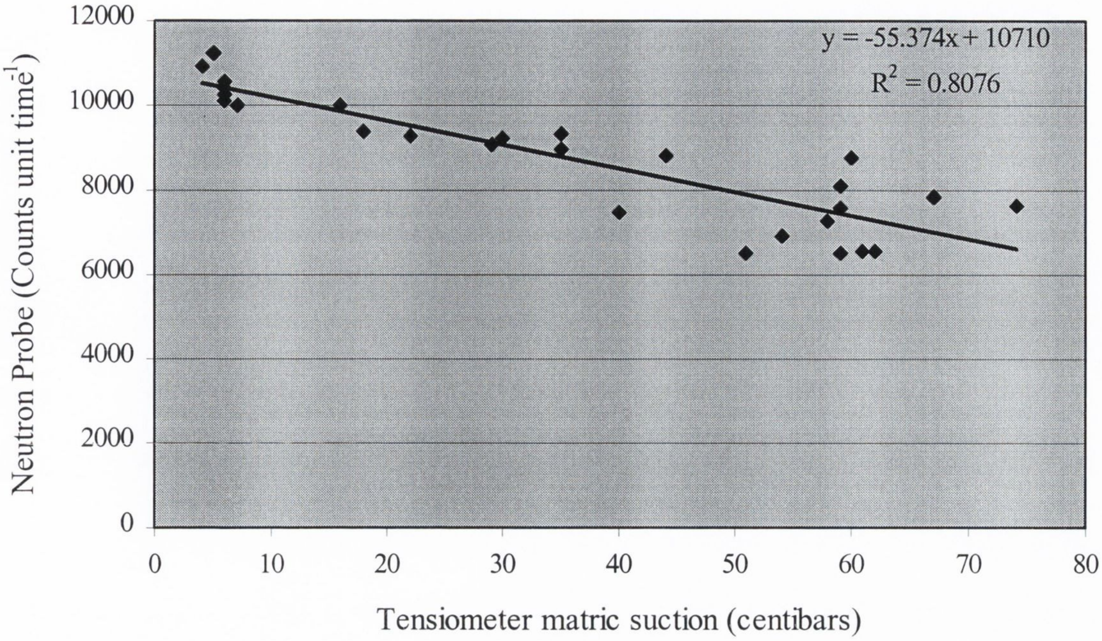


Figure 4.7 Relationship between tensiometer matric suction measurements and neutron probe measurements (counts unit time^{-1}) measured at 50 cm deep in plot 16.

The summary of regressions carried out between neutron probe soil moisture measurements and tensiometer matric suction measurements observed, at all tensiometer depths for each plot (plots 3a and 7 did not have tensiometers at the 150 cm depth), can be seen in Table 4.4. All the regressions were highly significant ($P<0.001$).

Table 4.4 Regression analyses between neutron probe soil moisture measurements and tensiometer matric suction measurements. The R^2 for comparison at each depth in each plot is presented, all are significant ($P<0.001$).

	Depth below the soil surface (cm)		
Plot	50	100	150
16	0.81	0.79	0.56
3a	0.75	0.69	ni
7	0.65	0.78	ni

ni indicates that tensiometers were installed at this depth.

A perfect relationship was not seen between soil matric suction and neutron probe measurements and the likely cause of variation between the two methods were the problems which were encountered with the tensiometers. A main problem with the use of tensiometers on the study farm was that during the summer the high matric suctions caused by the high smd, removed all the water from the tensiometers. Thus, even though tensiometers were refilled weekly during the summer and readings were taken 1 hour after refilling it is possible that the soil and tensiometer had not reached equilibrium during this period and thus the matric suction may not have been the true matric suction. The variation in matric suction caused by this fact is the likely cause of the differences between the two methods.

Observed soil moisture content, as indicated by neutron probe measurements were compared to estimated smd (Table 4.5) . A graphical example from plot 16 at a depth of 25 cm is presented in Figure 4.8. Regression analyses between estimated smd and observed soil moisture content showed a highly significant ($P<0.001$) relationship between the two methods.

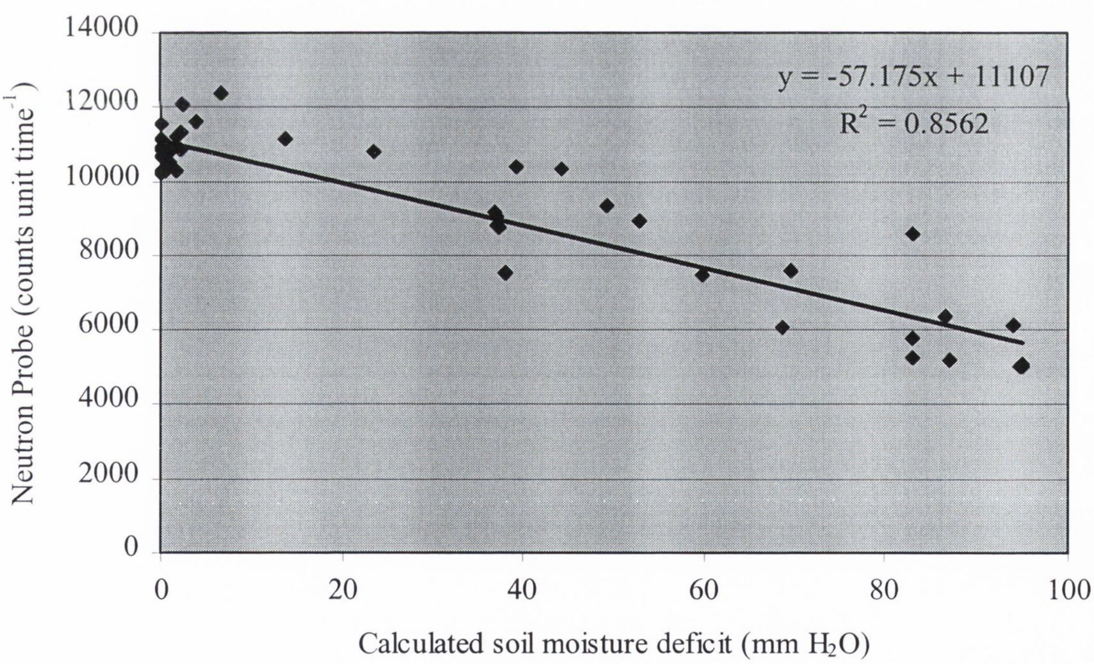


Figure 4.8 Relationship between neutron probe soil moisture measurements in plot 16 at the 25 cm depth and calculated soil moisture deficit.

There was a highly significant relationship between neutron probe measurements at all depths and calculated soil moisture deficit. At the deeper depths of 100 and 140 cm, a time lag had to be included in the regression as the development of a smd takes time to affect the deeper subsoil. The relationship between soil moisture content measured at depths and calculated soil moisture deficit can be seen in Table 4.5.

Table 4.5 Regression analysis between observed soil moisture content and estimated smd. All R^2 values are highly significant ($P<0.001$) except where indicated ns (not significant). Numbers in bold are the strongest relationships at each depth.

		Lag time (weeks) between SMD and neutron probe				
Plot	Depth (cm)	0 weeks	-1 weeks	-2 weeks	-3 weeks	-4 weeks
16	25	**0.86**	0.85	0.69	0.49	0.36
	50	**0.89**	0.84	0.63	0.42	
	75	0.67	**0.84**	0.83	0.70	
	100	0.69	0.83	**0.88**	0.81	
	140	ns	0.33	**0.41**	0.40	0.29
3a	25	**0.86**	0.73	0.52	0.36	
	50	**0.83**	0.81	0.63	0.45	
	75	0.69	0.73	**0.84**	0.69	
	100	0.54	0.82	**0.83**	0.82	
	140	0.32	0.50	0.68	0.77	**0.79**
7	25	**0.85**	0.77	0.60	0.45	
	50	**0.88**	0.85	0.67	0.47	
	75	0.60	0.51	**0.71**	0.59	
	100	0.35	**0.72**	0.61	0.59	

4.6 Herbage Production

The model developed by Brereton *et al.* (1982, 1987) which was used to calculate soil moisture deficit also estimated grass dry matter (DM) production and this is currently used for forecasting by Met Eireann. The grass production model is based on the principle that fractional depression of crop growth in drought conditions is proportional to the fractional depression of the evapotranspiration which is based on observations in perennial ryegrass dominant swards in Ireland.

The growth of grass is important regarding the potential uptake of N by the growing grass and for relating timing of fertiliser application to potential grass growth.

During 1994, predicted peak grass growth occurred between the end of April and mid-June. The highest predicted growth rate was during week 24 when there was 87 kg DM ha^{-1} day^{-1} (Appendix G). After this week the growth rate initially decreased very rapidly and then decreased less rapidly. The reason for the rapid decrease after week 24 was the increase in soil moisture deficit to above 50 mm (Appendix C2).

Simulated grass DM production during 1995 peaked from the beginning of May to the end of June. Peak DM production was estimated to be >90 kg DM ha^{-1} day^{-1}. The grass production peak for this year was projected to be broader than for other years, but also was more variable than other years. Once again DM production decreased as the soil moisture deficit increased.

4.7 Subsurface movement of soil water

4.7.1 Introduction

A tracing experiment using Br^- was designed to estimate the rate of movement through the unsaturated soil and quaternary deposits of an anion applied to the soil surface. The experiment was conducted in January 1996 at a time of maximum drainage and the experiment is detailed in this section. The groundwater was also monitored for the applied Br^- to ascertain a travel time from soil surface to the groundwater of a conservative anion, these results are presented in section 5.6.3.

4.7.2 Bromide natural occurrence in soils and use as a tracer

Bromide has been used by many workers to simulate nitrate movement through soils. Smith and Davis, (1974) showed that nitrate movement was identical to bromide (Br^-) movement through subsoils but was variable in top soils due to the effects of microbial activity on the nitrate ion. In a simultaneous tracing experiment on irrigated plots, nitrate and bromide travel times and peak amplitude were identical (Everts *et al.*, 1989). Soil bromide concentrations are typically low although values maybe be found in the range 0.3 to 852 mg kg^{-1} (Maw and Kempton, 1982; Flury and Papritz, 1993) with higher concentrations reported for soils closer to the sea. In the UK Wilkins (1978) reports soil Br^- concentrations from 30 to 73 mg kg^{-1}. Although data on Br^- content of soils is scarce Flury and Papritz, (1993) suggest a typical value of ~1 mg Br^- kg^{-1}.

Br^- is not a totally conservative tracer as Schnabel *et al.* (1995) reported that some up-take by ryegrass (*Lolium perenne* L.) occurred, ranging from 1.7 to 18.2 kg ha^{-1} with an average of 6.2 kg ha^{-1}. A well drained soil should have significantly higher Br^- uptake rates compared to a poorly drained soil. Owens *et al.* (1985) reported that 32% of the Br^- applied to orchard grass was taken up, the uptake of Br^- being similar to the uptake of N. At the time of maximum growth significantly more Br^- is taken up compared to periods of low growth. Kessavalou *et al.* (1996) also found Br^- uptake in corn to be similar to nitrate in that 27% and 23% of applied Br^- and N were taken up, respectively. Br^- is generally non-toxic at low concentrations, although in one experiment cows were killed after eating grass which had recently received 168 kg Br^- ha^{-1} (Owens *et al.*, 1985). A review of Br^- occurrence in groundwater is presented in section 5.6.2.

4.7.3 *Methodology*

At the beginning of January 1996 background samples were taken of the soil solution, at different depth as described in section 6.5.2, in plots 12 and 5, which contain boreholes 1 and 2, respectively (see Figure 2.7 for plot and borehole locations). These sites were also selected to examine groundwater flow direction.

On 16/1/96, KBr was applied in plots 12 and 5. A grid, 100 m^2, was marked out on the soil surface at each borehole, with the borehole in the centre of the grid. The grid was subdivided into 4 m^2 blocks (Plate 4.9); each block, with the exception of the block containing the borehole, had 2 l of deionised water containing 200 g KBr spread evenly by hand over it giving a total of 5 kg KBr on the 96 m^{-2} grid i.e., 528 kg ha^{-1} or 349.5 kg Br^{--} ha^{-1}. The solution was applied evenly using a 4 l watering can with a T-bar attached to the outlet to ensure even irrigation of the Br^- solution. The soil solution was sampled weekly at each site from 10 January to 27 April 1996.

Bromide concentration in the soil solution was determined in the Environmental Sciences Unit, Trinity College Dublin using ion chromatography with a Dionex ion chromatograph.

4.7.4 *Results*

The rate of Br^- application of 349.5 kg Br^- ha^{-1} was very high to counteract dilution of the tracer in the groundwater. It should be born in mind that Owens *et al.* (1985) applied 168 kg Br^- ha^{-1} and 19 cows died after grazing the plot two weeks after Br^- application. Cows did not graze the area used in this study for 8 weeks after Br^- application and no mortalities occurred.

When the Br^- was applied the soil moisture was at field capacity as indicated by the calculated soil moisture deficit of zero in Appendixes C.4 and D. During the experimental period, 16 January to 27 April 1996, 12 of the 15 weeks had effective rainfall events. There was a total of 517.2 mm rainfall during the experimental period and of this total, it was estimated that there was 445 mm of effective rainfall. The rainfall during the experimental period was above the 30-year average (1961-90) of 342 mm from January to April 1996 (Table 4.6).

Table 4.6 Monthly calculated effective rainfall, total rainfall and the 30-year average monthly rainfall (Fitzgerald and Forrestal, 1996).

Month	1996 Effective Rainfall (mm)	1996 Total Rainfall (mm)	30 Year Average (mm)
January	177.1	185.8	117.0
February	101.8	117.8	87.0
March	122.3	148.6	79.0
April	44.0	65.0	59.0

The Br^- concentration of soil solution sampled by ceramic cups at 0.5, 1 and 1.5 m depths are shown in Figure 4.9. The background concentrations of Br^- were low , i.e. <1 mg l^{-1}. In plot 12, the Br^- concentration in the soil solution began to increase on day 36 and peaked on day 83, 67 days after Br^- application. The peak Br^- concentration in the soil solution at the 0.5 m depth occurred after the second weekly effective rainfall event >75 mm with 247.5 mm of cumulative drainage since the Br^- was first applied. The Br^- concentration in the soil solution decreased to < 1 mg l^{-1} by day 118 when sampling ceased.

In plot 5, the soil solution Br^- breakthrough at 0.5 m depth occurred faster than in plot 12. The Br^- concentration in the soil solution began to increase on day 24, and peaked on day 50, 34 days after surface Br^- application. The peak Br^- concentration shown may not be the true peak in Br^- concentration as no sample was collected during the following 30 days following the observed peak concentration. The peak soil solution Br^- concentration at 0.5 m in plot 5 occurred after the first weekly effective rainfall >75 mm and after 128.5 mm of cumulative effective rainfall.

The Br^- concentrations in the soil solution at 1 and 1.5 m deep began to increase simultaneously on day 43, 27 days after Br^- application. The concentrations at the 1.0 and 1.5 m depths were very similar and peaked on day 81, 65 days after the experiment was started. The peak Br^- concentration in the soil solution at the 1 m depth was only 5 mg l^{-1} greater than

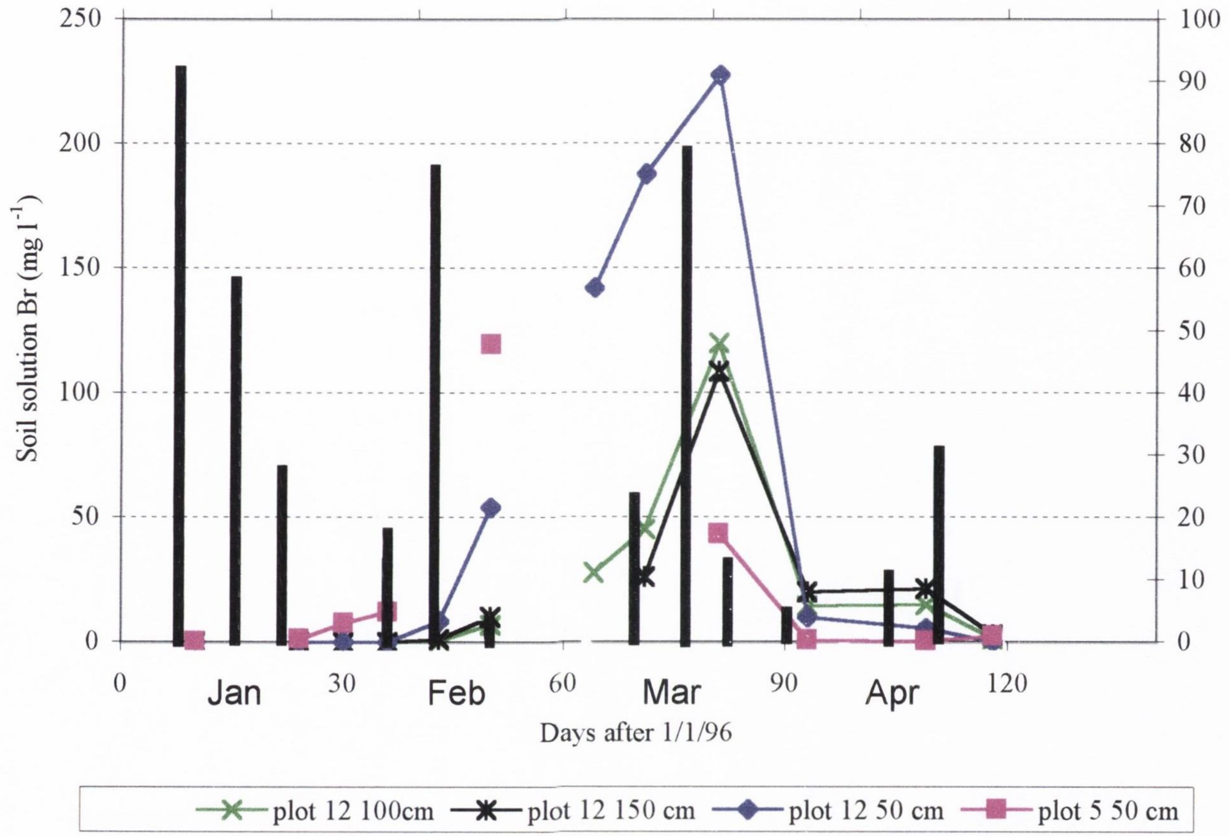


Figure 4.9 Temporal variation of soil solution Br^- concentrations (at various depths), vertical bars are calculated effective rainfall amounts (mm $week^{-1}$) which is the secondary Y axis, x axis series are plot no., sample depth.

the peak at the 1.5 m depth. At both sampling depths the Br^- concentrations in the soil solution decreased to 1 mg l^{-1} or less when sampling ceased on day 118.

From the Br^- tracing experiment through the unsaturated zone in plots 12 and 5 it is possible to see a relatively fast movement of the applied Br^- past the soil solution sampling points in each plot. Dils (1997) observed rapid movement, within 17 hours, of applied Br^- from the soil surface to the groundwater at a depth of 150 cm, which was attributed to preferential flow.

The Br^- tracer also indicates the risk of applied N being leached as NO_3^- during the period of the tracing experiment. Late January is a time of recommended Urea application, which upon hydrolysis and subsequent nitrification, would be at risk of being leached through the unsaturated zone.

The results of the groundwater monitoring for Br^- can be seen in section 5.2.3.

4.8 General discussion

For 1993 and 1994 leaching began in the first weeks of September and ceased during the following April. In 1995 leaching commenced in mid October and ceased in the following mid-February, after which date there was only one further effective rainfall event.

Thus application of nutrients during the period from September until April could be at risk to leaching for the years 1993 and 1994. The most critical period would appear to be from September until the end of February of the next year. The month of March would probably have a low NO_3-N leaching risk due to the increase in herbage dry-matter production occurring, because growing plants would be using significant quantities of N during this month.

CHAPTER 5 BEDROCK PHYSICAL PROPERTIES AND HYDROGEOLOGY

5.1 Introduction to the Bedrock Physical Properties

This chapter describes the physical characteristics of the bedrock which includes both unsaturated and saturated bedrock although much focus is given to the saturated bedrock. This chapter presents a revised bedrock geology of the study farm based on two new boreholes drilled during the project. Water table fluctuations are presented for the duration of the study and two water table maps are presented drawn on data collected during 1995. Pumping tests carried out on each borehole are described and analysed. Tracing experiments are presented which aimed to show groundwater flow direction beneath the farm.

5.2 Bedrock Geology

5.2.1 Introduction to the Borehole Geology

The bedrock beneath the study farm consists of Lower Carboniferous Limestone of the Ballysteen Formation which is a sequence of medium to dark grey , argillaceous, bioclastic limestone with shaley partings and inter beds. Ballysteen limestone can be subdivided into two distinct units; a lower unit consisting of a thin, basal sequence of fairly argillaceous packstones with argillite interbeds, overlain by relatively homogeneous, thicker-bedded, medium to dark grey, coarse-grained crinoidal packstones and grainstones. The upper part of the lower unit has mud present in fine whisps (c. 2 mm) and occasional thin interbeds (generally < 20 mm). The lower unit has an estimated thickness of c. 30 m.

The upper unit, which constitutes the major part of the Ballysteen Formation, consists of extremely argillaceous, dark grey to black, fine coarse-grained crinoidal calcarenites/packstones. Mud is present both as thick (>0.20 m) beds and as wisps and wispy interbeds. The mud content can reach up to 65-70%. Chert is present throughout the succession as irregular nodules and thick/thin nodular interbeds.

The Ballysteen Limestone Formation is underlain by the Ringmoylan Formation, which is a distinctive sequence of argillaceous limestones and dark shales. In the study area, the Ringmoylan Formation consists, predominantly, of interbedded, thin bioclastic limestones and dark grey to black, thick calcareous mudrocks. The limestones are dominantly grainstones and are commonly reddened in the lower part of the formation. They generally make up less than 35% of the sequence. The base of the formation is identified by the incoming of significant quantities of calcareous mudrocks. In the study area the top of the Ringmoylan Formation is not seen and is taken at the base of the overlying Ballyvergin Formation, which forms a distinctive, non calcareous, green-grey, laminated mudstone-siltstone unit which has been recognised as a widespread isochronous horizon (Clayton *et al.*, 1980). The estimated thickness of the Ringmoylan Formation is c. 45 m. Shearley (1988) subdivides the Ringmoylan Formation, in the study area, into a lower Air Hill Member (c. 11m) and an upper Ballyderown Farm Member (c. 35m). The Air Hill Member is described as consisting of calcareous, sand streaked, dark mudstones (with sandy laminae up to 10 mm), calcareous sandstones and siltstones and sandy calcarenites. Mudstones generally make up 40-60 % of the sequence.

The base of the member is taken as the top of a thin (0.75 m) resistate pebble conglomerate which occurs at the top of the Araglin Member of the Ballyderown Formation. The top of the member is taken as the highest sandstone bed of the sequence.

The Ballyderown Formation as defined by Shearley (1988) consists of yellowish-grey sandstones, which are commonly calcareous, thin interbedded mudstones and conglomerates. The formation is subdivided into two members; a lower coolalisheen Member, which is dominated by heterolithic sandstones and intraformational conglomerates; and an upper Araglin Member which is dominated by heterolithic/calcareous sandstones.

5.2.2 Preexisting Site Boreholes

The bedrock geology beneath the study farm was described by Shearley (1988) Lower

Carboniferous Limestone of the Ballysteen Formation which is a sequence of medium to dark grey , argillaceous, bioclastic limestone with shaley partings and inter beds. Boreholes 1 and 2 were drilled in Ballysteen limestone. Ringmoylan Formation, which underlies the Ballysteen Formation, is a distinctive sequence of argillaceous limestones and dark shales. The Ballyderown Formation as defined by Shearley (1988) consists of yellowish-grey sandstones, which are commonly calcareous, thin interbedded mudstones and conglomerates.

Borehole 3 was drilled through 18 metres of Ringmoylan shale and into 23 m of Ballyderown sandstone.

The detailed geology of the previous boreholes drilled on Ballyderown during the 1980's is presented here.

Borehole 1 38.25 m deep

The bedrock is overlain by Quaternary deposits <1 m thick. In borehole 1, 32 m of core is penetrated: c. 24 m of fairly thin-bedded, fine to medium grained, cherty calcarenites with shaley interbeds and laminae (shale content is generally <30%), which overlie a sequence (c. 8 m) of thin, highly argillaceous, cherty calcarenites and thick interbedded shales (with shale content up to 60%). These are assigned to the lower unit of the Ballysteen Limestone Formation, and are richly fossiliferous, containing crinoids, Bryozoa, solitary rugose corals, Michelonia, gastropods and large brachiopods.

Borehole 2 48 m deep

Penetrated the lower part of the Ballysteen Limestone Formation consisting of fossiliferous packstones and wackestones with thin shales. It becomes more coarsely fossiliferous downhole and the percentage argillite increases.

At a depth of 39 m a distinctive thinly laminated greenish-grey silty shale unit (c. 2 m) was penetrated.

Borehole 3 41.7 m deep

The bedrock was overlain by 4.5 m of loose gravel The entire Air Hill Member is exposed (c. 11.2 m). The top 6.75 m constitutes the lowest lithofacies of the predominantly mud-dominated sequence consisting of interbedded fine-grained sandstones and mudrocks with argillite content varying between 10-60% and forming discrete bands. The sandstones are green-grey, calcareous, and become highly bioturbated up section. The next 1.5 m consists of sand-streaked mudstones with thin, calcareous bands up to 10 mm thick. The bottom 3 m of the member consists of fossiliferous sandstones with interbedded siltstones and dark mudstones (25%).

To gain a better understanding of the bedrock geology of Ballyderown two new boreholes were drilled in late 1993 to add to the three existing monitoring wells which were installed during the 1980's.

To further investigate the extent of the Ringmoylan shale which forms an anticline which plunges from east to west and through which a fault was identified (Shearley, 1988) it was decided to drill a borehole (borehole 4) to the west of borehole 3. Borehole 4 was also located in this position to help clarify the anomalously high water levels which were observed in borehole 3 as found by McGuire (1991). A second new borehole location (borehole 5) was located in the north west corner of the farm to help improve the hydrogeological conceptual model of the farm.

5.2.3 New Borehole Methodology

The two additional boreholes 4 and 5 were drilled during November and December 1993 by the Geological Survey of Ireland (GSI) bedrock coring rig. The boreholes were drilled and wells installed in the same manner as the previous three monitoring wells on the farm (Figure 5.1). Two inch core samples of bedrock were recovered for the total bedrock depth and were returned to the GSI for cataloguing and storage awaiting formation identification and logging.

The bedrock cores from the two new boreholes (4 and 5) were logged in the GSI by the author

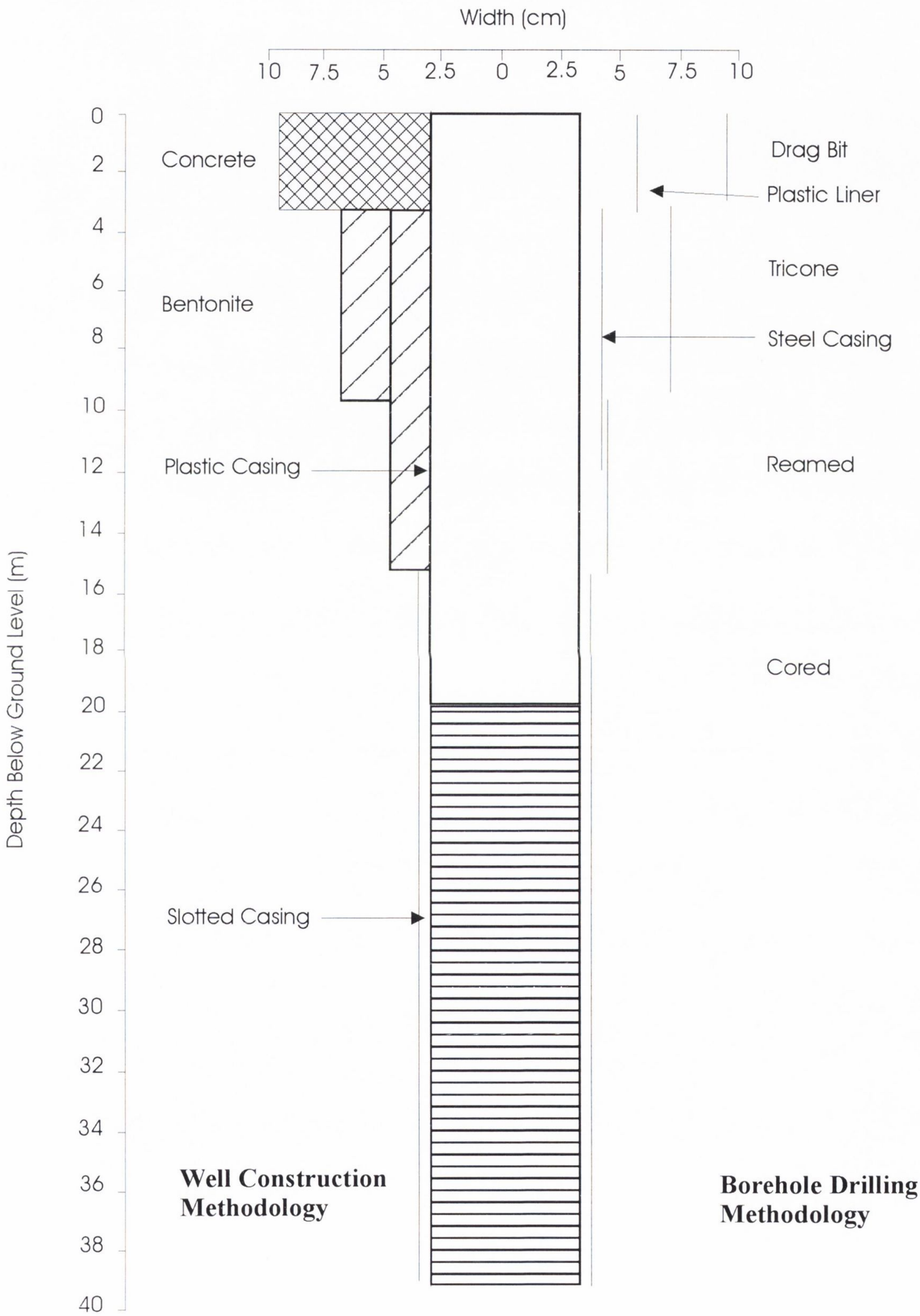


Figure 5.1 Borehole drilling methodology and monitoring well construction.

with assistance of a GSI bedrock geologist, David Smith. The three existing boreholes bedrock cores from Ballyderown were also examined to aid formation comparison with boreholes 4 and 5.

5.2.4 New Borehole Geology

Borehole 4 (93-39)

This borehole was drilled in November 1993. The overlying Quaternary deposits were 2.6 m thick. The total depth of the borehole was 40.3 m. The first 10 metres (2.6 to 13.8 m) penetrated lower Ballysteen limestone (bottom five cores in Plate 5.1) which was a mid to dark grey limestone which is well sorted in places with thin shale interbeds which increased with depth (Detailed logs can be seen in Appendix H.1 and H.2). The limestone was solutionally enlarged at the limestone/shale contacts, which was most common in the top 6 metres of the bedrock. The size of the solutional openings is unclear as the bedrock core was separated when there was a solutional gap (an example from borehole 5 can be seen in Plate 5.4). Ringmoylan shale was found from 14 to 22 m depth. The Ringmoylan shale was characterised by thin calcareous shales which were bioturbated in places and showed evidence of tectonic movement. Coarse limestones were interbedded with the shale. The frequency of shale interbeds increased down the hole which culminated in a thick shale bed 1.5 m thick which was fragmented and had calcite infillings in fissures due to the proximity of a fault. No rock was returned from 22 to 24.7 m (as seen by the fragmented core in Plate 5.2 between 19.8 m and 25.8 m); this is thought to be due to the borehole penetrating through a fault zone. Further evidence of the faulting was observed in the Ringmoylan shale where there were indications of tectonic movement. The Ballyderown sandstone was penetrated from 24.7 to 40.3 m which was the end of the borehole (as seen in plate 5.2 above the 25.8 m tag). The Ballyderown sandstone was a massive light grey sandstone in places with fine shale interbeds.

Borehole 5 (93-40)

This borehole was drilled in November 1993. The Quaternary deposits overlying the bedrock were 3.5 m deep. The total depth of the borehole was 45 m deep. The borehole penetrated the middle Ballysteen Limestone Formation which consisted of coarse limestones/packstones with shaley partings and thin shale interbeds (Plate 5.3 and 5.4).

The limestone-shale bedding contacts appear to be solutionally enlarged for the full extent of the core. The degree of enlargement is difficult to gauge as the core is fragmented due to the solutional enlargement. The top 10 m of the core appears to have significant solutional enlargement as seen in Plate 5.3. Further solution is evident at 26 m below ground level, where the water table is located (Plate 5.5).

A summary of the five boreholes on Ballyderown can be seen in Figure 5.2 which includes the water table variation, expressed in m AOD, in each borehole as observed from 1994 to 1996.

5.2.5 Farm Bedrock Geology Map

The bedrock geology map of Ballyderown constructed by Sherley (1988) was revised, by the author with assistance from Professor G. Sevastopulo (Trinity College Dublin) and D. Smith (Geological Survey of Ireland), to include the additional geological information from boreholes 4 and 5 (Figure 5.3). The fault highlighted on Sherley's (1988) map was revised to run through borehole 4. The fault which was located to the south of Borehole 3 on Sherley's geology map was moved to the north of borehole 3 in the revised geology map which placed borehole 3 on the south limb of the anticline. The northern limb of the Ringmoylan shale anticline was extended slightly further across the farm than it was on Sherley's geology map due to the occurrence of Ringmoylan Shale in borehole 4 from 14 to 22 m below ground level.

5.3 Water table variation and mapping

5.3.1 Introduction

Water levels were recorded weekly in the five monitoring boreholes on the farm as part of the regular sampling regime. In this section the water levels from each borehole are presented.

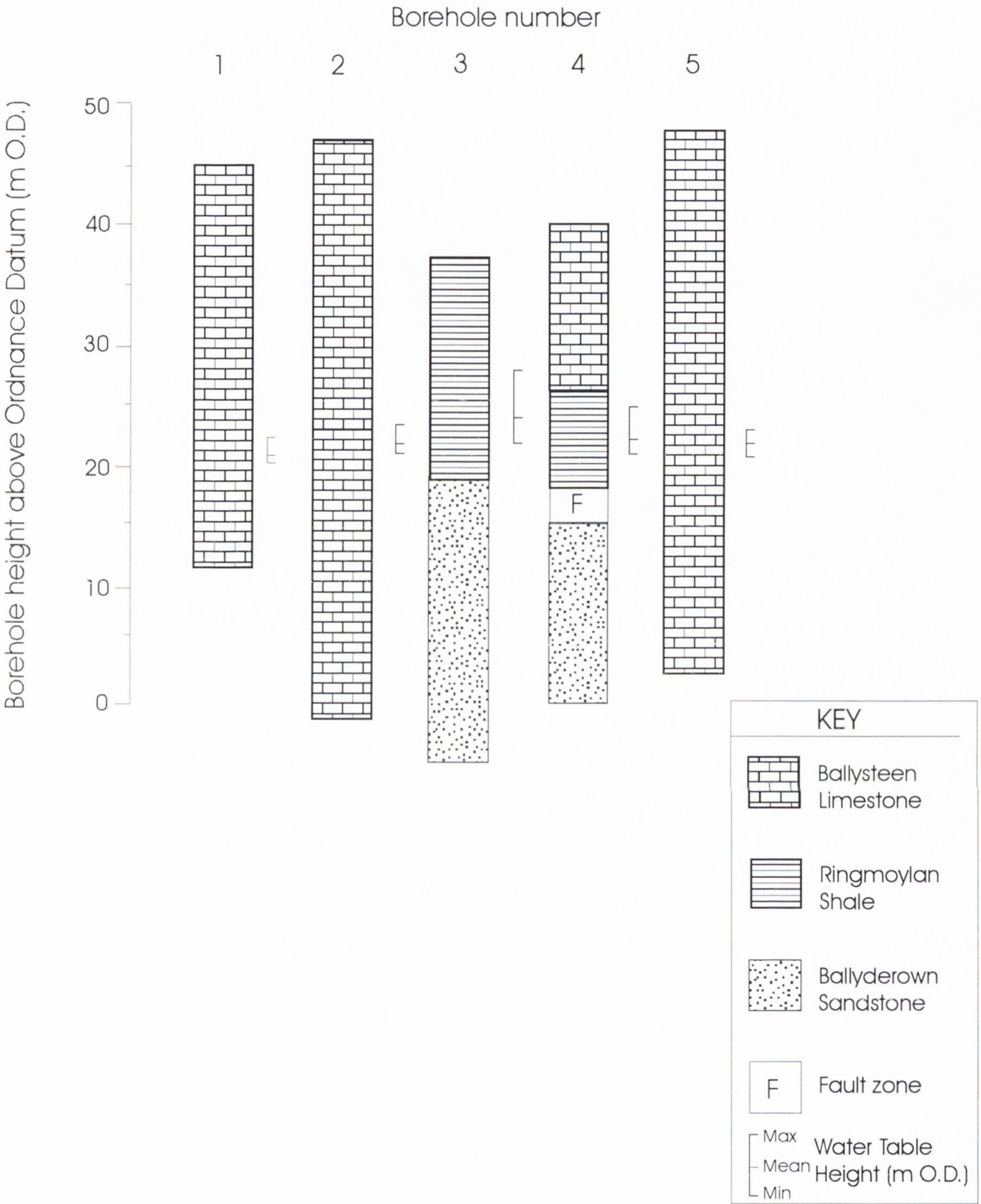


Figure 5.2 Summary geologies of boreholes 1 to 5. With water table heights indicated for max, mean and minimum observations (m O.D.)

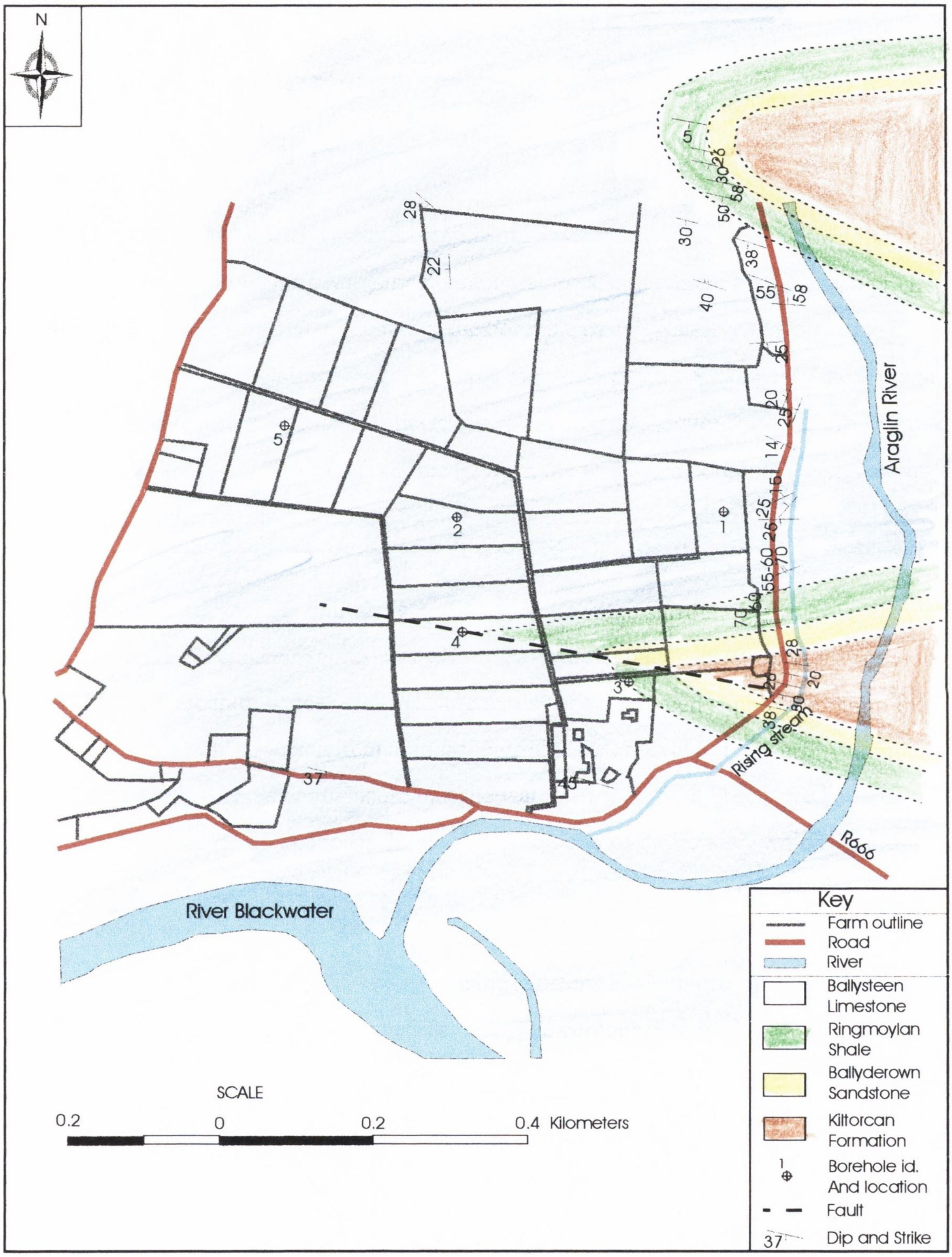


Figure 5.3 Bedrock geology map of Ballyderown farm and surrounding area

Water table fluctuations for the five monitoring wells on the farm are presented and compared to determine the relationships between each borehole. Two water table maps are then presented based on water table measurements carried out during 1995.

5.3.2 Methodology

Water levels in each borehole were measured using a water level indicator with a 50 m tape graduated every 10 mm with a audio signal when the probe entered the standing water (from ELE international, EE 450-010). The top of the borehole casing was levelled to metres above Ordnance Datum (m O.D.) with assistance from Teagasc surveying personnel (A topographic map was constructed from level data collecting while surveying, Figure 5.4). The dipped water level in each borehole could then be subtracted from the top of the borehole casing height to express groundwater levels as m O.D.

Due to the limited number of monitoring wells on the farm the surrounding river levels were also levelled and the canteen supply was also used to assist in construction of a water table map. To ensure accurate water level measurements for the canteen supply the pump in the borehole was turned off over night enabling the groundwater level to recover. A number of measurements were then taken to ensure that the water level had fully recovered and that the water level measurement was not influenced by the cone of depression which would have developed around this production well.

Water table maps were constructed digitally using Surfer 32 which drew contour lines using kriging which is a geostatistical gridding method. The contours produced were then overlain on the area base map using Corel draw 8.

5.3.3 Water Table Temporal Variation

A summary of the results of water table measurements carried out between 1/1/94 and 2/4/96 can be seen in Table 5.1.

Table 5.1 Summary of water table fluctuations (m O.D.) in boreholes 1 to 5 between 1/1/94 and 2/4/96.

Statistical summary	Borehole number 1	2	3	4	5
Mean	20.79	21.25	23.72	21.93	21.52
Median	20.89	21.29	24.13	21.85	21.35
Maximum	22.04	23.38	27.51	24.55	23.79
Minimum	20.30	20.65	21.48	20.80	20.60
Range	1.74	2.73	6.03	3.75	3.19
Borehole casing altitude	44.21	47.35	36.69	39.94	48.24

The mean water table height in the boreholes varied from 20.79 (borehole 1) to 23.72 (borehole 3) m O.D. The range (the difference between the maximum and minimum) in water table fluctuation in a single borehole ranged from 1.74 m (borehole 1) to 6.03 m (borehole 3). In summary boreholes 1, 2, 4 and 5 had similar mean water table heights of 20.79 to 21.93 m O.D., while borehole 3 had a higher mean water table height of 23.72. Borehole 5 is located 48.24 m O.D. and has a mean water table height of 21.52 m yet borehole 3 and 4 had mean water tables higher than borehole 5 although they are located topographically lower at 36.69 and 39.94 m O.D..

Temporal variation of the water levels in boreholes 1 to 5 from 1/1/94 until 2/4/96 can be seen in Figure 5.5.

Aquifer recharge timing, as indicated by increased water table heights, could be observed during 1994 and 1995. Aquifer recharge from 1990 to 1993 could also be assessed based on monthly monitoring conducted by Teagasc. The date of the first increase in water table levels after the summer period can be seen in Table 5.2.

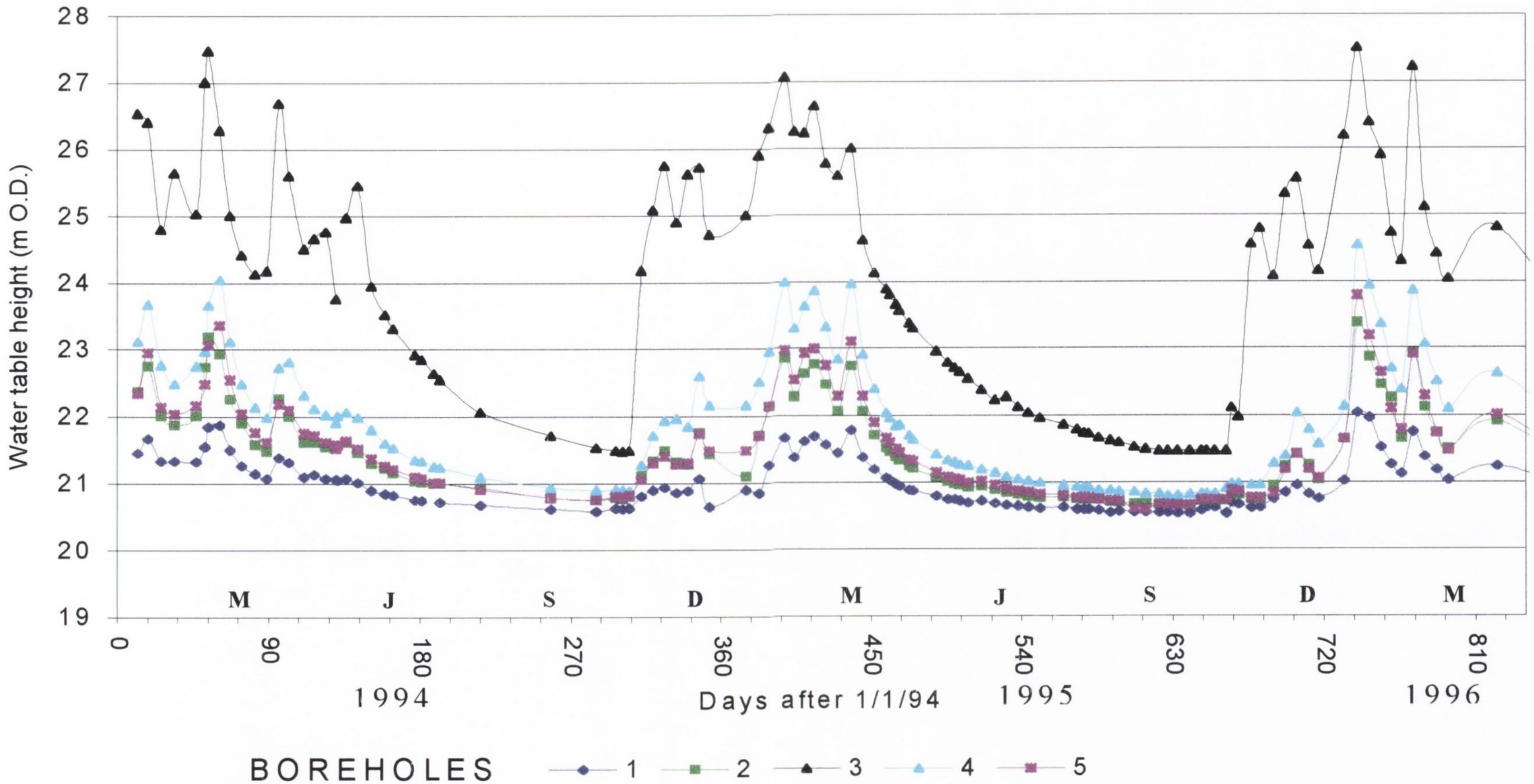


Figure 5.5 Water table temporal variation observed in boreholes 1 to 5 (1/1/94 to 8/4/96).

Table 5.2 Date of first observed increase of water table height after the lowest observed height (start of recharge) from 1990 to 1995 in boreholes 1, 2 and 3.

	Borehole		
Year	1	2	3
1990	7/7/90	7/7/90	11/11/90
1991	8/10/91	8/10/91	1/11/91
1992	5/9/92	5/9/92	4/10/92
1993	18/9/93	18/9/93	18/9/93
1994	8/11/94 (day 312)	8/11/94 (day 312)	8/11/94 (day 312)
1995	8/11/95 (day 677)	8/11/95 (day 677)	8/11/95 (day 677)

From 1990 to 1992, inclusive, the water table heights in boreholes 1 and 2 increased before borehole 3, indicating a faster travel time of recharge from the soil surface to groundwater than in borehole 3. However, from 1993 to 1995 inclusive, the water table in borehole 3 increased on the same date as boreholes 1 and 2 which tends to contradict the findings from 1990 to 1992. Boreholes 4 and 5 also increased on 8/11/94 and 8/11/95 and are not presented in Table 5.2.

To compare the water table fluctuations in each borehole the temporal variation of water levels in each borehole were compared using regression analysis, a summary of which can be seen in Table 5.3.

Table 5.3 Regression analysis between all boreholes water table height temporal variation (all R^2 values are significant at the $P<0.0001$).

Borehole	Borehole Number				
Number	1	2	3	4	5
1	1				
2	0.964	1			
3	0.686	0.755	1		
4	0.886	0.924	0.795	1	
5	0.970	0.978	0.722	0.922	1

From this comparison of the temporal variation of water table heights in each borehole using regression analysis, it is can be seen that borehole 3 had significantly lower R^2 values than the other boreholes. Regressions between borehole 3 and boreholes 1, 2, 4 and 5 had R^2 values ranging from 0.686 to 0.795 whereas boreholes 1, 2, 4 and 5 had R^2 values ranging from 0.886 to 0.970. Statistically borehole 4 had temporal variation significantly similar to boreholes 2 and 5 (R^2=0.964 and 0.970, respectively) and the relationship with borehole 3 was less strong (R^2=0.795).

Comparison of the temporal variation of water heights in each borehole indicates that borehole 3 has a different water table fluctuation than the other boreholes. Although all the boreholes appear to respond similarly as they all increase and decrease at the same time, the extent to which they vary is different in each borehole.

Borehole 3 increases and decreases the most such as during early aquifer recharge each year on days 312 (8/11/94) and 677 (8/11/95).

Boreholes 2 and 5 had very similar water table heights and temporal fluctuations as they are located at similar topographic heights of 47.35 and 48.24 m O.D., a difference of 0.89 m. Borehole 1 has a the lowest water table height, it is located at 44.21 m O.D. and thus is located at a lower altitude than boreholes 2 and 5 but higher than 3 and 4.

Boreholes 3 and 4 had consistently higher water tables than boreholes 1 and 2 although they are topographically lower. The temporal variation and overall water table height in borehole 4 appears to be more similar to boreholes 2 and 5 than borehole 3. Thus the Ballysteen limestone in borehole 4 appears to be influencing it to a greater degree than the Ringmoylan shale which is located in both 3 and 4.

5.3.4 Water Table Map of Ballyderown

Water table maps were constructed for two different occasions from water table measurements in the five monitoring wells on site. These measurements were supplemented using the canteen supply and the Araglin, the Funshion and the Blackwater rivers and the rising stream using the assumption that the rivers intersected the water table. Measurements of the water height in m O.D. were carried out on 16/8/95 and 9/11/95. The maps are presented in Figures 5.6 and 5.7

From Figures 5.6 and 5.7 it is possible to observe groundwater flows from the NNE to SSW, (assuming that flow occurs perpendicular to the piezometric contours). In August 1995 there was a maximum observed piezometric contour of 21 m O.D. which was located to the North of Ballyderown. The minimum piezometric contour was 19 m O.D. which was located to the South of Ballyderown, near the Blackwater river. The elevated water table heights in boreholes 3 and 4 were interpreted as reflecting the lower permeability of the bedrocks through which these boreholes were drilled. This is represented by a slight mound around boreholes 3 and 4 which occurred both in August and November 1995.

5.4 Pumping Tests

5.4.1 Pump Test Introduction

Pump testing is a traditional groundwater hydrology technique used to determine reliable estimates of hydraulic characteristics of the geological formations through which the groundwater is moving. Pumping tests have proved to be one of the most effective ways of obtaining such values as specific capacity (SC), transmissivity (T) and specific yield (S). Transmissivity is a product of permeability (K) and saturated thickness of the aquifer and is defined as the rate of flow under a unit of hydraulic gradient through a cross-section of unit width over the whole saturated thickness of an aquifer. Specific capacity (S.C.) is a term used by well drillers to indicate the productivity of a well (Freeze and Cherry, 1979; Domenico and Schwartz, 1998). Dividing the pumping rate by the total drawdown in a well gives the S.C. normally for a given day.

It is realised that carrying out pump tests on narrow diameter boreholes is very difficult and fraught with difficulties. Having taken this into account the tests which were carried out on these boreholes were trial pump tests but will be referred to as pump tests although caution is warranted in the interpretation of the results.

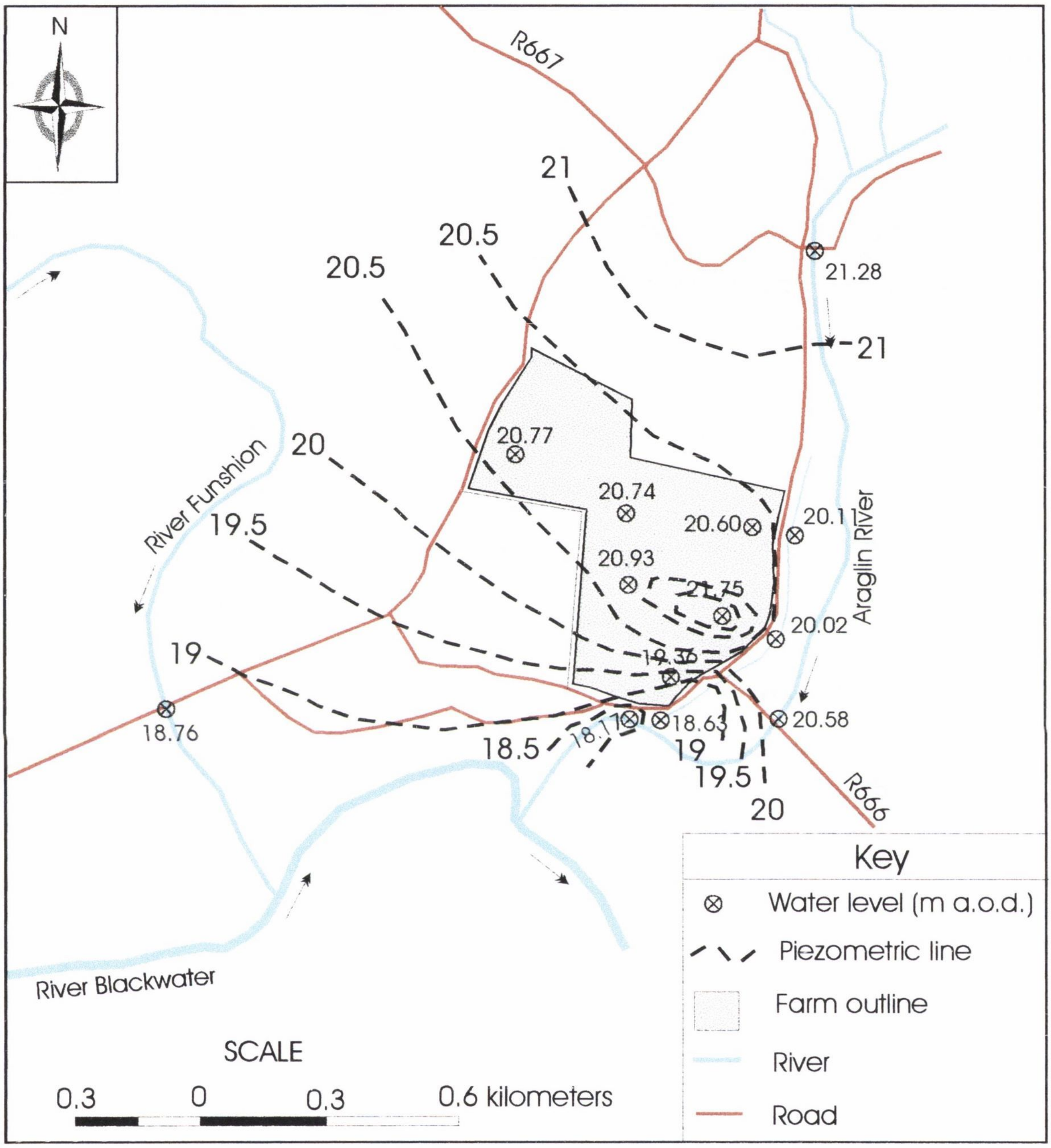


Figure 5.6 Water table map constructed from groundwater and surface water levels (m a.o.d.) on 16/08/95.

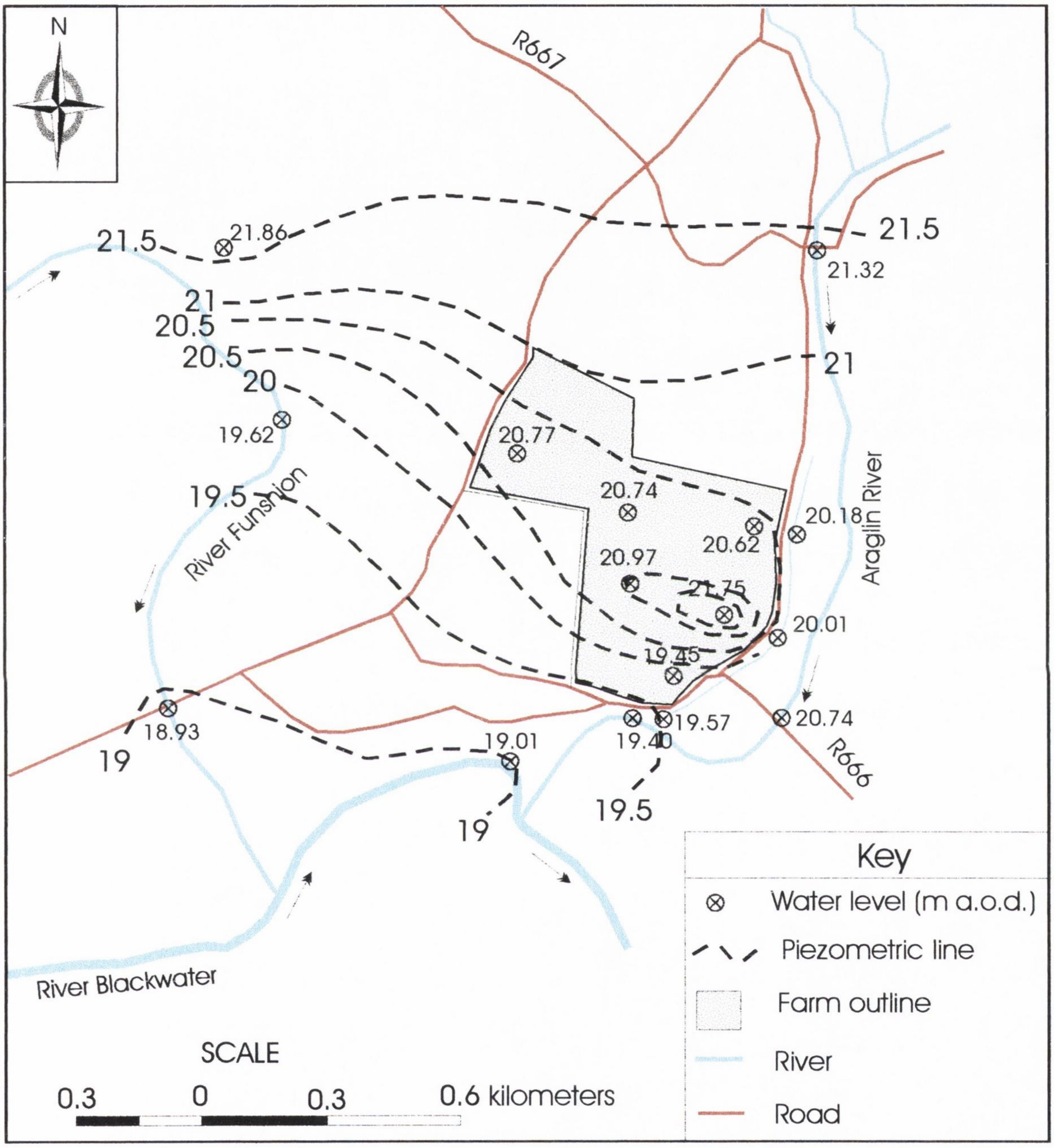


Figure 5.7 Water table map constructed from groundwater and surface water levels (m a.o.d.) on 9/11/95.

This section presents summaries of pumping tests carried out previously to the current study on the Ballyderown by the Geological Survey of Ireland. Pumping test data for boreholes 4 and 5 from pumping tests carried out by the author in conjunction with the GSI are also presented and compared to the existing boreholes 1, 2 and 3.

5.4.2 Drawdown Observation Methodology

Trial pumping tests were carried out using a Seba hydrometrie, a pneumatic-submersible pump for sampling groundwater from 5 cm boreholes which was on loan from the GSI. The pump specifications are 4.5 cm diameter, 650 mm length, 6 kg weight, constructed of brass and produces head up to 100 m and had a maximum pumping rate of 7 litres per minute (10 m^3 per day). A portable petrol-engine driven compressor is used to power the pump capable of a 10 bar suction.

Standing water levels in all boreholes were determined and recorded before pumping tests were carried out in a specific borehole. The pump was lowered down the borehole to a depth of 10 m below the standing water level. Water level readings were recorded in the pumping well every 30 seconds for the first 5 minutes of pumping after which the measurement time was extended. The other boreholes, 1, 2, 3 and either 4 or 5 depending on which borehole the pumping test was being conducted in, were dipped every 10 minutes after the start of the pumping test. Boreholes were pumped for a total of 120 minutes after which the pump was turned off and recovery of the water table in the borehole was monitored.

Pump tests were carried out by the author on boreholes 4 and 5 in 1994. The GSI carried out numerous pump tests on boreholes 1, 2 and 3 in 1985, 1987, 1988 and 1990 which are also presented with permission of the G.S.I. The same methodology was used for each pump test although there was some variation in the total pumping time.

Due to the short pumping times in this study the drawdown over 100 minutes was used for borehole comparisons divided by the estimated discharge (m^3 day^{-1}) to produce the 100 min S.C.

Transmissivity was estimated for pumping and recovery cycles using the Jacob straight line method which can be applied to single-well constant discharge tests (Kruseman and de Ridder, 1994). Drawdown and recovery are plotted against time as a semilogarithmic graph with time expressed on the logarithmic x axis. In theory the curve becomes a straight line and the slope of the line drawn through the graph points over one log cycle is used to calculate transmissivity (T) in m^2 day^{-1} where Q is the discharge (m^3 day^{-1}) and ΔS is the slope of the straight line over one log cycle.

$$T = \frac{2.30Q}{4\pi\Delta S}$$

5.4.3 Pump Test Results and Discussion

Summary details of all trial pumping tests carried out on the farm can be found in Table 5.4 and 5.5.

Table 5.4 Trial pumping test details from Ballyderown.

Borehole Identity	Test Date	Pumping time (min)	S.W.L. m b.g.l.	Drawdown m	Mean Q m^3 day^{-1}	100 min S.C. (m^3 m^{-1} drawdown)
1	6/11/85	105		0.03	6.5	217
	4/12/85	300	23.01	0.02	6.5	325
	28/7/88	60	23.32	0.02	6.5	-
	15/5/90	100	23.60	0.015	5.4	360
2	11/3/87 AM	62	25.41	10.23	6.1	<1
	11/3/87 PM	150	25.41	4.71	6.1	1
	28/7/88	140	26.32	0.61	5.7	9
	16/5/90	120	26.57	0.42	5.2	12
3	28/7/88 #1	44	14.06	9.3	7	<1
	28/7/88 #2	150	14.06	9.11	5.8	<1
	16/5/90	120	13.59	6.35	5.2	<1
4	14/6/94	120	18.68	1.03	7.9	8
5	15/6/94	120	27.32	0.22	7.3	33

Summary of pumping tests carried out in boreholes 1, 2 and 3 on four occasions from 1985 to 1990 can be seen in Table 5.4. The ability of the aquifers intersected by each borehole to supply water maybe summarised by the 100 minute specific capacity (SC) for each pumping test, at each borehole.

Borehole 1 had the highest SC of >200 m^3 m^{-1} drawdown and borehole 3 had the lowest SC of <1 m^3 m^{-1} drawdown. At borehole 2, 4 and 5 observed SCs of 12, 8 and 33 m^3 m^{-1} drawdown which are significantly higher than observed SCs from borehole 3 but not as high yielding as borehole 1. Boreholes 1, 2, and 5 have SCs greater than 10 whereas boreholes 3 and 4, which are drilled into Ringmoylan shale and Ballyderown sandstones (see borehole geology summary, Figure 5.2), have SCs less than 10 indicating that they are poorer, less permeable aquifers than the three boreholes which are drilled into Ballysteen limestone. The limestone aquifer intersected by borehole 1 is high and the shale/sandstone aquifer at borehole 3 is extremely low.

The pumping tests from borehole 2 are interesting as the drawdown observed decreased from a high of 10.23 m in the initial pump test to less than 1 m during the third, fourth and fifth pump tests (Table 5.4). Borehole 2 developed whereby fissures which were blocked by drilling mud were opened up during the first two pump tests which were carried out on 11/3/87. The water during the first two pump tests was muddy, but the mud cleared after 35 minutes in the afternoon pumping test on 11/3/87. A second factor supporting the well development hypothesis is the fact that after the first two pump tests the water level in borehole decreased from 25.41 (b.g.l) to greater than 26 m for the pump tests in 1988, 1990, and 1994.

No transmissivity values were calculated for borehole 1 as during both pump tests in 1988 and 1990 the water level dropped 2 cm, after 30 seconds of pumping, and remained at this level for the duration of the pumping tests (Figure 5.8). The pumping rate used for the pump tests was less than the transmissivity of the aquifer at this point. No pumping test analysis could be carried out due to a constant water level being reached almost immediately after pumping began.

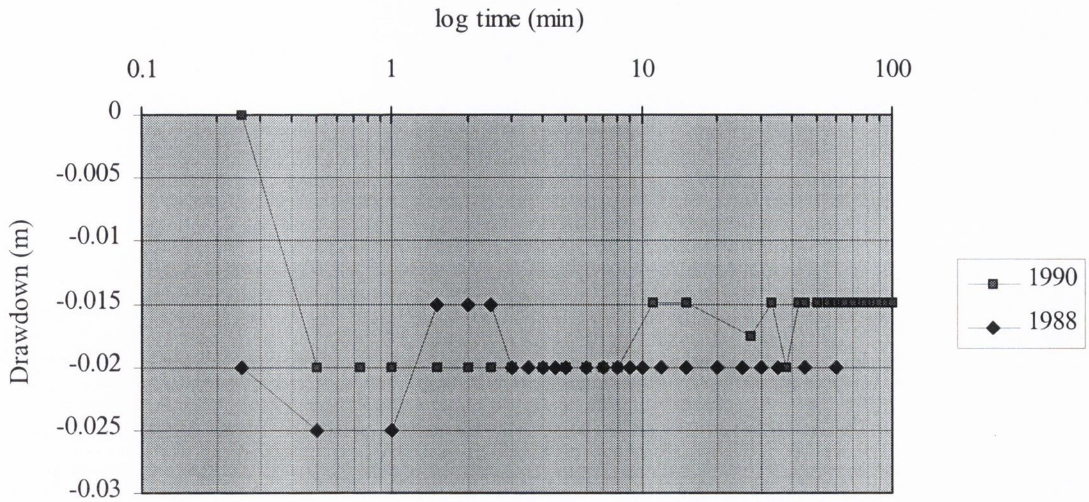


Figure 5.8 Draw down observations carried out in borehole 1 in 1988 (Q=6.5) and 1990 (Q=5.4).

In borehole 2 the pump tests carried out in 1988 and 1990 were used for determination of T, due to the well development during 1987, although in 1990 only the recovery was used due to variation of discharge during pumping causing water table fluctuation. Calculated T values varied between 17 and 95 m^2 day^{-1}.

The three pumping tests carried out in borehole 3 were all very similar. Generally three straight lines could be fitted to the drawdown and recovery graphs. During pumping the slope of the lines increased indicating the decreasing permeability of the aquifer over time. The SCs for all three pump tests were less than 1 m^3 m^{-1} drawdown and calculated transmissivity ranged from 0.1 to 1.5 m^2 day^{-1}. Thus the aquifer within which borehole 3 was located had an extremely low transmissivity.

The pump test carried out in 1994 at borehole 4 had a 100 min SC of 8 m^3 m^{-1} drawdown. Just before the pumping ceased at 120 minutes there was a decrease in the borehole water level of 3 cm after a period of static water levels. Continuation of the pump test after 120 minutes may have proved useful as this decrease towards the end of pumping may have been due to the dewatering of a permeable zone. The decrease in the water level indicates less permeable rocks were being dewatered towards the end of pumping. Three straight lines with different slopes were used to estimate T during pumping in borehole 4 (Figure 5.9). This is likely to be due to different storages in the karst limestone on site and not indicative of a larger regional scale.

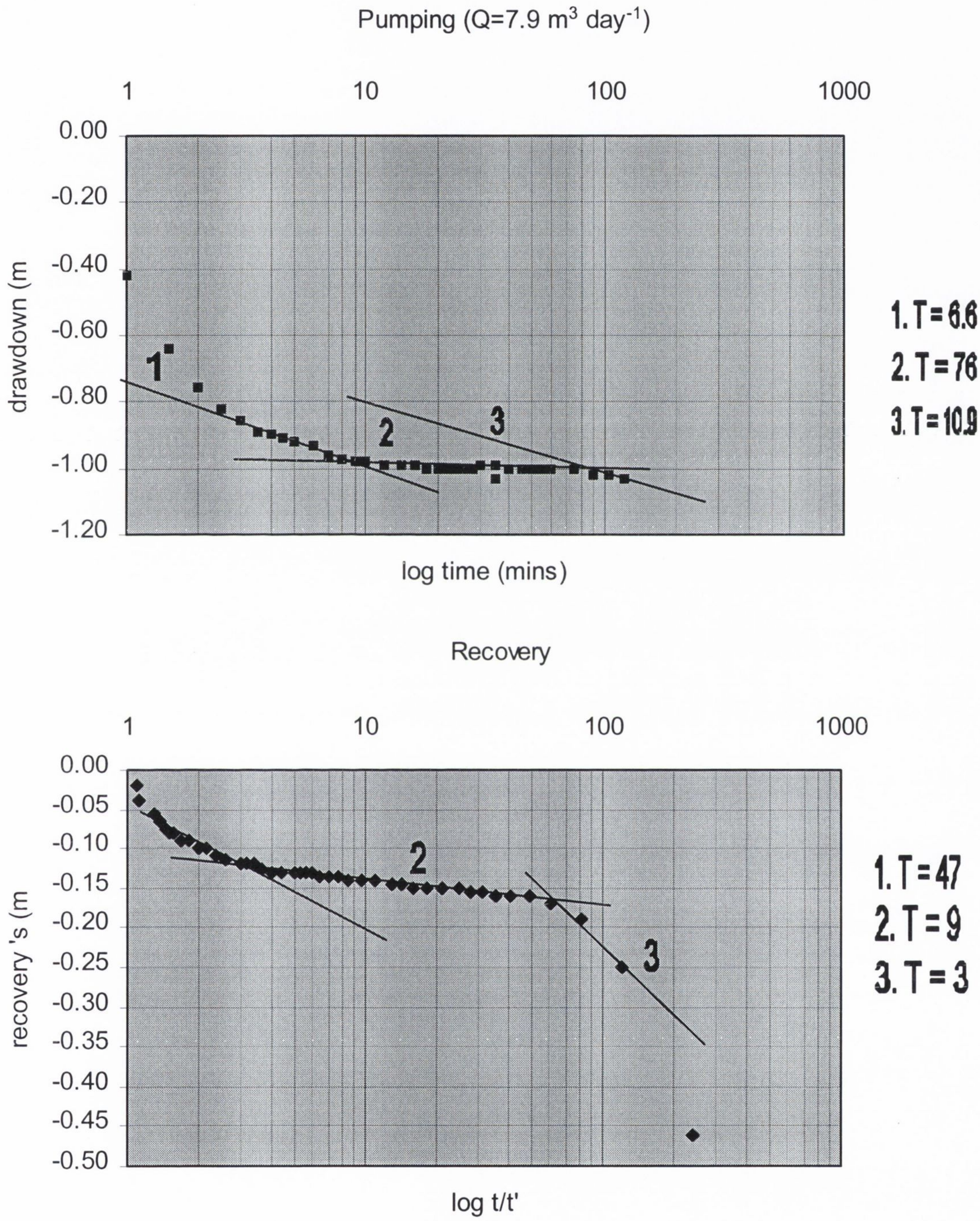


Figure 5.9 Pumping (Q=7.9 m^3 day^{-1}) and recovery graphs for borehole 4, in 1994, showing the straight lines used for calculation of transmissivity values, T values for each line are presented (m^2d^{-1}).

The calculated transmissivity values for borehole 5 ranged from 167 to 267 (m^2day^{-1}) for the pumping test and 34 to 668 (m^2day^{-1}) for the recovery of the water level in the borehole (Figure 5.10).

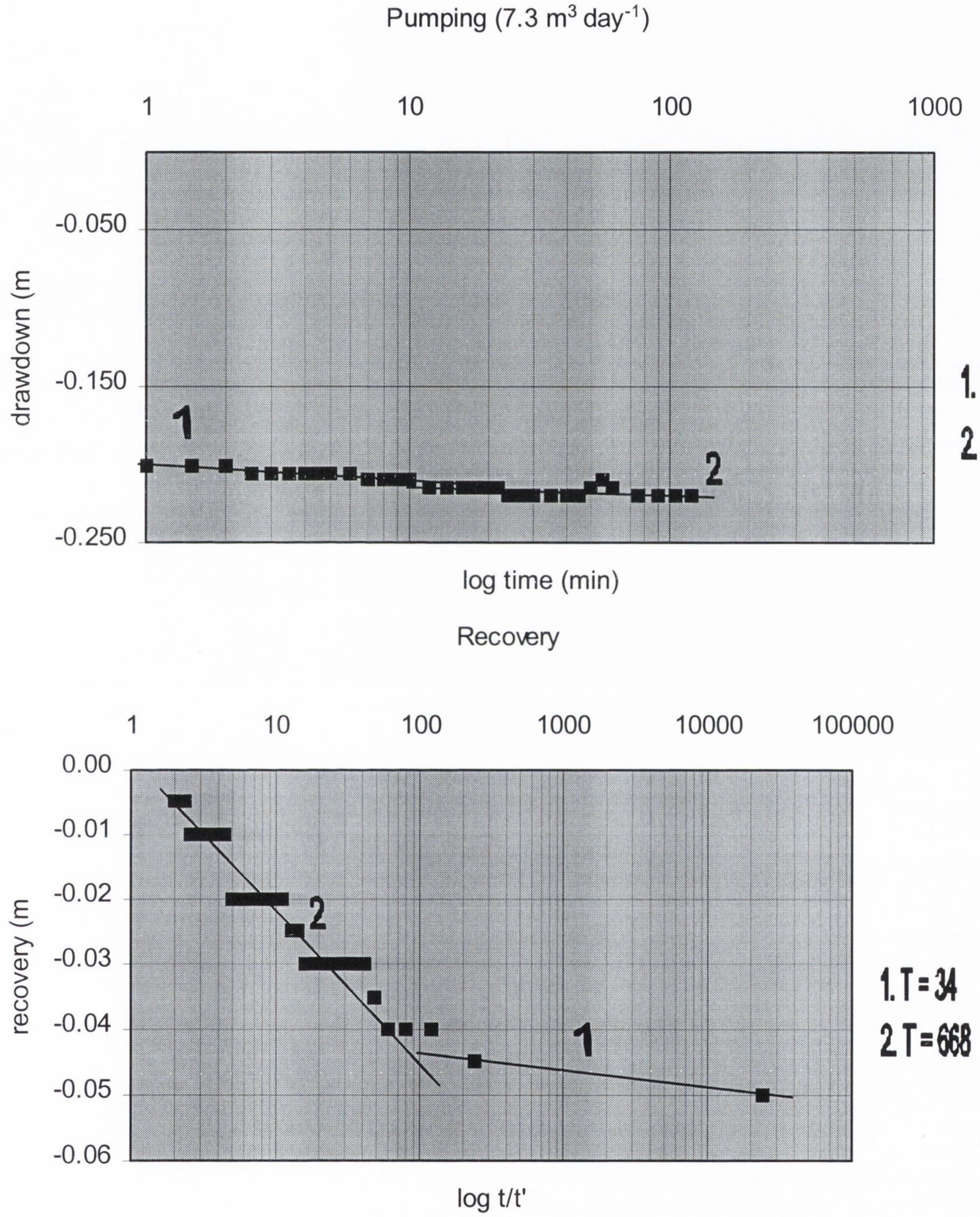


Figure 5.10 Pumping and recovery graphs for borehole 5, in 1994, showing the straight lines used for calculation of transmissivity values, T values for each line are presented (m^2day^{-1}).

Calculated transmissivity values for pump tests carried out on boreholes 1 to 5 can be seen in Table 5.5. A range of transmissivity values is given for the pumping tests corresponding to a number of lines which can be drawn on a single drawdown or recovery curve.

Table 5.5 Transmissivity values (m^2 day^{-1})as calculated from pump and recovery tests using the Jacob equation.

Borehole No.	Test date	T (pumping)	T (recovery)
1			
2	27/7/88	17	80
	16/5/90		95
3	28/7/88 #1	0.1 to 0.3	0.2 to 1.5
	28/7/88 #2	0.2 to 0.6	0.1 to 0.7
	16/5/90	0.2 to 0.8	0.2 to 1.4
4	14/6/94	7 to 76	3 to 47
5	15/6/94	167 to 267	34 to 668

From the pumping tests carried out on the boreholes at Ballyderown it is possible to observe that borehole 3 had extremely low 100 min S.C. of less than 1 m^3 m^{-1} drawdown and had transmissivity values of generally less than 1 m^2 day^{-1}. The pumping tests confirm that shale bedrock has extremely low permeability whereas the limestone bedrock has variable permeability but this was significantly higher than shale. The pumping tests from borehole 4 were interesting as transmissivity values ranged from 3 to 76 m^2 day^{-1} which was not as high as observed in the other boreholes located in limestone bedrock (1, 2 and 5) but was not as low as borehole 3.

The observed transmissivity values for each borehole corresponds well with the range of water table heights (difference between maximum and minimum water table heights) observed in each borehole over the study period as presented in section 5.3. Borehole 3 had the highest range of water table height observations of 6.03 m, this borehole also had the lowest transmissivity values observed. Boreholes 1, 2 and 5 had water table heights ranging from 1.74 to 3.19 m and these boreholes had the highest observed transmissivity values.

The range of water table heights in borehole 4 was 3.75 m which had a transmissivity which was also located between limestone and shale. At this site the shale/sandstone aquifer has a low transmissivity value and this is reflected in the large water table fluctuation range whereas the limestone aquifer has higher transmissivity values and has a corresponding lower water table fluctuation range. Borehole 4 located in limestone/shale has both transmissivity and water table fluctuation ranges between the shale/sandstone and limestone aquifers.

The limitations of the pump tests carried out should be born in mind when interpreting the results presented here. Pumping rates during the tests ranged from 5.2 to 8 m^3 day^{-1} which is extremely low compared to the most pump tests carried out by hydrogeologists. The pump used for the tests was the only pump suitable for pumping water from 5 cm diameter boreholes with deep water tables. Caution should be used due to the low discharge rates of water pumped from each well and the pump tests were short ~ 120 minutes. Nevertheless the pump tests presented do provide a relative basis for comparison of the monitoring boreholes in Ballyderown.

5.5 Groundwater Tracing Experiments

5.5.1 Introduction

In order to ascertain groundwater flow directions beneath Ballyderown a number of groundwater tracing experiments were designed. This section highlights three tracing experiments carried out from borehole to borehole tracing experiments, a fourth tracing experiment from the ground surface is presented in section 5.6.

The first groundwater tracing experiment used sodium fluorescein which was injected in to borehole 3 on 8/7/95. The second and third groundwater tracing experiments used Leucophor which was injected into borehole 5 on two occasions, namely 8/7/95 and 16/1/96.

5.5.2 Methodology

On 8/7/95, the beginning of the tracing experiments, background groundwater samples were taken from all boreholes and surface water sampling points around the farm perimeter.

Na Fluorescein

Borehole 3 was selected for Na flourescein injection to ascertain the groundwater flow direction in this area of the farm as this was complicated by the elevated water table heights observed in both boreholes 3 and 4 (section 5.3.3). On the morning of the tracing experiment 0.5 kg of Na flourescein was dissolved in two litres of de-ionised water. The solution was then stored in a dark container awaiting transport to the field site. The solution was then poured into borehole 3 at 3 pm on 8/7/95.

Samples were taken from sampling points 1 to 12 in Figure 5.11. Sampling points 1 to 6 were borehole groundwater water samples; points 8, 9 and 11 were spring water samples from the rising stream to the East of the farm; and points 7, 10 and 12 were river water samples. For the first days after tracer injection samples were taken twice a day after which point daily samples were taken. Samples were taken by using dedicated bailers for sampling the monitoring boreholes at Ballyderown. Surface water samples were taken by submersing 50 ml glass bottles in the surface water body. The samples were stored in dark boxes in a cool box at 4°C for return to the laboratory where they were stored in the dark at 4°C until fluorescence measurements were made.

Fluorescence was determined for each sampling using a Perkin Elmer luminescence spectrometer. Standards were made using reagent grade Na Fluorescein and fluorescence was determined at an excitation of 486 nm and emission of 515 nm which were the maximum excitation and emission for the top standard as determined by scanning the sample. The results of the Na fluorescein tracing experiment are presented in section 5.5.3.

Leucophor

Leucophor optical brightener was injected in to borehole 5 to ascertain groundwater flow direction from this area of the farm. Leucophor adheres to cotton and cotton ball detectors were constructed from non fluorescent hospital grade cotton wool. The cotton wool was examined under UV light to determine if there was any fluorescence before it was used for the experiment. The cotton wool was encased in a fine nylon mesh to try to prevent organic matter discolouring the cotton. The cotton ball detectors were placed at the sample locations, points 1 to 17 with the exception of 5 (Figure 5.11), before the injection of the Leucophor in to the groundwater. Five litres of Leucophor were poured in to borehole 5 at 16:00 on 8/7/95. This experiment was repeated again on 16/1/96.

The cotton ball detectors were renewed twice daily for the first few days after which they changed regularly as presented in Table 5.6. When renewing the cotton balls, the ball was removed from the water and placed into a marked plastic bag which was then placed in a light proof container for return to the laboratory for examination under UV light. A new cotton ball was then placed in the water body using nylon builders line with a weight attached. The results of the Leucophor tracing experiment are presented in section 5.5.4.

5.5.3 Sodium Flourescein Trace Results

The trace commenced on 8/7/95 and monitoring continued until 14/9/95. There was a total of 10 sampling points on and surrounding Ballyderown. These are points 1 to 12 (excluding 3 and 5, which both had tracers injected into them) Figure 5.11. The results of water sampling at points 1 to 12 are presented in Table 5.6.

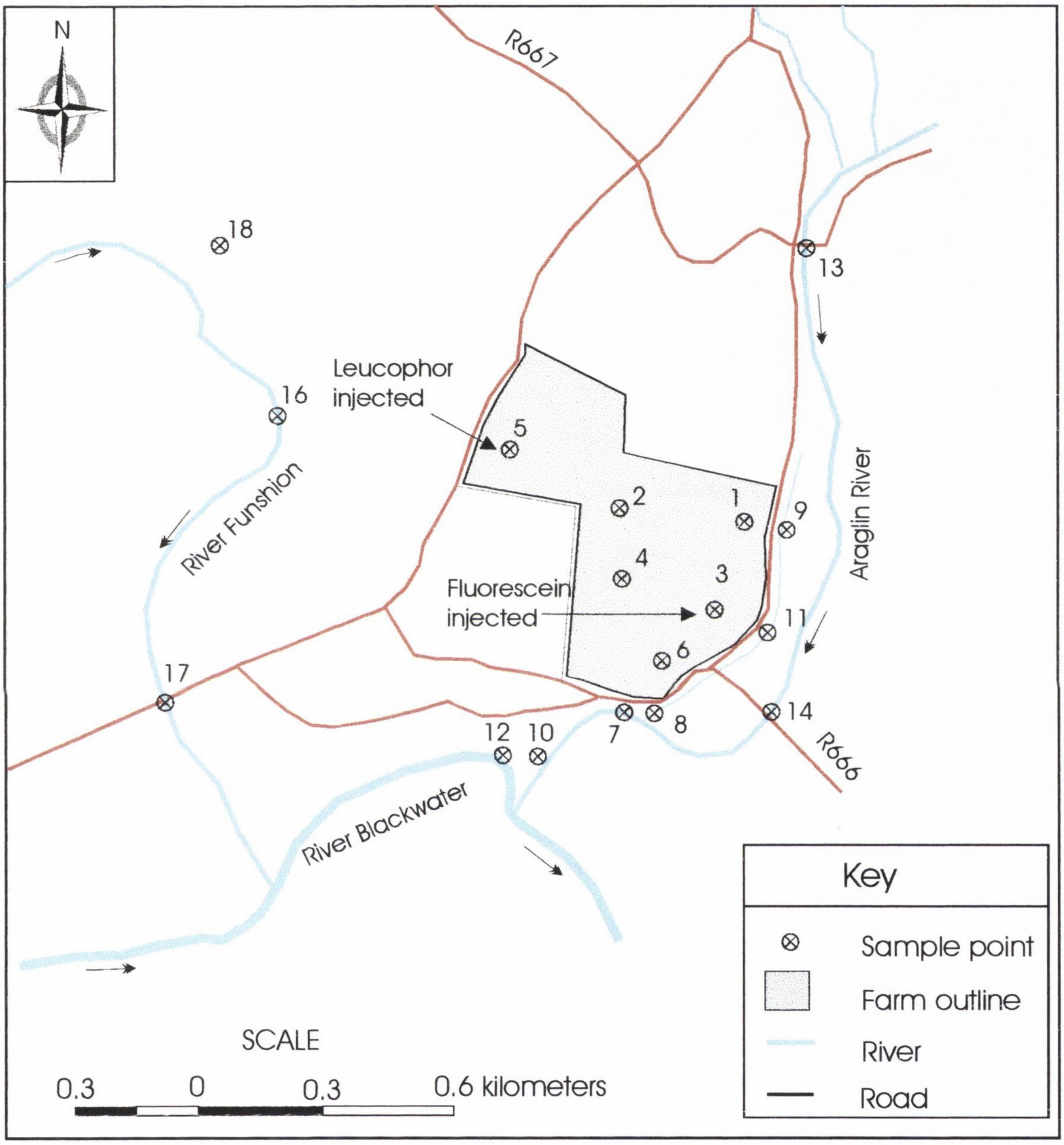


Figure 5.10 Sample locations for Leucophor and Na Fluorescein tracing experiments.

Table 5.6 Water sample Fluorescence expressed as $\mu g\ l^{-1}$ of Na Fluorescein.

	Sampling location identity									
Date	**1**	**2**	**4**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
05/07/95	0	0	0	0	1	0	0	1	0	1
08/07/95	0	0	0	0	1	0	0	1	0	1
08/07/95	0	0	0	0	1	0	0	1	0	1
09/07/95	0	0	0	0	0	0	0	1	0	1
09/07/95	0	0	0	0	0	0	0	1	0	1
10/07/95	0	0	0	0	0	0	0	1	0	1
10/07/95	0	0	0	1	0	0	0	1	0	1
11/07/95	0	0	0	1	1	0	0	1	0	1
12/07/95	0	0	0	1	1	0	0	1	0	1
13/07/95	0	0	0	1	0	0	0	1	0	1
14/07/95	0	0	0	0	1	0	0	2	0	2
15/07/95	0	0	0	0	2	0	0	2	0	10
16/07/95	0	0	0	0	1	0	0	2	0	15
17/07/95	0	0	0	0	2	0	0	2	0	15
19/07/95	0	0	0	0	2	0	0	10	0	25
24/07/95	0	0	0	0	1	0	0	1	0	10
27/07/95	0	0	0	0	0	0	0	0	0	1
31/07/95	0	0	0	0	0	0	0	5	0	1
03/08/95	0	0	0	0	0	0	0	2	0	1
09/08/95	0	0	0	0	0	0	0	1	0	0
21/08/95	0	0	0	0	0	0	0	0	0	1
14/09/95	0	0	0	0	0	0	0	0	0	0

During the monitoring period only three of the sampling locations yielded water samples which had fluorescence readings which were above background. The three sample locations were surface water bodies surrounding Ballyderown.

Site 7, the Araglin river to the south of Ballyderown, had fluorescence concentrations equivalent to 1 to 2 $\mu g\ l^{-1}$ from 14/7/95 to 19/7/95. These concentrations were extremely low but were significantly above the background concentrations.

Site 10, the Araglin river to the south of Ballyderown close to the Blackwater river, had a background fluorescence of 1 $\mu g\ l^{-1}$, this increased and peaked at 10 $\mu g\ l^{-1}$ on 19/7/95. The fluorescence concentration then decreased to between 0 and 1 $\mu g\ l^{-1}$ from 24/7/95 to 27/7/95. When sampled on 31/7/95 the fluorescence increased to 5 $\mu g\ l^{-1}$.

Site 12, the Blackwater river to the south of Ballyderown, had a background fluorescence equivalent to 1 $\mu g\ l^{-1}$, on 15/7/95 the concentration began to increase and it peaked at 25 $\mu g\ l^{-1}$ on 19/7/95. The concentration then decreased to the background concentration again on 27/7/95.

At site 12 there does appear to be a significant increase in fluorescence from 15/7/95 to 27/7/95. This increase was much larger than at sites 7 and 10. The increase in fluorescence at sites 7 and 10 could be just a natural fluctuation in fluorescence. If the increase in fluorescence at site 12 is due to the Na flourescein, which was put in borehole 3, then this would indicate that the groundwater has flowed southwest from borehole 3 and emerged in the Blackwater river.

From 1/7/95 until 10/7/95 inclusive, a total of 0.4 mm of rainfall was recorded at Moorepark. The first significant rainfall after the tracing experiment began occurred between 11/7/95 and 20/7/95, a total of 51.3 mm of rainfall occurred during this period. It is possible that the increase in fluorescence at sites 7, 10 and 12 were due to this rainfall. The rain might have transported compounds from the land and urban areas in to the river water thus increasing the fluorescence of the water. The Blackwater river would have been affected by runoff from towns and villages in its catchment, such as increased flow from the Town of Fermoy.

A further increase in river water fluorescence was observed in the Araglin on 31/7/95 and this also was associated with a significant rainfall as a total of 11.6 mm of rainfall fell between 28/7/95 and 31/7/95, with 7 mm falling on 30/7/95. This further illustrates the association between increase fluorescence of river water and periods of rainfall.

Thus it is unclear whether the increases in fluorescence in the surface water samples discussed are truly a result of the flourescein applied or whether the increases are due to a week of heavy rainfall which mobilised and transported luminescent compounds to the river such as organic matter. Comparison of the fluorescein injection location, borehole 3, to the groundwater flow direction of NNE to SSW, as indicated from Figures 5.6 and 5.7, would suggest that the fluorescence could be due to the tracing experiment. A flow direction from borehole 3 to the SSW could transport the tracer to the Araglin river and into the Blackwater river.

5.5.4 Leucophor Trace Results

Table 5.7 presents the date of cotton ball indicator sampling from 8/7/95 to 15/3/97.

Table 5.7 Sampling dates for cotton balls used to determine the presence of Leucophor.

08/07/95	12/07/95	16/07/95	24/07/95	16/08/95	17/01/96
09/07/95	13/07/95	17/07/95	27/07/95	21/08/95	24/01/96
10/07/95	14/07/95	19/07/95	03/08/95	10/10/95	15/03/97
11/07/95	15/07/95	21/07/95	09/08/95	07/11/95	

No fluorescence of the cotton balls was observed under Ultra violet light. There were occasions when there was partial fluorescence (areas of 2 to 5 mm) of the cotton ball. If Leucophor was present in the groundwater there is no reason why partial fluorescence would occur as the cotton ball should absorb the Leucophor reasonably uniformly. On test cotton balls in the laboratory uniform fluorescence was observed. Comparison of the test cotton ball to the field cotton balls suggested that none of the field cotton balls had absorbed the Leucophor from the tracing experiment.

Cotton ball indicators placed in surface water bodies surrounding the farm were continuously tampered with. It appears that fishermen on these rivers considered the cotton balls, which were tied to pieces of string, to be a danger to their fishing. On many sampling dates the cotton balls could not be found and the string attaching the cotton balls to the river banks had been cut. This meant that there was incomplete sampling of the surface water bodies for the presence of Leucophor.

There were a total of 16 monitoring sites for the Leucophor trace. There were 9 monitoring sites in the groundwater and springs surrounding Ballyderown. There was a total of 7 surface water monitoring sites. The monitoring of the groundwater, springs and surface water was located at Ballyderown or immediately surrounding the farm. There was only three sampling sites located to the west of borehole 5 and the majority of the monitoring sites were located on the east and southern side of Ballyderown. The monitoring in the Blackwater river to the south of Ballyderown was interfered with continuously and only a few samples were taken in the Blackwater.

After the second Leucophor tracing experiment (16/1/96) in borehole 5 the top 1 to 2 metres of groundwater contained no visible sign of Leucophor, yet when samples were taken from 10 metres below the water table the groundwater appeared to be cloudy with Leucophor precipitate in suspension in the water (from February to April 1996). The Leucophor was still visibly present in the groundwater at borehole 5 when sampling ceased in April 1996.

From the water table maps presented in Figures 5.6 and 5.7 the groundwater flow direction to the SSW could have resulted in the transportation of the Leucophor tracer from borehole 5 towards the Blackwater river between sampling points 17 and 12. The lack of indicators returned from sampling point 12 indicated that there would have been little chance of observing the tracer if it had followed the groundwater flow direction which is indicated from the water table maps.

5.6 Soil surface Br trace

5.6.1 Introduction

To further investigate the groundwater flow beneath Ballyderown farm and to estimate the travel time from the soil surface to groundwater another tracing experiment was designed. A soil surface bromide tracing experiment was designed to both estimate the travel time through the soil and Quaternary deposits (as presented in section 4.7) to groundwater. It was also hoped to detect bromide in the other monitoring wells on the farm.

5.6.2 Groundwater Br Occurrence

As outlined in section 4.7, Br^- has been used by many workers to simulate nitrate movement through soils (see section 4.7.2 for a review of the use of Br^- as a tracer and occurrence in soils). Groundwater Br^- concentrations are on average very low. Houghton (1946) reported Br^- concentrations in groundwater from the southeast of England to range from 0.026 to 2.26

mg l^{-1} with high concentrations attributed to salt water intrusion due to Cl:Br ratios in the groundwater being similar to salt water.
Typical groundwater Br^- concentrations have been reported in the UK to range from 0.06 to 0.09 mg l^{-1} (Luong *et al.*, 1980). Lundstrom and Olin (1986) reported Br^- concentrations ranging from 0.016 to 0.08 mg l^{-1} from springs sampled in Sweden. Owens *et al.* (1985) reported a rainfall Br^- concentration of 0.1 mg l^{-1} which amounted to a net annual deposition of 1.1 kg ha^{-1}. Bowen (1979) reported concentrations of 0.014 mg l^{-1} for surface water. The Br^- concentration in both soil and groundwater decreases with increasing distance from the sea (Yuita, 1983). Schuh *et al.* (1997) observed increases in groundwater Br^- concentration of one order of magnitude almost immediately after surface application and this was attributed to preferential flow through the soil to the water table which varied from 3 to 4.8 m b.g.l..

The longevity of Br^- in a catchment after a single surface application was noted by Schuh *et al.* (1997) who observed elevated Br^- concentrations in saturated till for 3 years (the end of monitoring) after a single surface application. Owens *et al.* (1985) observed no significant decrease of groundwater Br^- concentrations for 4.5 years following a single surface applied Br^- application.

It should also be noted that Br^- can have serious health effects as Owens *et al.* (1985) observed when 19 cattle from a herd of 25 died after grazing a plot which had received KBr, at a rate of 168 kg Br^- ha^{-1}, two weeks earlier.

Many authors have used Br^- tracing in field and laboratory investigations to examine the importance of preferential flow as a mechanism of water movement through soils to recharge aquifers (Caron *et al.*, 1996; Jabro *et al.*, 1994; Kelly and Pomes, 1998; Schuh *et al.*, 1997; and Timlin *et al.*, 1998).

5.6.3 Methodology

The detailed methodology was described in section 4.7.3. To summarise: On 16/1/96 (Figure 5.12 uses days after 1/1/96, Br^- applied day 16) KBr was surface applied to a grid (100 m^2) surrounding boreholes 1 and 2, with the borehole in the centre. No KBr was applied to 4 m^2

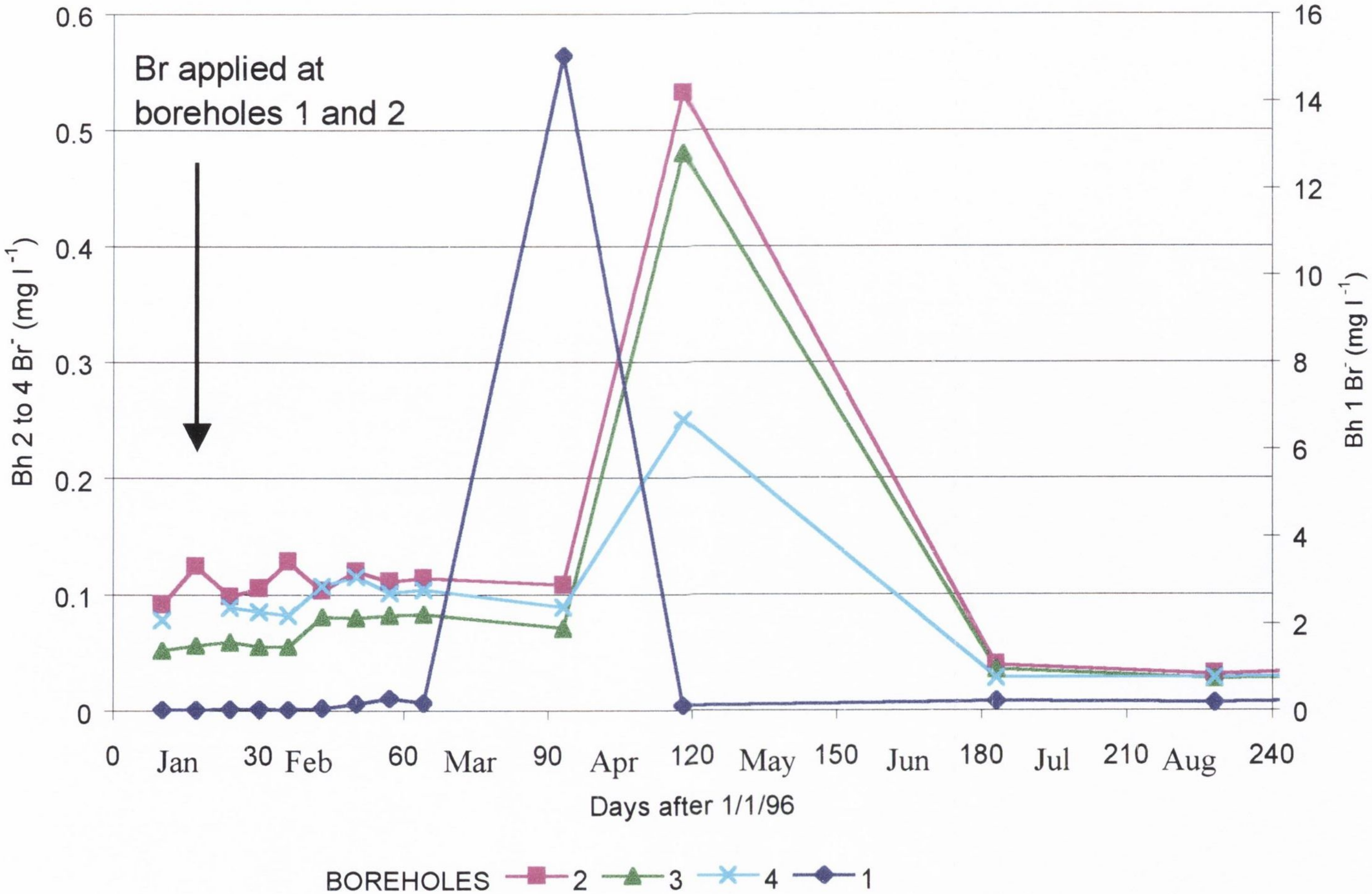


Figure 5.12 Groundwater Br^- concentrations as measured in boreholes 1 to 4. (Note borehole 1 is on the secondary y axis).

immediately surrounding each borehole. Soil solution was sampled as outlined in section 4.7.3. Groundwater was sampled weekly between 10/1/96 and 4/3/96 (days 10 to 64) after which date occasional samples were taken until 27/3/97 (day 452). Each borehole was sampled with a dedicated bailer to prevent cross contamination.

5.6.4 Groundwater Br^- Results

The results of the effect of the soil surface Br^- trace on groundwater Br^- concentrations can be seen in Figure 5.12.

Background groundwater Br^- concentrations measured between days 10 and 30 were 0.05, 0.11, 0.06 and 0.09 mg l^{-1} for boreholes 1 to 4, respectively. Generally the background groundwater Br^- concentration was <0.1 mg l^{-1} with the exception of borehole 2. A very slight increase in groundwater Br^- concentration of 0.02 to 0.03 mg l^{-1} was observed on day 43 (27 days after Br^- application) in boreholes 1, 3 and 4. On day 93 (77 days after Br^- application) the groundwater Br^- in borehole 1 increased to 15 mg l^{-1} and by day 118 (102 days after Br^- application) the groundwater Br^- in this borehole decreased to 0.133 mg l^{-1}. Groundwater Br^- concentrations in boreholes 2, 3 and 4 increased from ~ 0.1 mg l^{-1} on day 93 to peak at 0.53, 0.48 and 0.25 mg l^{-1}, respectively, on day 118. The Br^- concentrations in boreholes 2, 3, and 4 decreased again to <0.1 mg l^{-1} on day 183 (167 days after Br^- application).

Further sampling of groundwater in 1996 and 1997 showed that a slight increase of groundwater Br^- concentrations one year after surface application of Br^- (Figure 5.13).

In 1997 the was a significant increase of groundwater Br^- concentration sampled in borehole 1 from 0.2 mg l^{-1} on day 228 to 0.47 mg l^{-1} on day 386 before decreasing again to <0.3 mg l^{-1} when sampling ceased on day 452. There were also slight increases of groundwater Br^- as sampled in boreholes 2, 3, and 4 to 0.07, 0.04 and 0.04 mg l^{-1}, respectively, on day 452, which were less than the background levels observed in early 1996.

The pattern of observed increases of groundwater Br^- concentrations in 1997 was similar to 1996 with borehole 1 having the highest observed Br^- concentration on day 386 and boreholes

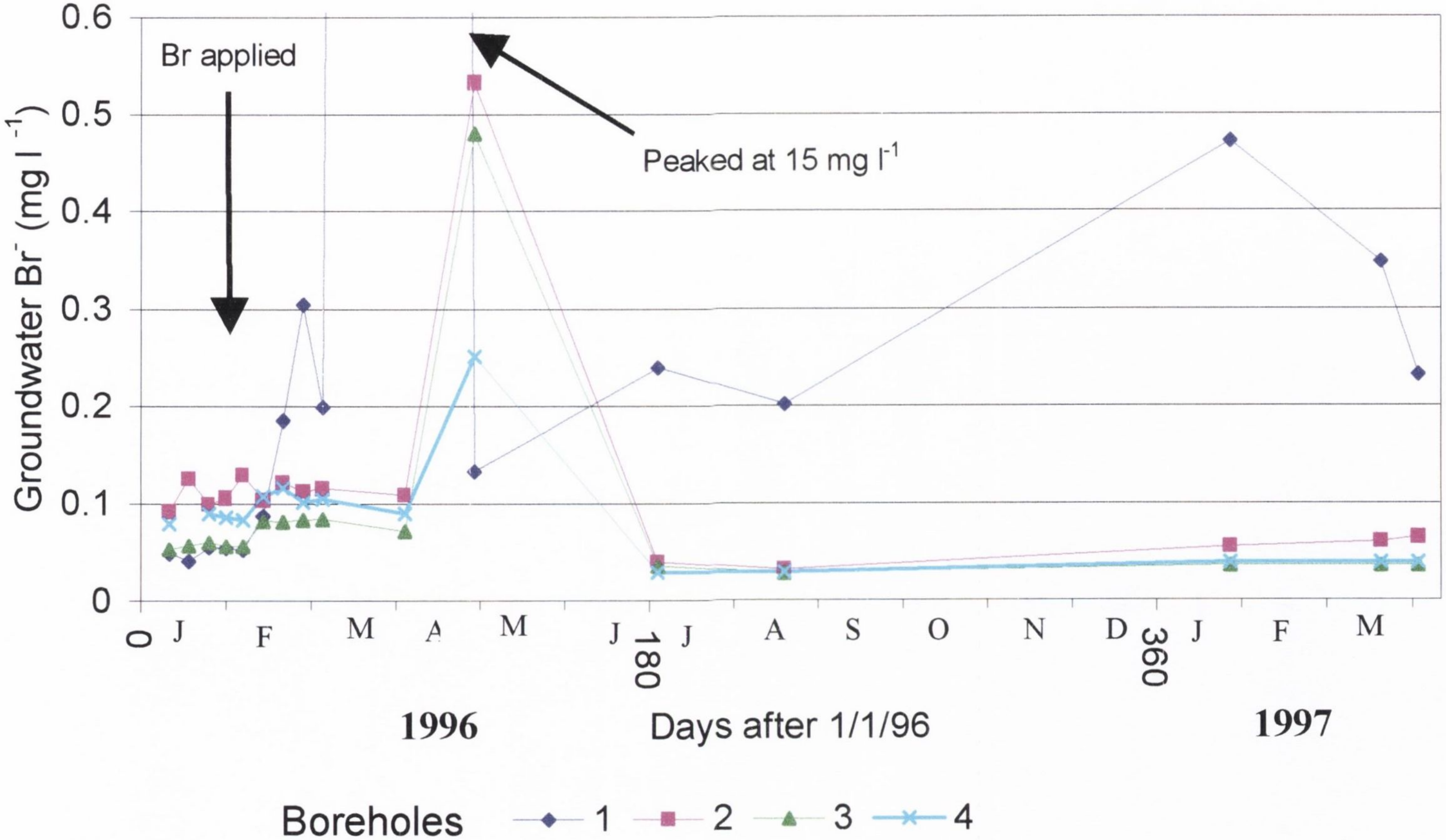


Figure 5.13 Temporal groundwater Br^- fluctuations from 1/1/96 to 27/3/97.

2, 3, and 4 all had similar Br^- concentrations which were highest when sampling ceased on day 452, 66 days after the Br^- peak observed in borehole 1.

Thus surface application of Br^- affected groundwater Br^- concentrations for the 436 days of observations after the application of Br^-. As mentioned previously, the longevity of surface applied Br^- in catchment was also reported by Owens *et al.* (1985) and Schuh *et al.* (1997).

The rapid movement of Br^- from the soil surface to the groundwater implies that if nitrate or other water soluble substances were in the soil, available for leaching, then groundwater would be at risk of contamination. The application of fertilisers, manures and the grazing of cattle during periods of drainage increases the risk of groundwater contamination. Due to the rapid movement of Br^- to groundwater any changes in groundwater quality/chemistry could reflect management practices which occurred in the zone of contribution in the recent past (in the order of months/weeks). Increased groundwater NO_3-N concentrations from agriculture each winter can be attributed to the agronomic practices from the previous summer.

The concentrations of Br^- measured in groundwater at the different boreholes sites were variable as boreholes 2, 3, and 4 had similar peak Br^- concentrations which ranged from 0.25 to 0.53 mg l^{-1}. The peak Br^- concentration observed in borehole 1 was 15 mg l^{-1}, which appears to be significantly higher than the observed peaks at the other borehole sites. Increases in groundwater Br^- concentrations were expected at boreholes 1 and 2 as this is where the Br^- was applied to the soil surface. Increases in Br^- concentrations in boreholes 3 and 4 mean that the groundwater at the two sites was being influenced by the Br^- applied to the soil surface at boreholes 1 and 2.
A further factor confusing the issue of which site where Br^- was applied was effecting the groundwater Br^- concentrations at boreholes 3 and 4 and that was the fact that the water tables in boreholes 3 and 4 were higher in altitude than in boreholes 1 and 2 (Figure 5.14).

Thus the occurrence of Br^- in boreholes 3 and 4 can not be explained by saturated flow as water can not flow from a low altitude to a higher altitude. To explain the occurrence of Br^- which has moved from an area which is topographically higher (boreholes 1 and 2) to an area topographically lower (boreholes 3 and 4) it likely that there was unsaturated flow of the Br^- which entered the groundwater in the vicinity of boreholes 3 and 4.

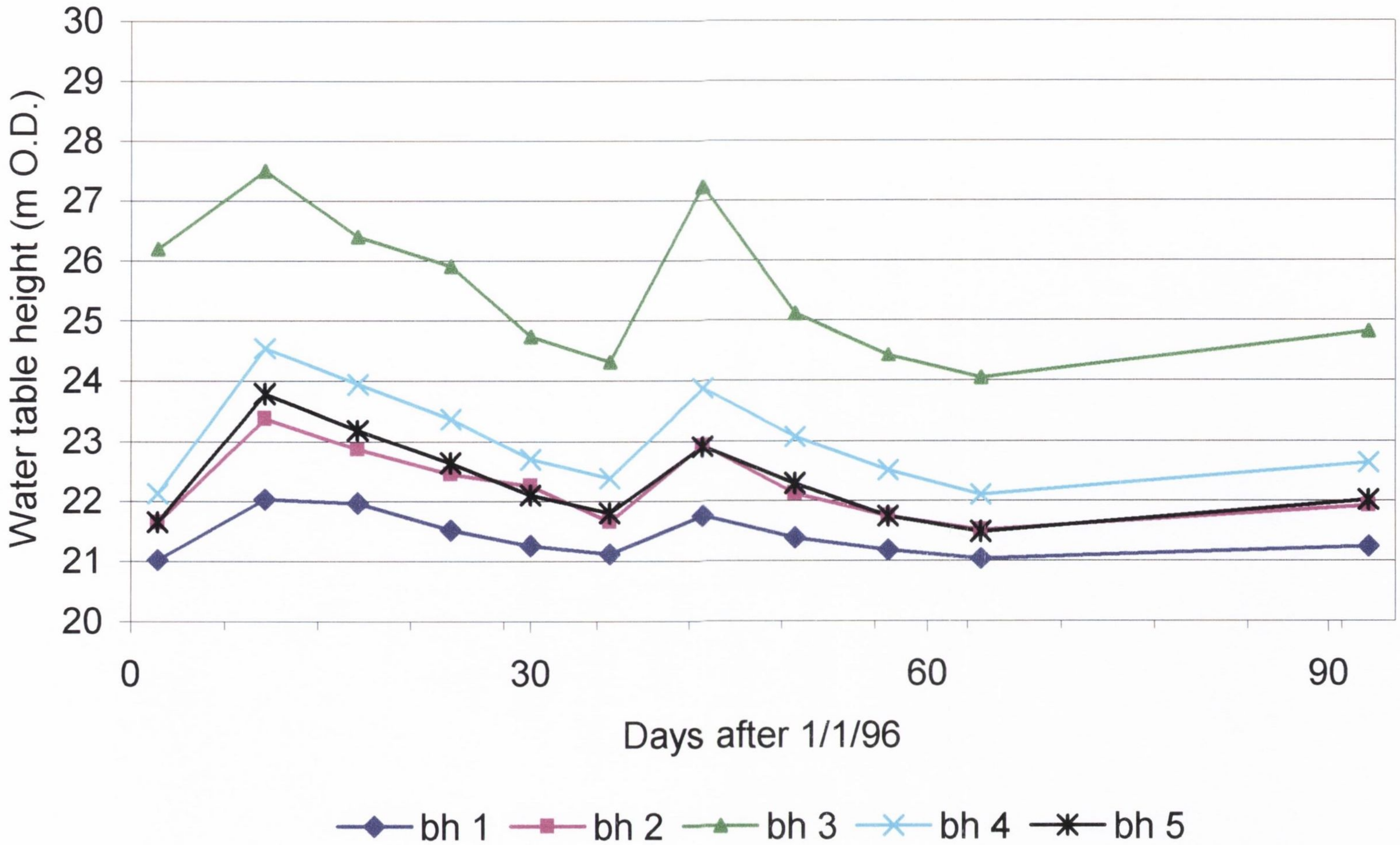


Figure 5.14 Water table heights (m O.D.) Observed in boreholes 1 to 5 during the Br^- tracing experiment (2/1/96 to 2/4/96).

Based on unsaturated flow being the transport agent for the applied Br^- a total of five possible flow directions are outlined in Figure 5.15.

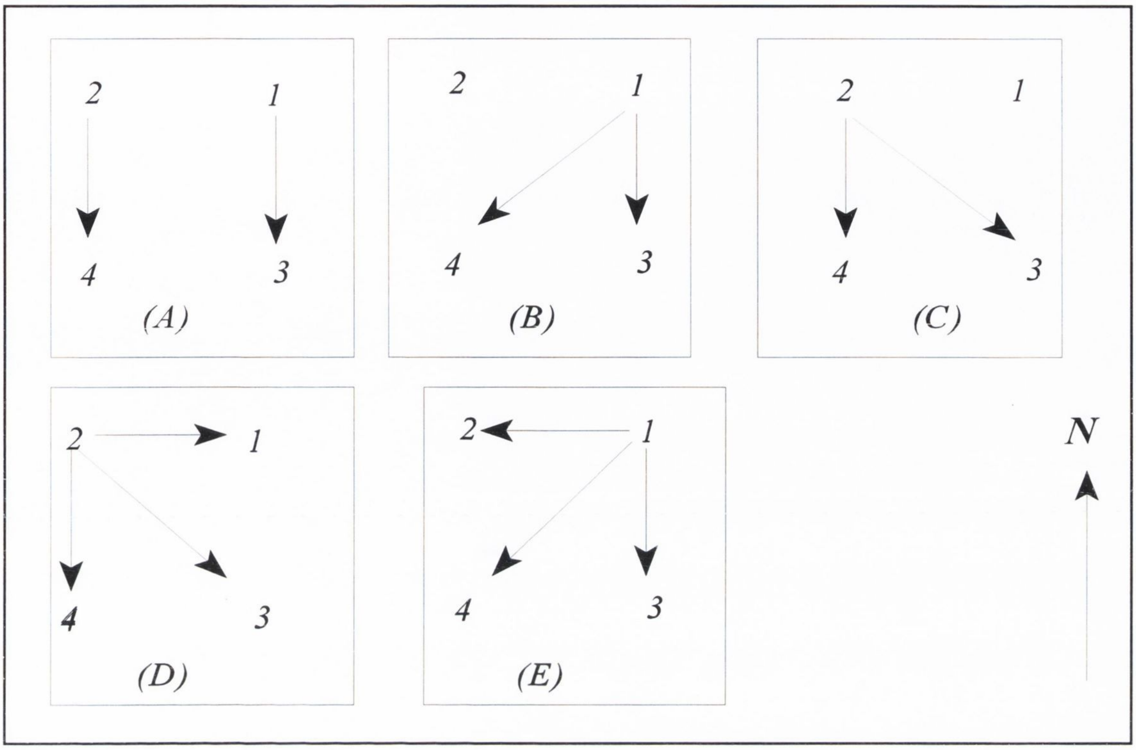


Figure 5.15 Five possible flow directions of surface applied Br^- from boreholes 1 and 2 to boreholes 3 and 4.

Option A, southerly movement of Br^-, is that the Br^- in borehole 4 sources from borehole 2 and the Br^- in borehole 3 sources from borehole 1 to the north. Movement of Br^- from borehole 1 to 3 and from borehole 2 to 4 could occur if there was unsaturated flow down dip from each borehole.

Option B, Br^- movement from borehole 1 to the south to borehole 3 and to the south west to borehole 4. This option is also possible with Br^- moving down dip from borehole 1 to 3 and diverging to the west down the strike of the fold from borehole 1 to 4. The Br^- observed in borehole 2 could be from the surface applied Br^- at this site.

Option C is southerly movement of Br^- from borehole 2 to borehole 4 and south eastern movement from borehole 2 to borehole 3. This is unlikely as the bedrock is striking to the west and flow normally occurs down strike and dip and so movement of Br^- from borehole

2 to borehole 3 is unlikely.

Option D, divergent flow from borehole 2 to the southeast influencing borehole 1, 3 and 4. This is unlikely as the peak Br^- concentrations in borehole 1 was significantly higher than in borehole 2 and the peak concentration in borehole 1 occurred 25 days before the observed peak in borehole 2. Again it is unlikely that Br^- movement would occur up strike to boreholes 1 and 3.

Option E, divergent flow from borehole 1 to the southeast. This is a likely hypothesis as the observed groundwater Br^- concentrations in boreholes 2, 3 and 4 are similar which could indicate a common Br^- source. It is unlikely that saturated groundwater flow is occurring from borehole 1 to 2, 3 and 4 as boreholes 2, 3 and 4 have higher water table heights than borehole 1. But unsaturated flow may occur in the unsaturated bedrock down gradient from borehole 1. From geological logs of borehole 1 it is possible to hypothesise unsaturated flow between bedding partings such as limestone/shale interfaces where horizontal flow must occur to flow around the more impermeable shale band. Thus unsaturated flow down bedrock dip and down strike of the plunging fold, upon which borehole 1 is located, would be expected. Flow to the south occurs due to beds dipping to the south which transports Br^- towards borehole 3. Flow to the west is possible along the strike of the fold which plunges to the west and dips at 15° which would transport Br^- towards borehole 2. A mixture of south and western unsaturated flow could explain the occurrence of Br^- in borehole 4 which is located to the south west of borehole 1.

5.7 Conclusions

The bedrock geology of the farm area was revised based on new information gained from two additional boreholes on the farm. The main revisions involved the extension of the Ringmoylan shale anticline limb further across the farm. A fault which was believed to be to the south of borehole 4 actually intersected in borehole 4.

From the two water table maps constructed the groundwater flow direction was estimated to be from NNE to SSW. There appeared to be a groundwater mound around the Ringmoylan shale anticline. Elevated water table heights were observed in both boreholes 3 and 4. The effect of this mound might be to force the groundwater to flow to the west around the shale anticline.

Aquifer characteristics determined from short duration, constant rate, pumping tests indicated that the boreholes which intersected the Ballysteen limestone had higher transmissivity values than Ringmoylan shale. Boreholes which had higher transmissivity values had a narrower range of observed water table fluctuations, which may indicate high specific yields in the Ballysteen limestone.

Groundwater borehole to borehole tracing experiments were inconclusive. Elevated fluorescence observations in the rivers to the south of Ballyderown may indicate a positive trace from the Na Fluorescein or may indicate increased background fluorescence due to the heavy rainfall during the elevated observations.

The Br^- applied to the soil surface around boreholes 1 and 2 was observed in boreholes 3 and 4, although the water table maps would suggest that this was not possible by saturated flow. A hypothesis of unsaturated flow was proposed to explain the occurrence of Br^- in boreholes 3 and 4. The most likely source of the elevated groundwater Br^- in boreholes 3 and 4 is Br^- applied at borehole 1 as the bedrock beneath the application area dips to the south and with the bedrock strike to the west. Thus flow to the west and south could affect both boreholes 3 and 4.

Rapid movement of the soil surface applied Br^- to groundwater within 77 days was observed in borehole 1. The short travel time would suggest that if contaminants were present in the soil that groundwater contamination could occur rapidly. This finding also suggests that changes in groundwater chemistry, in particular nitrate, could be attributed to recent agricultural activity. Changes in nitrate concentrations are likely to reflect changes in applied N rates to plots during the previous year.

CHAPTER 6 UNSATURATED ZONE NITRATE LEACHING

This chapter details the quantification of nitrate leaching through the unsaturated zone in the plots which contain the boreholes 1 to 5 and also in plots 6 and 6a which were affected by excessive dirty water irrigation. The literature review introduces the reader to the area of unsaturated zone nitrate leaching, methodologies used to quantify nitrate leaching and the effect which agriculture has on nitrate movement through the unsaturated zone.

6.1 Methodologies for quantifying nitrate leaching

There are four principal methodologies for estimating the quantity of nitrate leached through soil: lysimeters, soil sampling, porous suction cups, and field drainage sampling.

6.1.1 Lysimeters

In general a lysimeter is a column of soil which is encased with an impermeable barrier or by placing an impermeable barrier beneath a soil block, with an outlet for drainage collection. A system for the collection of soil water is attached to the outlet from the impermeable barrier (Whitehead, 1995). The most common lysimeter used is the monolith lysimeter (Goulding and Webster, 1992) and these are made by cutting an undisturbed soil block from the ground and encasing the sides and base of the block with an impermeable barrier such as fibre glass; an outlet from the base of the lysimeter allows collection of soil drainage water (Belford, 1979). Thus it is possible to quantify both the volume of drainage and the particular pollutant being investigated.

A second type of lysimeter which is less used now is the back filled lysimeter. This is made by re-packing a container with soil which is dug layer by layer from the field. The disadvantage of this type of lysimeter is that there is a large amount of soil disturbance which may cause changes in the soil N dynamics possibly by causing mineralisation of organic N or immobilisation of N.

Although lysimeters have the advantage of obtaining a true measurement of leaching loss from a block of soil, they do not resemble field soils in every aspect (van Babel, 1961). Cracks may develop at the inside edge of the lysimeter, especially in soils with a high clay content, thus water may bypass the soil column giving a non representative sample. The second main problem with lysimeters is that the water draining through the lysimeters may be delayed compared to the field as there is no subsoil matric potential in lysimeters whereas there is in a field soil (Webster *et al.*, 1993).

6.1.2 Suction Cups

Suction cups are constructed of hydrophilic materials with fine pores. When suction is generated within the sampling system, water is sucked inwards through the pores of the cup until a corresponding capillary pressure occurs in the soil and cup pores. If the capillary pressure of the cup is lower than the surrounding soil, water flows from the soil to the cup until the capillary pressure in the suction cup and the soil are equal. In order to achieve suction in the system no air must pass through the cup pores (Grossman and Udluft, 1991).

The suction in the sampling system creates a potential gradient around the suction cup and this results in seepage water flowing into the cup from a specific space. Krone *et al.* (1952) measured this potential field around the suction cup using tensiometers; the potential field can be seen in Figure 6.1. This diagrammatic representation is only valid for completely homogenous soils. The extent of the potential field disturbance may reach 1 m but the radius of the recharge area lies between 0.1 m and 0.5 m, depending on the capillary pressure in the soil, the suction in the cup and its diameter, and on the pore size distribution (Germann, 1972 as cited in Grossmann and Udluft, 1991).

The extent of the soil volume from which the water sample is removed depends on the moisture content of the soil and on the size of the sample removed. It is suggested by Grossmann and Udluft (1991) that sample sizes should be kept as small as possible to minimise disturbance to the soil. Webster *et al.* (1993) gave sampling of the water as a reason why there are differences between results from lysimeters and suction cups since sampling by suction cups can accelerate the downward movement of soil water.

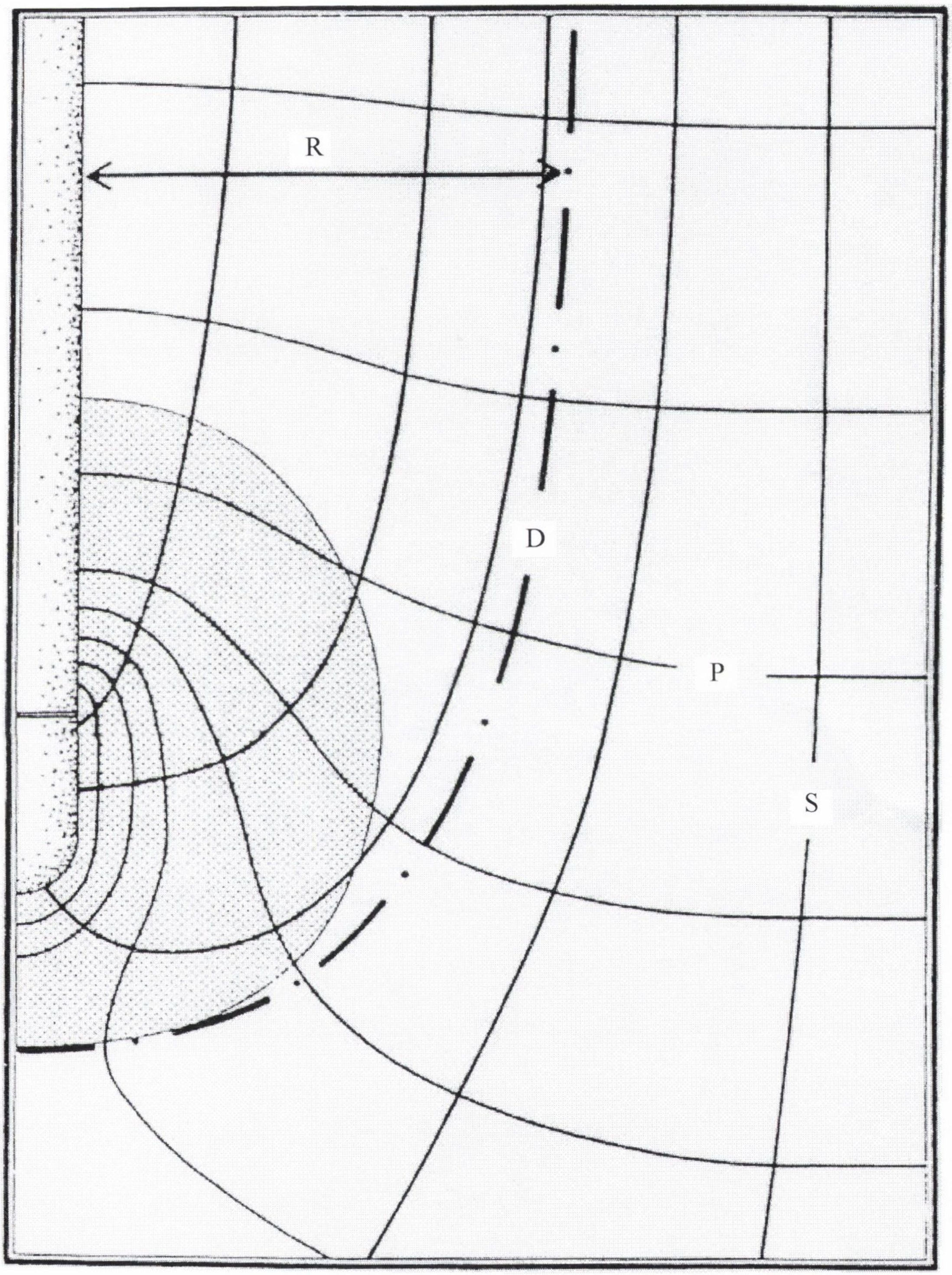


Figure 6.1 Potential field around a suction cup in a homogeneous soil (R, radius of the recharge area; D, dividing stream line; P, iso-potential line; S, stream line; dotted field, space from which the sample is taken.) (From Grossman and Udluft, 1991).

There have been suggestions in the literature that suction cups sample `loosely bound' seepage water from the bigger pores, with the pore size sampled being dependent on the suction size (Williams and Lord, 1997). The suction created acts on all pores and therefore movement of water occurs from all pore sizes with velocities depending on the pore size. The difference of N concentration between pore sizes should not be great due to diffusion and dispersion, although this is not the case for macro pores.

No sediment type is homogenous and thus a channelling effect on the seepage water will occur. If there is a concentration gradient in the soil then the suction could have an effect on the sample composition due to a higher influx from the larger soil pores (Hansen and Harris, 1975).

Preferential flow through macro pores is the most serious problem which affects suction cups as the soil water can by-pass the suction cups. This could mean that the samples removed are the static water in the soil rather than the major portion of the water which is moving along the preferential flow-paths through the soil profile. In some studies this has explained differences between suction cups and suction plates (Beasley, 1976; Shaffer *et al.*, 1979; Barbee and Brown, 1986.)

The variability of nitrate concentrations taken from the suction cup samplers has been reported as high in the literature (Alberts *et al.*, 1977; Cuttle, 1992); thus a large number of replications are needed to account for field variation. When fields are grazed by ruminant animals, the natural soil heterogeneity becomes exacerbated by the random excretion of dung and urine (Alberts *et al.*, 1977; Grossmann and Udluft, 1991; Cuttle, 1992).

6.1.3 Soil Sampling

The simplest and cheapest method to estimate leaching losses is to take a sample of soil to whatever depth is required and extract the nitrate and ammonium (NO_3-N and NH_4-N= 'Mineral N') (Goulding and Webster, 1992). The most common extractant for mineral N is 2 M KCl (Bremner, 1965). By sampling to 90 cm deep the method gives the mineral N profile of the soil and it estimates the quantity of N which is at risk of leaching. The quantity of nitrate leached is estimated from the difference between successive sampling dates combined with an estimate of drainage. The method is somewhat imprecise (Goulding and Webster, 1992) due to removal of nitrate by other processes such as denitrification, immobilisation and plant uptake, while fresh N can be added through mineralisation of soil organic matter.

When nitrate concentrations estimated by soil sampling and suction cups, were compared, differences were found by Webster *et al.* (1993). The differences in the two methods were attributed to analytical error and sampling variability; it was also noted that at the EU limit of 11.3 mg l^{-1} the soil inorganic N concentration was close to the limit of detection due to dilution in the extractant (Webster *et al.*, 1993). Whereas Djurhuus and Jacobsen (1995) found no significant differences between soil core extracts and suction cup samples on a coarse sand and sandy loam. Observations suggest that soil sampling over-estimate N loss to drainage water and suction cups under estimate losses due to preferential flow (Magnesan *et al.*, 1994; Alberts *et al.*, 1977).

A study by Alberts *et al.* (1977) comparing suction-cup samples and soil solution extractions with regard to nitrate concentrations found that the latter usually contained higher concentrations. A possible explanation for this finding could be soil variability and samples taken from different locations within a plot complicates methodological comparison due to the inherent soil heterogeneity (Alberts *et al.*, 1977). Webster *et al.* (1993) also made comparisons between sampling methodologies and they concluded that suction cups and lysimeters measured the same concentration of mineral N in the leachates, but the concentrations obtained from soil cores were lower than those obtained from the other methods.

6.1.4 Field Drainage Systems

On heavy clay soils, with artificial drainage systems installed beneath a field, it is often possible to analyse and quantify the amount of N leaving the field. The technique has the advantage of the plot being large enough to overcome heterogeneity caused by grazing animals but it is unlikely that the drainage system will intercept all the drainage water percolating beneath a field (Whitehead, 1995).

6.1.5 Methodologies used in the present study

For the purpose of this investigation suction cups were chosen to estimate the concentration and load of nitrate leaching through the unsaturated zone to groundwater. Suction cups were chosen as they provided the most economical method since it is possible to replicate measurements easily. Lysimeters would have been preferable but they are expensive to construct which means that only a few replicates can be used to study nitrate movement. It was decided to carry out soil sampling in autumn to estimate the amount of N available for leaching during the period of maximum aquifer recharge. Since there was no field drainage present on the farm due to the highly permeable nature of the unsaturated soil and the deep water table present beneath the farm it was not possible to use this sampling method.

6.2 Nitrate leaching from Dairy Farming

6.2.1 Introduction

Nitrate leaching from dairy farming can be studied on the basis of two main land-uses, firstly silage areas or cut grass and secondly grazed areas. These two land-uses will be dealt with separately as they behave extremely differently with regard to nitrate leaching.

Nitrate leaching occurs when soil which is at field capacity receives water via rainfall in excess of evapotranspiration causing displacement of water down the soil profile. As the excess rainfall moves through the soil profile anions such as nitrate are dissolved in the soil solution and are transported from the soil to the groundwater and surface water. Nitrate is the most mobile form of N in soils with other forms of N less susceptible to leaching, although ammonium may leach under high concentrations such as beneath urine patches. Urea also may leach under suitable conditions such as at high concentrations at low temperatures which inhibit ammonification. It is unusual for organic forms of N to be leached from the root zone although organic N in slurry may be leached when applied to highly permeable soils or where macropores or preferential flow paths occur. Nitrous oxide, released through the processes of nitrification and denitrification, also may become dissolved in the soil solution and be leached.

The nitrate ion is susceptible to leaching as it is negatively charged and thus is not adsorbed to clay or to organic matter colloids which are also negatively charged. Ammonium, in contrast, is positively charged and is adsorbed on the soil by the process of electrostatic attraction.

In grassland ecosystems nitrate leaching has traditionally been considered to be very low since grass has a large capacity to take up nitrate and in temperate climates this capacity is maintained throughout much of the year. This was the accepted case until 1984 when Ryden *et al.* (1984) showed that nitrate leaching below a grazed sward in the U.K. was greater than 5.6 times the nitrate leached below a cut sward and that this was due to the random deposition of urine and dung containing large amounts of N in the field. Since 1984 numerous workers have observed high rates of nitrate leaching from grazed grassland (Barraclough *et al.*, 1992; MacDuff *et al.*, 1992; Younie and Watson, 1992; Scholefield *et al.*, 1993; Ledgard *et al.*, 1996 a and b; Stout *et al.*, 1997 and Vertes *et al.*, 1996).

The underlying problem is that ruminant animals are not efficient at converting N ingested to the end products of milk and protein as described in section 3.4.2 and as little as 20 to 25% of ingested N is utilised by the grazing ruminant. Urine patches contain the highest loads of N excreted which can equate to N application rates of 400-1200 kg N ha^{-1}, which vastly exceeds plant requirements thus causing a nitrate leaching risk.

When grass is grown and cut, in the absence of ruminants, the quantity of nitrate leached is very low, normally less than 20 kg N ha^{-1} $year^{-1}$ (Whitehead, 1995) due to the homogenous application of N to the grassland and the removal of harvested N. Under grazed grassland however, the quantity of nitrate leached is often greater than 100 kg N ha^{-1} $year^{-1}$, the actual amount being dependent on the intensity of grazing carried out. The more intensively a field is grazed the more N is returned to the field in the form of dung and urine, thus the quantity of nitrate leaching from grazed grassland is related to the amount of N excreted in the field by grazing ruminants. High rates of nitrate leaching from grassland indicate that the plants' requirements have been exceeded by the application of N fertiliser and the return of unutilised herbage N from ruminants (which includes slurry and dirty water); the excess also includes mineralised soil organic matter and atmospheric deposition.

6.2.2 Quantity of nitrate leached from cut grassland

As mentioned earlier, nitrate leaching from cut grassland is generally low. Webster and Dowdell (1984a) observed that when no fertiliser was applied annual losses of nitrate were 3.8 kg N ha^{-1} with a mean soil drainage water concentration of 1 mg NO_3-N l^{-1}. Nitrate leaching from cut grassland is low if the rate of fertiliser N is no more than the optimum for grass growth at the particular location. Barraclough *et al.* (1983) observed that fertiliser additions up to 400 kg N ha^{-1} $year^{-1}$ could be applied to cut grass without breaching the EU MAC of 11.3 mg NO_3-N l^{-1}. This safe rate of 400 kg N ha^{-1} $year^{-1}$ applied to cut grass was also observed by Prins *et al.* (1988). Estavillo *et al.* (1996) estimated that only 5% of the 240-290 kg N ha^{-1} applied to cut grass was lost via leaching.

When cut grassland receives fertiliser N >400 kg ha^{-1} $year^{-1}$ substantial amounts of nitrate can be lost via leaching. Garwood and Ryden (1986) showed increases in the quantity of nitrate leached on a well drained soil from 15 to 145 kg N ha^{-1} leached when the fertiliser application was increased from 250 to 500 kg N ha^{-1} $year^{-1}$.

Application of nutrients to plots in amounts greater than the immediate plant requirements or before heavy rainfall events increases the risk of nitrate leaching to groundwater. Ryan and Fanning (1996) applied 300 kg N ha^{-1} as fertiliser to a growing sward in lysimeters containing a range of Irish soils after which they applied slurry in December and February at a rate of 120 kg N ha^{-1}. They found that the leachate from all but one soil type breached the EU limit of 11.3 mg N l^{-1}. Froment *et al.* (1992) also observed that 40% of N in manures applied during autumn and winter was lost by leaching; the loss of nitrate was proportional to the inorganic N content of the manures. Thus there was no apparent uptake of manure N by the crop.

Climatic control on the quantity of nitrate leached from cut grassland includes leaching after the grassland was exposed to drought conditions, such as observed by Garwood and Ryden (1986) who found increased nitrate leaching under drought conditions from 15 to 184 kg N ha^{-1} $year^{-1}$ and from 145 to 590 kg N ha^{-1} $year^{-1}$ for N fertiliser application rates of 250 and 500 kg N ha^{-1} $year^{-1}$, respectively. Webster and Dowdell (1984b) observed a doubling of nitrate concentration in drainage water from cut grass lysimeters when a drought was imposed on the lysimeters. Drought conditions in grassland soils decrease plant uptake of N thus increasing the amount of N at risk of leaching upon re-wetting of the soil after the drought when there is an increase in soil organic matter mineralisation (Whitehead, 1995). This issue is discussed in greater depth in section 6.2.4.

To summarise, the quantity of N leached from cut grassland swards is low when the N application rate is < 400 kg N ha^{-1} and if the N is applied corresponding to the need of the grass. Extreme weather events such as heavy rainfall after fertiliser application or after drought periods if N was applied during the drought when plant growth would be limited by lack of water both can cause rates of N leaching which breach the EU MAC of 11.3 mg N l^{-1}.

6.2.3 Quantity of nitrate leached from grazed grassland

As discussed in section 3.4.2 grazing dairy cows excrete between 80 and 115 kg N ha^{-1} $year^{-1}$ in the urine form and about 45 kg N ha^{-1} $year^{-1}$ in faecal form (Salette, 1996); thus the actual amount of N received by grazed grassland is considerably higher than the load of N received by cut grassland. Nitrate leaching is therefore affected more by the presence of urine patches than dung patches as the majority of the N in urine is in an available form whereas in faeces 45-64% of the N is in an insoluble organic form.

The proportion of grassland affected by excreta depends on stocking density, length of grazing period, frequency of excretion, the area covered by individual excreta patches and the degree of uniformity with which excreta are distributed (Garrett, 1991). Afzal and Adams (1992) estimated that after a 200 day grazing season with a stocking rate of 3 cattle ha^{-1}, 30% of the pasture was affected by dung and urine excretal returns with greater than 90% of this due to urine. An estimated 200 kg N ha^{-1} was excreted non uniformly to an area equating to 30% of the plot, representing a load of 667 kg N ha^{-1} to excreta-affected areas. Addiscott (1996) reports areas affected by urinal N returns of 15-20% of the plot whereas faecal affected areas were ~50% smaller than urine affected areas ranging from 7 to 10% of the plot. Hack-ten Broeke *et al.* (1996) estimated that between 5 and 23% of their monitoring plot was affected by urine deposition.

The first report of nitrate leaching occurring from intensively grazed swards came from New Zealand, when Walker (1962) reported substantial amounts of nitrate lost through leaching. The paper which really highlighted the effect of grazing on the quantity of nitrate leached was Ryden *et al.* (1984) who showed 5.6 times more nitrate leached from grazed grassland versus cut grassland.

Using higher rates of N fertiliser enables more animals to be kept i.e. up to a maximum of 6 to 10 ha^{-1}, and the productivity per hectare increases accordingly (van Burgh *et al.*, 1981). However productivity per animal shows a sharp decrease as the stocking rate increases. More N applied thus seems to imply more animals excreting and more excretion per animal. Scholefield *et al.* (1993) showed a larger increase in the quantity of nitrate leached when the fertiliser input was increased from 200 to 400 kg N ha^{-1} than when the fertiliser application was increased from 0 to 200 kg N ha^{-1}. Thorn (1985) reported no significant relationship between nitrate leaching and fertiliser application rate in Ireland, although at N fertiliser application rates <210 kg N ha^{-1} nitrate leaching varied from 8 to 40 kg N ha^{-1}. At rates >210 kg N ha^{-1} the quantity of nitrate leached varied considerably from 9 to 221 kg N ha^{-1}.

In Northern Ireland on drained plots grazed by beef cattle, which received N fertiliser at the rate of 100, 200, 300, 400, and 500 kg N ha^{-1}, average N leaching losses were 18, 25, 42, 72, and 64 kg N ha^{-1}, respectively (Watson *et al.*, 1992).

Ledgard *et al.* (1996a) observed that on grass/clover swards a fertiliser rate of 360 kg N ha^{-1} was excessive compared to a rate of 225 kg N ha^{-1} as there was only a little extra milk produced and N losses were enhanced, the maximum drainage water concentrations observed being 60 mg N l^{-1}. At 360 kg N ha^{-1} the clover and N_2 fixation was severely restricted and thus the actual N available to the plants in plots receiving 225 kg N ha^{-1} was larger than just fertiliser N applied (due to the contribution by clover) and this may account for only slight differences in milk production from the two treatments.

6.2.4 Effects of drought on nitrate leaching

Drought is defined as a period of 15 consecutive days, during which not more than 0.2 mm of rain fell and dry spells are when no more than 1.0 mm of rain fell in the same period (Keane, 1992). Tyson *et al.* (1997) reported a significant correlation between winter nitrate leaching and the preceding summer's maximum soil moisture deficit (SMD) over a 13 year period with the highest losses following dry summers. Jordan and Smith (1985) observed high nitrate export in drainage water from a six hectare grazed grassland and attributed the higher than average losses to be due to more rapid mineralisation and nitrification upon soil re-wetting after a prolonged drought. Harpstead and Brage (1958) and Birch (1960) observed that the longer a soil is in an air-dry state, the more N and C are mineralised upon re-wetting. The quantities of C and N mineralised are proportional to the C content of the soil and are a linear function of the log of the time the soil was in an air-dry state. Garwood and Tyson (1973) recorded an increase in nitrate losses in drainage from grassland lysimeters receiving 250 kg N ha^{-1} from 15 to 145 kg N ha^{-1} following a summer drought.

Increased mineralisation of soil organic matter was observed by Herlihy (1979) when mineralisation rates in three Irish soils, which were subjected to fluctuating soil moisture, were compared to soils which were artificially kept at field capacity. Mineralisation peaks increased from 64 to 79 μg N g^{-1} dry soil per unit time when the fluctuating soil moisture was compared to a soil incubated at field capacity.

When uptake of N during the growing season is restricted by drought the quantity of nitrate leached is likely to be high (Jordan and Smith, 1985). This was observed by Garwood and Ryden (1986) who observed a dramatic increase in the quantity of nitrate leached from an average of 145 kg N ha^{-1} $year^{-1}$ to 590 kg N ha^{-1} $year^{-1}$ due to drought and the fact that N fertilisation was applied at the pre-determined rates despite the summer drought conditions.

Irrigation of grassland is generally assumed to increase the risk of nitrate leaching, but under controlled conditions, when irrigation is not excessively applied, it can decrease the quantity of nitrate leached from the soil due to increased uptake of applied fertiliser N by the grass crop (Rawitz *et al.*, 1980). Webster and Dowdell (1984b) observed increased nitrate leaching when grass lysimeters were subjected to a two week drought, whereas an irrigation of 120% of the average rainfall caused no increase in nitrate leaching.

6.2.5 Application Timing

Hack-ten Broeke *et al.* (1996) estimated that urine deposition in July had a 10% risk of increasing the soil solution nitrate-N concentration to greater than the EU MAC of 11.3 mg N l^{-1} whereas urine application in September had a 25% risk. Stout *et al.* (1997) also observed that the quantity of nitrate leaching increased from 18% when applied in spring to 28 and 31% of the urine N applied in summer and autumn. Only 2% of N applied as faeces during the summer was leached which was not significantly different from the zero N control treatment.

In Ireland, Sherwood and Fanning (1986) observed that 3% of N applied as urine in May and August remained in the soil profile in late November whereas 30-50% of that applied in September and November remained and was therefore susceptible to leaching. This finding has implications for the recently increased practice of extended autumn grazing.

Garwood and Ryden (1986) marked urine patches and sampled them in November to estimate the amount of nitrate available for leaching and they concluded that there were substantial amounts of nitrate found at depths greater than 1 m although a soil moisture deficit of 15 mm was present. This indicated that there may have been preferential flow of urine through macropores in the soil which is supported by an earlier study (Ryden *et al.*, 1984) which observed peak ammonium concentrations at a depth of 1 m whereas the nitrate peak was found slightly deeper. The possible movement of urine via macropores was also observed by Williams *et al.* (1990) as urine moved rapidly to a depth greater than 15 cm in soils with an appreciable number of macropores and less than 50% of the urea at this depth had been hydrolysed. The rapid infiltration of urine into soils reduces the effect which ammonia volatilisation would have on decreasing the amount of nitrate which would subsequently be available for leaching.

6.2.6 The effect of soil physical properties on nitrate leaching

The quantity of nitrate leached from a soil depends greatly on its porosity and water holding capacity, as these factors affect the quantity of water required to re-wet the topsoil and to cause leaching from it. The more water a soil can hold before leaching occurs, the lower is the risk of nitrate being leached from that soil. A heavy rainfall event during a summer period when soils have high concentrations of nitrate present may cause movement of nitrate beneath the rooting zone on soils with a low water-holding capacity but this may not occur in a soil with a high water-holding capacity.

The pore distribution in a soil is very important affecting the ratio of mobile to non-mobile water and thus the extent to which water and nitrate in micropores is by-passed. Bergstrom (1995) compared soils with and without preferential flow paths and found lower nitrate concentrations in drainage from lysimeters with preferential flow paths due to leachate by-passing the majority of the soil matrix where the nitrate was evenly distributed. Booltink (1995) found low nitrate leaching on a structured soil when the top soil was depleted of N by plant uptake. However, when N in the top soil increased then nitrate leaching increased but the subsoil nitrate concentrations did not change due to the by passing of the soil matrix at depth. The presence of preferential flow paths was characterised by an almost immediate increase in the water table level after rainfall, with a time lag of between 30 and 100 minutes after rainfall ceased.

Applications of 380 kg N ha^{-1} $year^{-1}$ to cut grassland led to the leaching of 20 kg N ha^{-1} $year^{-1}$ for a clay soil and 70 kg N ha^{-1} $year^{-1}$ for a sandy soil (Steenvoorden *et al.*, 1986). A study on cut grass lysimeters showed higher rates of nitrate leaching from a sandy free-draining soil of 87 kg N ha^{-1} $year^{-1}$ compared to 34 kg N ha^{-1} $year^{-1}$ from a loam soil (Garwood and Ryden, 1986). When irrigation was applied to the lysimeters the quantity of nitrate leached was reduced from 87 to 64 kg N ha^{-1} $year^{-1}$ for the sandy soil and from 34 to 14 kg N ha^{-1} $year^{-1}$ for the loam soil due to increased uptake by the grass which was limited by water availability in the non irrigated lysimeters.

Ryan and Fanning (1996) also report the significant effect that soil type had on nitrate concentrations in drainage water from cut grass lysimeters. Peak drainage nitrate concentrations were significantly lower from a poorly drained organic clay loam soil than from a well drained coarse sandy loam, with the clay loam remaining below the EU MAC for the duration of the two year trial whereas the coarse sandy loam breached the EU MAC of 11.3 mg N l^{-1} on six occasions.

The installation of field drainage to grazed or cut grassland has a number of effects on the quantity of nitrate available for leaching. The lowering of the water table when field drainage is installed increases the aerated zone in the soil, thus decreasing denitrification and increasing the soil organic matter mineralisation rate. Scholefield *et al.* (1993) showed that 3 times more nitrate was leached from plots which had mole drains installed at a depth of 55 cm compared to similar plots with no drains.

Scholefield *et al.* (1988) observed, when drainage was installed in old grassland, an increase in nitrate leaching from 48 to 187 kg N ha^{-1} $year^{-1}$ for a sward receiving 400 kg N ha^{-1} $year^{-1}$ and denitrification decreased from 110 to 80 kg N ha^{-1} $year^{-1}$. The larger increase in leaching compared to the reduction in denitrification was attributed to soil organic matter mineralisation.

In a 13 year study Tyson *et al.* (1997) correlated the quantity of nitrate leached from a drained grazed grassland with the maximum soil moisture deficit from the preceding summer. The effect of low soil moisture during the summer would limit uptake of fertiliser N, reduce denitrification and upon re-wetting of the soil, cause an increase in soil organic matter mineralisation, all contributing to more N being leached during the winter. Soils with low water holding capacities which are highly permeable are likely to develop higher soil moisture deficits thus forming conditions for higher nitrate leaching rates later on.

6.2.7 Nitrate Leaching from slurry/manure and dirty water applications

As discussed in section 3.4.2, N in slurry is ~ 50% available as ammonium and the remaining 50% is in an insoluble organic form. When slurry is applied to grassland, N in the ammonium form is subject to volatilisation and runoff. The remaining ammonium-N is nitrified, forming nitrate which is then available for plant uptake and leaching. Application of slurry to grassland also increases the organic matter content of the soil, thus increasing the potential quantity of N mineralised. The quantity of N mineralised after the first year of slurry spreading has been reported as between 20% of the slurry organic N with cattle manures to >70% with poultry manures (Beauchamp and Paul, 1989). When plots receive repeated slurry applications then the quantity of N mineralised is cumulative, reflecting the historical application of slurries and manures.

The most important factors influencing nitrate leaching from animal manures are the load of N applied and the time of application. Sherwood and Fanning (1986) studied the effect which 3 yearly applications of pig slurry, containing 1400 kg total N ha^{-1} $year^{-1}$, had on nitrate leaching. On a free-draining soil 15% of the slurry N applied was estimated to have been lost by nitrate leaching whereas only 2% was lost on an impermeable gley soil. Chang and Entz (1996) observed increased nitrate leaching from 93 to 341 kg N ha^{-1} $year^{-1}$ when the rate of slurry application was increased from 60 to 180 m^3 ha^{-1}.

Timing of slurry applications follows the same general rules as for any fertiliser, whereby N should be applied when required by the growing crop to maximise plant uptake and minimise losses to the environment. However land application of manures and slurries has generally been carried out in autumn in Ireland due to a number of factors which include animals not being present on the land, farm machinery being used less in autumn, reduction of odour, and lack of storage capacity for the winter housing period.

Nitrate leaching from slurry and manure application to grassland is reduced considerably by ammonia volatilisation which can reduce the inorganic N content available for leaching by up to 60% within 24 hours of spreading (Carton *et al.*, 1994; Richards, 1998).

Techniques which reduce the amount of ammonia volatilised from land spread slurry, such as shallow injection, also increase the amount of soil N which increases the risk of nitrate leaching. Landspreading of slurries and manures during the autumn and winter, when soil temperatures are low and rainfall is greatest, reduces the amount of ammonia volatilisation with the result that the majority of the applied ammonium is available for nitrification and subsequent leaching.

Literature on the effect which the irrigation of dirty water has on nitrate leaching through the unsaturated zone is limited. An introduction to dirty water quality was presented in section 3.5.2. To summarise, the ammonium content of dirty water varies during the year; Ryan and Sherwood (1990) reported concentrations of 43 and 126 mg N l^{-1} for the winter and summer whereas ADAS *et al.* (1994) reported mean ammonium concentrations of 94 and 586 mg N l^{-1} for the winter and summer, respectively.

The effect of dirty water irrigation on nitrate leaching is presented in section 6.6.1. The irrigation of dirty water on grassland has a number of aspects which affect nitrate leaching through the unsaturated zone. The irrigation with dirty water could have two effects on nitrate leaching. If the soil is at field capacity, the application of dirty water would increase the amount of leaching, organic and ammoniacal N added in the dirty water would be nitrified in the soil thus forming nitrate which would be available for leaching. If the soil has a moisture deficit then the irrigation of dirty water provides moisture for plant uptake, thus reducing the amount of N in the soil, but the dirty water also contains nutrients which may be greater than the plant's requirements.

The summer period is generally characterised by soil moisture deficits in grassland soils due to evapotranspiration exceeding rainfall. Thus the application of dirty water could provide moisture which would increase plant uptake but the concentration of N in dirty water during the summer is high, possibly greater than the plant's requirements.

Winter application of dirty water occurs when the soil is normally at field capacity thus application of dirty water would increase the amount of water leaching through the unsaturated zone.

Although the ammoniacal content of dirty water is lower in the winter, it is high enough to breach the EU MAC for NO_3 in drinking water. Nitrification of the ammonium during the winter may be slow, thus increasing the period of time for the slow plant growth to utilise the applied N.

ADAS *et al.* (1994) found no effect of dirty water irrigation on nitrate leaching measured using ceramic cups which were installed at a depth of 100 cm, whereas dirty water was found to affect land drainage beneath areas of dirty water irrigation and rapid increases in BOD were observed after application rates of 2 mm hour^{-1}. Nitrate in drain flow was very low whereas ammonium concentrations were found to increase significantly up to 500 mg N l^{-1}.

ADAS *et al.* (1994) observed drain flow when soil moisture deficit was near 0 mm, but when dirty water was irrigated on soil which had a high soil moisture deficit (>100 mm) rates of up to 45 mm over two days could be applied with no subsequent drain flow. This indicates that at high soil moisture deficits soil could absorb high rates of dirty water applications with no effect on drainage.

Ryan (1990) observed increases in soil solution mean NO_3-N concentrations from a mean of 0.4 mg l^{-1} when no N was applied to the grazed grassland plot increasing to a mean of 29.5 mg l^{-1} in grassland plots which received dirty water.

6.2.8 Ploughing of permanent grassland

The ploughing of permanent grassland can cause a dramatic increase in the rate of nitrate leaching because of the amount of N released due to increased mineralisation of soil organic matter. At Rothamsted in the U.K., an average loss of 490 kg N ha^{-1} year^{-1} was reported for 3 years after the ploughing of old pasture (Jenkinson, 1986).

The historical fertilisation of grassland prior to ploughing controls how much N will be mineralised after ploughing; the more N applied to the grassland, the higher the rate of N mineralisation. When grassland was ploughed Webster and Dowdell (1984a) observed that plots which received no fertiliser N and 400 kg N ha^{-1} year^{-1} had nitrate leaching quantities of 7 and 70 kg N ha^{-1}, respectively. Young (1986) observed that the amount of nitrate leached from ploughed grassland increased with the age of the grassland, i.e. the amount of N leached in the 3 years after ploughing ranged from 100-120 kg N ha^{-1} for a one year old sward to 280-380 kg N ha^{-1} for a four year old sward.

6.3 Examination of nitrate leaching from study farm using inorganic soil N

6.3.1 Introduction

The objective of soil sampling to quantify nitrate leaching to groundwater was to supplement the information which was obtained using ceramic cups which sampled the active soil solution. This section estimates the quantity of N in the soil which is at risk of being leached to groundwater. The relationship between N leaching and the quantity of N applied to plots will then be examined.

6.3.2 Inorganic Soil N Methodology

Field Sampling

Soil samples were taken at 15 cm intervals down the soil profile using a 1 cm diameter screw auger to a depth of 75 or 90 cm. A total of 20 cores were taken randomly (although dung patches were deliberately not sampled) in each plot containing a borehole. Soil samples from the same depth were bulked together and returned to the laboratory for inorganic N determination. The samples were collected by staff at Teagasc, Johnstown Castle and analysed for the years 1990, 1991, 1992 and these analyses are included as part of the results section 6.3.3 so as to present some historical data on the quantity of N available for leaching. Soil samples for 1993, 1994, and 1995 were collected by the author.

Laboratory N Determination

Between 1990 and 1993 the laboratory methodology was slightly different i.e. 100 g of soil had 100 ml of KCl added in a 1 l Buchner flask after which the solution was shaken vigorously by hand and left to settle. The shaking process was repeated every 15 minutes for two hours. After two hours the samples were filtered through Whatman No. 2 filter paper and stored at <4°C before being analysed colorimetrically by a Teagasc technician. In 1994 and 1995 soil inorganic N was determined as described in the soil organic N mineralisation monitoring methodology in section 3.6.3.

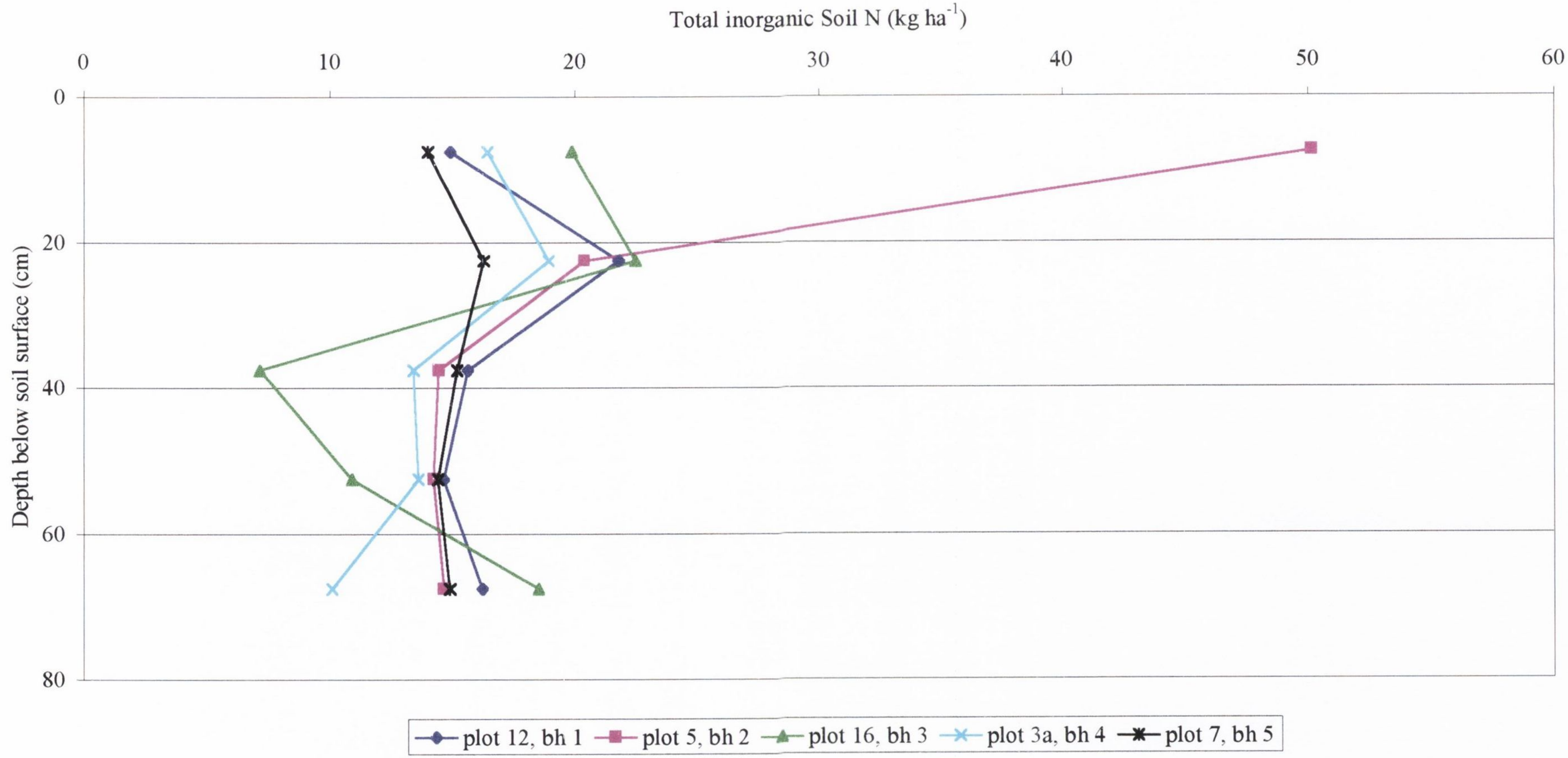


Figure 6.2 Inorganic soil N profiles from the 5 borehole plots in November 1993.

6.3.3 Soil Inorganic N Results

Concentrations of inorganic soil N

The results of the quantity of inorganic N available for leaching are presented separately for the years 1990 to 1993 and for 1994/95 to 1995/96 due to the different laboratory extraction methodologies used to determine soil inorganic N content.

The soil inorganic N profiles of the five borehole plots sampled in November 1993 can be seen in Figure 6.2. It is possible to see a wide variation in the N concentration at the 0-15 cm depth, with plot 5 containing borehole 2 having the highest N load, of 50 kg N ha^{-1}, available for leaching; plot 7, containing borehole 5, had the lowest N load of 14 kg N ha^{-1} available for leaching at the 0-15 cm depth.

In all plots, except plot 5, the soil inorganic N increases between the 0-15 and 15-30 cm sampling depths decreasing again to an almost constant level of 16 kg N ha^{-1}. At lower depths in plot 5 the soil inorganic N concentration decreases from 50 kg ha^{-1} at the 0-15 cm depth to an almost constant level at the 30-45 cm depth.

It is likely that N leaching in plot 16 occurred before the soil samples were taken as there was a significant increase in soil inorganic N concentration from 7 kg N ha^{-1}, at the 30-45 cm, to 19 kg N ha^{-1}, at the 60-75 cm depth. There appears to have been little movement of N down the soil profile in the other plots due to no similar increase occurring at the 60-75 cm depth and generally an increase in N concentration at the 15-30 cm depth.

The results of the investigation of soil N down the soil profile in November 1994 can be seen in Figure 6.3.

There is a wide variation in the initial soil N quantities from 0-15 cm below the soil surface, with the quantities varying from 19 to 39 kg N ha^{-1}. As in 1993, plot 5, which contains borehole 2, had the highest quantity of soil N at the 0-15 cm sampling depth and plot 16, which contains borehole 3, had the lowest quantity of soil N at the same depth.

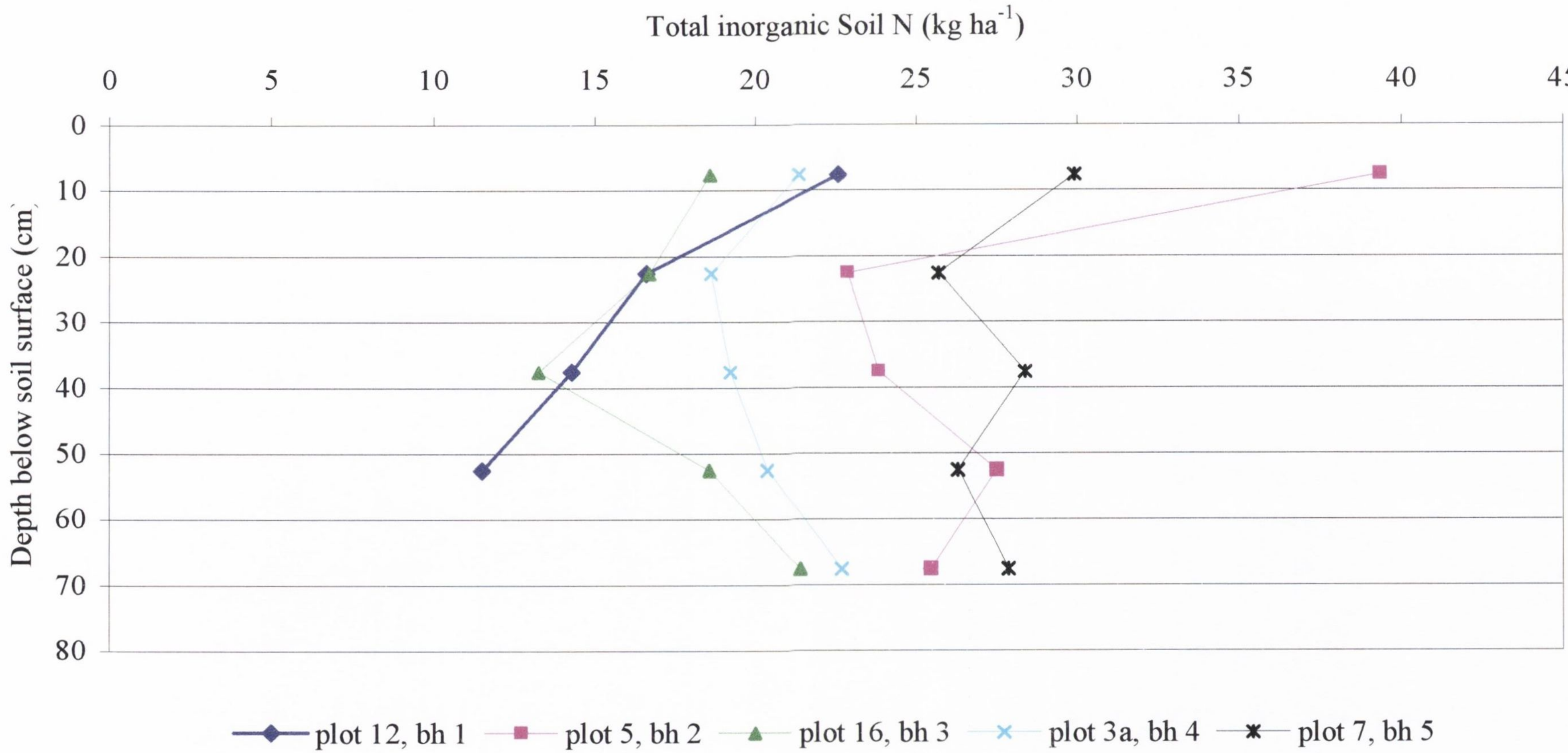


Figure 6.3 Inorganic soil N profiles from the 5 borehole plots in November 1994.

The distribution of inorganic soil N down the soil profile is interesting. As in 1993, the inorganic soil N in plot 16 increased dramatically from the 30- 45 to the 60-75 cm sampling depths, which again indicates movement of soil N before the soil samples were taken. Plots 5 and 3a also exhibit similar but smaller increases in soil N concentration down the profile, also indicating movement of N before soil samples were taken.

Inorganic soil N profiles of soil samples taken in November 1995 can be seen in Figure 6.4.

The soil samples taken in November 1995 had initial soil inorganic N levels at the 0-15 cm sampling depth varying from 8 to 16 kg N ha^{-1} which is significantly lower than in 1993 and 1994. An even more dramatic increase than previous years the inorganic soil N in plot 16 increased from 10.5 kg N ha^{-1} at the 0-15 cm depth to 43 kg N ha^{-1} at the 75-90 cm sampling depth, which indicates that soil inorganic N movement had commenced before soil sampling was carried out.

The other four plots also had increases of inorganic soil N quantity down the profile which confirms the observed movement of soil inorganic N in plot 16.

By examining the soil inorganic N distributions down the soil profile for the years 1993 to 1995, it is possible to observe that plot 16 always had high inorganic soil N at the 60-75 cm sampling depth and this indicates that N movement through the soil profile was faster in this plot than the other plots, suggesting a higher permeability of the soil or sub-soil in this plot.

In 1993 and 1994 all plots, except plot 16, had higher inorganic soil N quantities near to the soil surface than deeper down the soil profile, indicating a slower rate of N movement. In 1995 the soil sampling appears to have missed the start of leaching, with peak concentrations occurring down the soil profile. The timing of soil sampling and depth of soil sampling is therefore crucial to get a best estimate of the quantity of N leaching to groundwater.

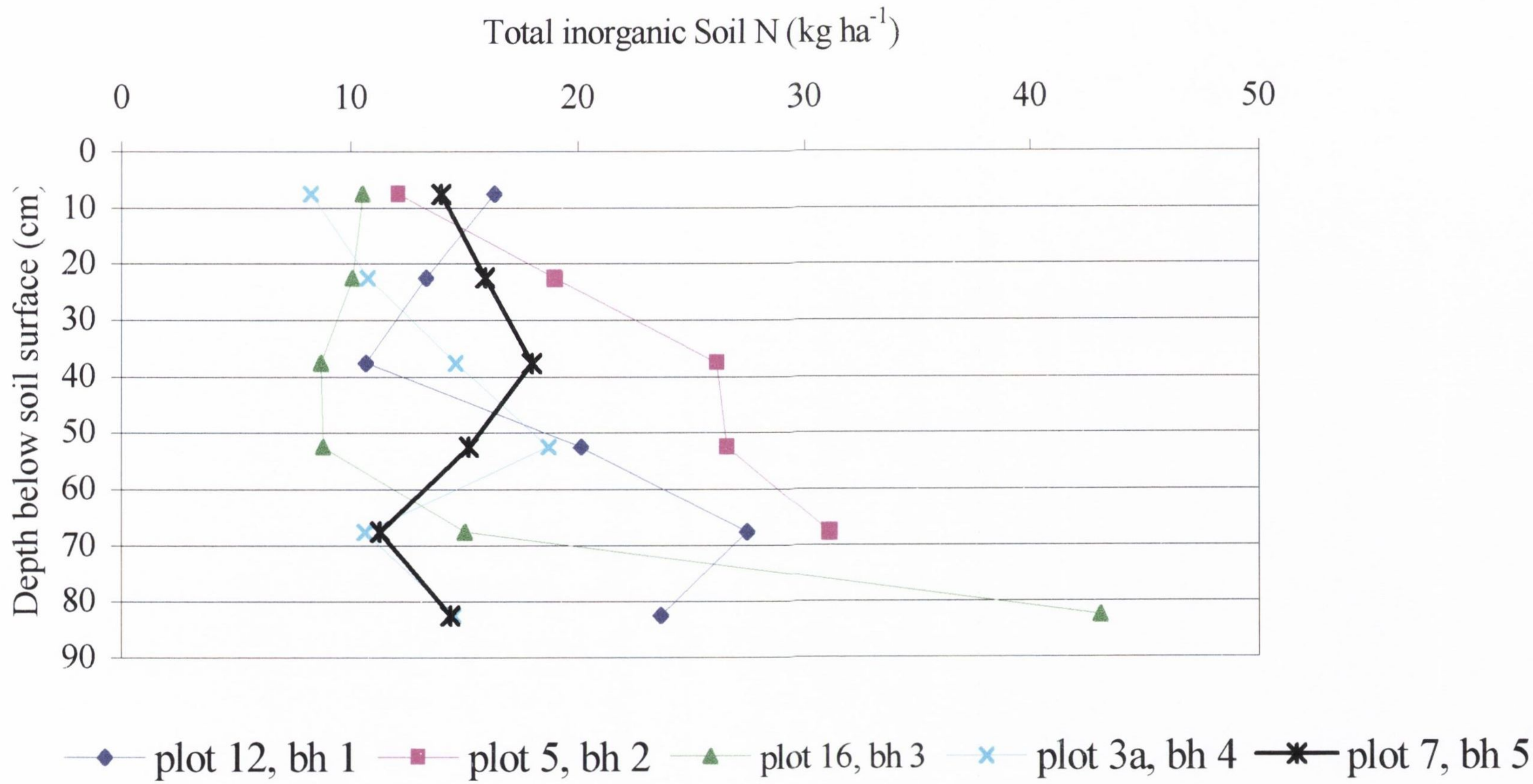


Figure 6.4 Inorganic soil N profiles from the 5 borehole plots in November 1995.

Quantity of soil inorganic N available for leaching, 1990 to 1993

The results of the four years 1990 to 1993 can be seen in Table 6.1. The annual mean quantity of N available for leaching varied from 59 to 78 kg N ha^{-1}.

Table 6.1 Total inorganic N in soil samples taken from 0 to 75 cm, (kg N ha^{-1}).

	Plot Number								
Year	12(1)‡	5(2)	16(3)	3a(4)	7(5)	4a	14	15	Mean
1990	28	43	43	ns	ns	36	207	ns	71
1991	52	89	53	ns	ns	ns	ns	79	68
1992	42	112	35	ns	ns	ns	45	ns	59
1993	84	89	58	75	86	ns	ns	ns	78

‡ Borehole number.
ns No sample taken.

There are three main observations which can be made from Table 6.1. Firstly, there is large variation in the quantity of inorganic soil N available for leaching between plots and years. The most extreme example of this can be seen in 1990, when the quantity of soil N available for leaching varied from 28 kg N ha^{-1} to 207 kg N ha^{-1}.

Secondly, there is tremendous annual variation in any plot in the quantity of soil N available for leaching. The most extreme example can be seen in plot 5, which contains borehole 2, where the quantity of soil N available for leaching varies between 43 kg N ha^{-1} in 1990 to a high of 112 kg N ha^{-1} in 1992.

Thirdly, it possible to see the effect which dirty water irrigation has on the quantity of N available in the soil to be leached to groundwater. Dirty water was applied to plot 14 during 1990 and plot 5 during 1992 and these plots had the highest inorganic soil N quantities of 207 and 112 kg N ha^{-1} available for leaching, respectively.
The 1995 soil sampling was carried out to a total depth of 90 cm, which was 15 cm more than in other years. The data (Table 6.2) show that when sampled to this deeper depth there was considerably more inorganic N available for leaching.

The total soil inorganic N load available for leaching in 1995 is shown in Table 6.2.

Table 6.2 Total inorganic N in soil samples taken from 0 to 75 cm for 1994 and 1995a, and 0 to 90 cm for 1995 b, (kg N ha^{-1}).

	Plot Number (borehole no.)						
Year	12 (1)	5 (2)	16 (3)	3a (4)	7 (5)	6	6a
Nov 1994	65	139	88	102	138	ns	ns
Nov 1995a	88	115	53	63	74	143	275
Nov 1995b	112	-	96	78	89	168	320

For 1995, the results are expressed as the total inorganic N (kg ha^{-1}) to a depth of 75 cm which is available to be leached. The 1995b results express the total inorganic nitrogen to a depth of 90 cm which is available to be leached. For borehole 2 the results for 1995a and 1995b are the same as it was not possible to take samples from 75-90 cm due to the stoniness of the soil and the presence of a fragipan at this depth prevented deeper augering.

Soil inorganic N quantities available for leaching in 1995 ranged from 53 to 275 kg N ha^{-1} at the 0-75 cm depth and the levels ranged from 78 to 320 kg N ha^{-1} from 0-90 cm. For the 0-75 cm depth the lowest amount of nitrogen which was available for leaching was observed in plot 16. The highest quantity of inorganic soil N available for leaching in a plot containing a borehole was 115 kg N ha^{-1} in plot 5.

Significant relationships ($P<0.02$) were observed between the quantity of inorganic soil N available for leaching (y) and the N loadings of TN (total N=x) and AN (available N=x) applied to each plot (as calculated in section 3.9.3). Figures 6.5 (a) and (b), show the years 1994 and 1995 respectively, which were the years when the soil N was extracted using a higher soil to KCl extractant ratio.

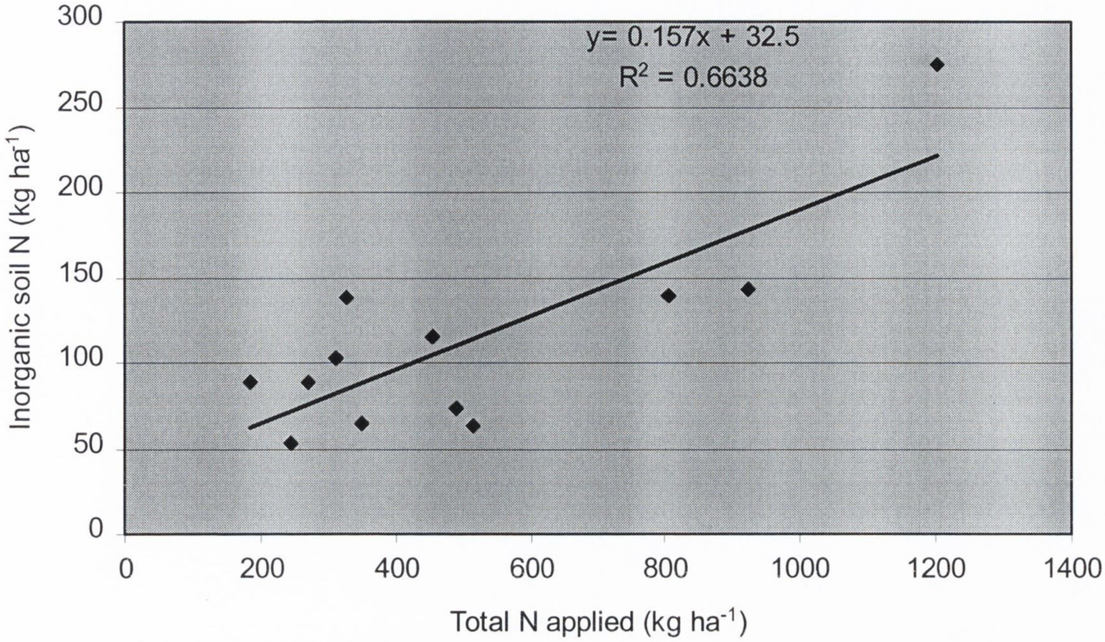


Figure 6.5 (a) Significant ($P<0.02$) relationship between inorganic soil N available for leaching 1994 and 1995 (0 to 75 cm depth) and TN applied to the plot.

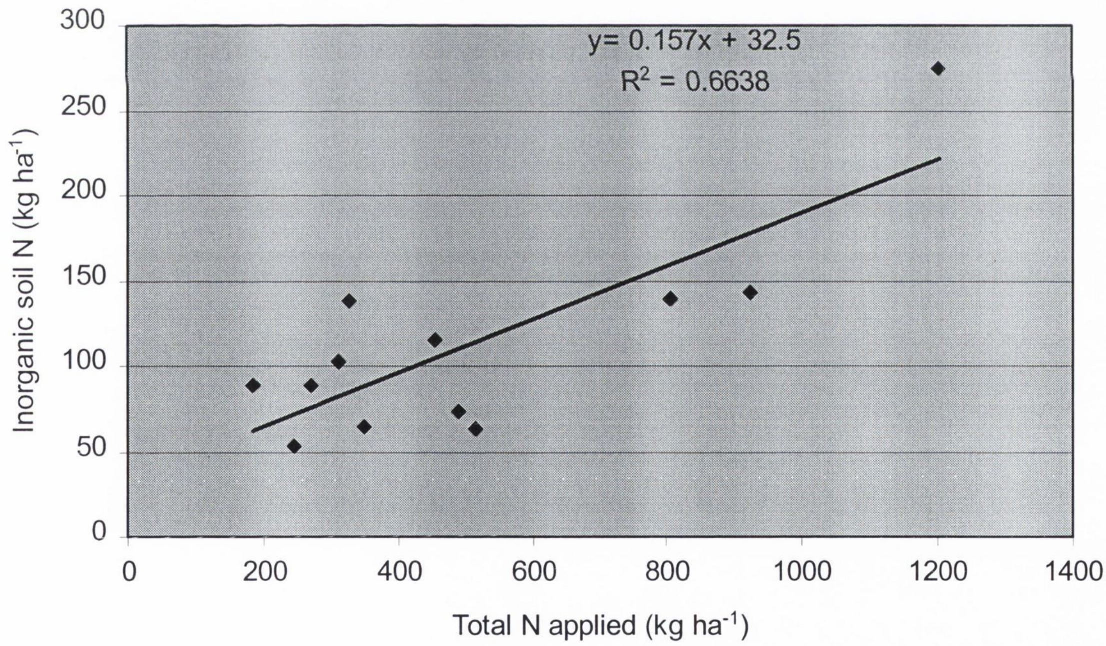


Figure 6.5 (b) Significant ($P<0.02$) relationship between inorganic soil N available for leaching 1994 and 1995 (0 to 75 cm depth) and AN (available N) applied.

6.4 Inorganic Soil N dynamics during 1995/96

6.4.1 Introduction

During the course of the soil organic N mineralisation determination, as described in section 3.6, soil inorganic N quantities from 0 to 10 cm below the soil surface were quantified for the purpose of calculating the pre-incubation soil inorganic N concentration. Pre-incubation soil inorganic N concentrations provide information about the temporal variation in soil inorganic N.

6.4.2 Methodology

The methodology for the field soil sampling and laboratory determination of inorganic soil N is described in 3.6.3. To summarise, 4 soil cores (3 cm wide by 10 cm deep) were taken, in plots 5, 16, 3a, and 7. On return to the laboratory the soil inorganic N was extracted with 1m KCl. The inorganic NH_4-N and NO_3-N was then determined colorimetrically by a Teagasc technician.

6.4.3 Results

Weekly variation of soil inorganic N was observed throughout the mineralisation monitoring period from April 1995 to March 1996 (Figure 6.6). The highest peak inorganic soil N level of 233 μg N g^{-1} dry soil occurred in plot 5 in late September. This large peak is directly attributable to the application of herbicide to the plot before ploughing and re-seeding. The increase in soil inorganic N from 15 to 233 μg N g^{-1} dry soil in 1 week, between the herbicide application and ploughing of the plot, can be seen in Figure 6.6. The application of herbicide led to a rapid degradation of the grass roots which released a large amount of N into the soil.

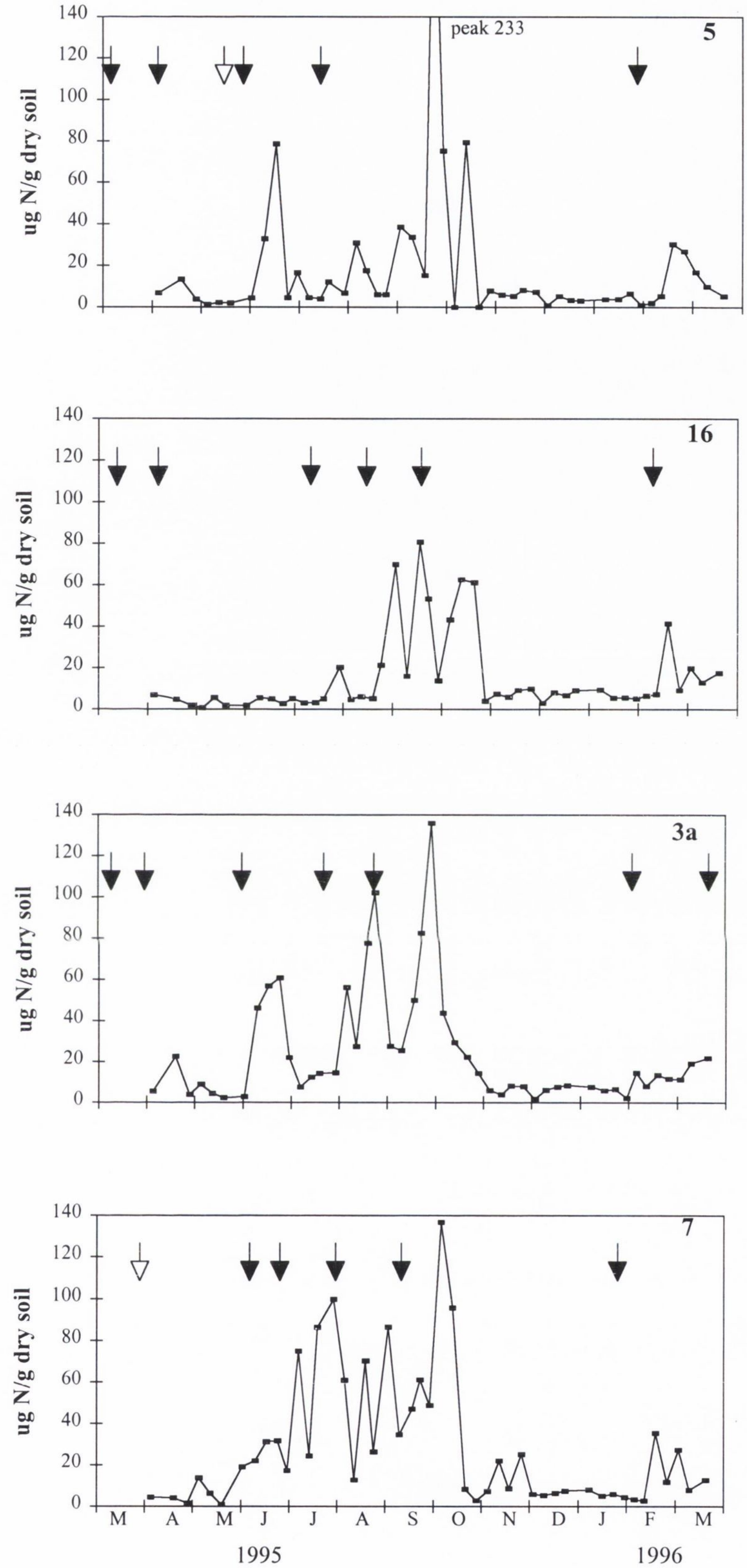


Figure 6.6 Temporal variation of inorganic soil N measured in plots 5, 3a, 16 and 7. (Solid arrows are fertiliser application dates, hollow arrows are slurry application dates.)

Plot 5 had three soil inorganic N peaks >50 μg N g^{-1} dry soil (Figure 6.6), i.e. in June, September and October. The increase in June was due to N fertilisation of the plot with inorganic and slurry fertilisers during May, whereas the increases in September and October were due to a combination of the spraying of the plot with herbicide in preparation for ploughing and re-seeding and the effect of soil re-wetting which was described in section 3.6.4.

Soil inorganic N levels in plot 3a had four peaks >50 μg N g^{-1} dry soil (Figure 6.6). There was one peak in June, two in August and one in late September/early October. Once again the highest peak soil inorganic N level was observed in late September/early October. The peaks in June and August are likely to be due to inorganic N fertilisation applied to the plots on the following dates 31/05/95, 25/07/95 and 22/08/95.

Plot 16 had the lowest inorganic soil N concentrations, between April and late August at <20 μg N g^{-1} dry soil (Figure 6.6). But during September and October there were 3 peaks > 50 μg N g^{-1} dry soil which are likely to be due to a combination of inorganic fertilisation and re-wetting of the soil causing N mineralisation. The sharp decreases in soil inorganic N between the 3 peaks could be due to a combination of plant uptake, nitrate leaching or immobilisation.

Inorganic soil N levels in plot 7 had the largest number of peaks >50 μg N g^{-1} dry soil, i.e., a total of 6 (Figure 6.6). The highest level of inorganic soil N was found in late September/early October again coinciding with the re-wetting of the soil after the summer drought which was observed in section 3.6.4, Figure 3.5.

Mean soil inorganic N on the farm, for the duration of the mineralisation monitoring period, ranged from 15 to 29 μg N g^{-1} dry soil (Table 6.3). Peak soil inorganic N concentrations ranged from 81 to 233 μg N g^{-1} dry soil, and the highest peak values occurred in late September/early October 1995.

Table 6.3 Summary of pre-incubation soil inorganic N concentrations for the duration of the monitoring period ie April 1995 to March 1996, (μg N g^{-1} dry soil).

Plot No. and Borehole No.	Range	Mean	SE of Mean	No. Samples
5 (2)	1-233	20	±5.7	44
16 (3)	1-181	15	±2.9	46
3a (4)	2-136	25	±4.2	47
7 (5)	1-137	29	±4.7	47

6.4.4 Discussion

Hatch *et al.* (1991) observed, in plots which received 420 kg N ha^{-1} $year^{-1}$ and which had been grazed the previous year but which was cut during the mineralisation measurements, generally low concentrations of inorganic soil N at ~20 μg N g^{-1} dry soil but on one occasion this increased to 57 μg N g^{-1} dry soil after a fertilisation event. Frequent peaks above 50 μg N g^{-1} dry soil were observed in the present study which were attributed to a combination of mineralisation and fertilisation.

Maximum soil inorganic N levels were observed in all plots in late September/early October. This period is also the start of leaching on the farm and thus this increased soil N is at risk of being leached to groundwater. At this time of high soil N levels, plots 16 and 7 had inorganic fertiliser applied to them in mid September. It is likely that the fertiliser addition would have increased the concentration of inorganic soil N but plots 5, and 3a showed similar increases in soil N during this period with no artificial fertiliser addition. Hatch *et al.* (1991) also observed increased inorganic soil N levels in autumn which were probably due to mineralisation of soil organic N. Herlihy (1979) observed peak mineralisation rates and peak inorganic soil N in three Irish soils in April/May and August to October. Herlihy (1979) also observed that when soil moisture was allowed to vary, the inorganic soil N concentrations were higher than when the soil moisture was kept constant. The soil moisture contents in the present study varied widely during September/October (Figure 3.5).

Jamieson *et al.* (1998) also observed that the highest mineralisation of soil organic N occurred in autumn and winter although the actual rate was significantly reduced with increased summer rainfall but summer drought increased the observed autumn/winter mineralisation.

6.5 Ballyderown Soil Solution Nitrate

6.5.1 Introduction

Nitrate concentration in the soil solution is a direct measure of the N lost from agricultural fields. The benefit of measuring the concentration of nitrate in soil solution percolate is that it helps determine whether or it is at risk of exceeding the EU MAC for nitrate concentration in drinking water. Soil analyses have traditionally been used to estimate the concentration of nitrate in percolation water but only soil solution sampling and analyses provide a direct measure of nitrate concentration.

Soil solution sampling was carried out in this project to determine the effect of agricultural practices on the concentration of nitrate leaching through soils. To ascertain the relationships between nitrate leaching and N applied loads, soil solution was sampled at different depths down the soil profile to evaluate whether denitrification was important in reducing the amount of nitrate reaching groundwater.

6.5.2 Methodology

Field equipment installation and sampling

Beside each borehole site ceramic cups (CCs) were installed in the soil at three depths, 50 cm, 100 cm and 150 cm (except at borehole 1 where CCs were installed at 50 cm only due to the depth to bedrock being ~ 70 cm); there were 3 replicates per depth at each site. The CCs were purchased from Soil Moisture Incorporated, California.

Vertical holes were drilled to the required depth, the soil was placed in stratigraphic sequence on a clean plastic sheet and a soil slurry was made by mixing de-ionised water with sieved soil from the same depth at which the CC was to be inserted (plate 6.1). The soil slurry was then poured into the hole and the CC was then pushed into the base of the hole to ensure good hydraulic contact. The hole was then stratigraphically back filled with native soil, tamped down using a wooden dowel and a bentonite seal was formed by pouring dry bentonite in to the hole (Figure 6.7) at 10 cm below the soil surface. Nylon tubes were then buried just below the grass sod and attached to Buchner flasks which were located beside the boreholes.

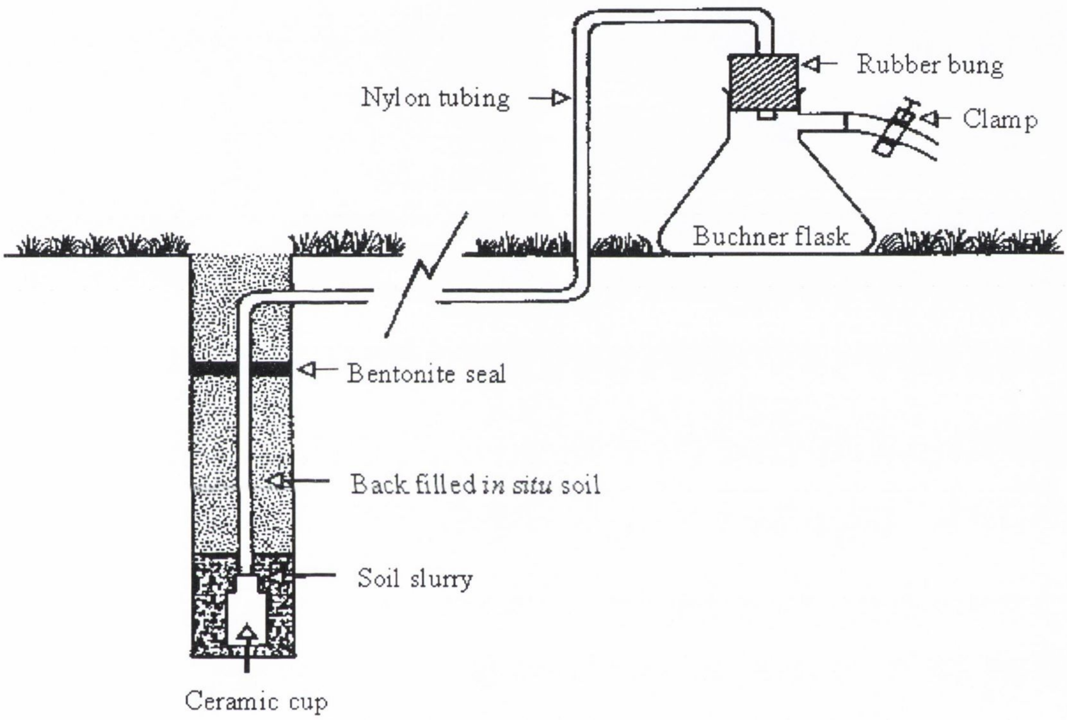


Figure 6.7 Schematic insertion of a ceramic cup.

The holes were drilled using a 5 cm diameter hand auger or when the soil was stony, a Giddens soil exploration drilling rig with a 12 cm diameter auger was used. All CCs at the 50 cm depth and all CCs at plot 7 were installed by hand, whereas the CCs at 100 and 150 cm in plots 5, 16, and 3a were installed using the Giddens drilling rig. In plot 12, CCs were installed only at 50 cm due to the thin soil at this site.

Soil solution was sampled using the falling head method whereby a 0.6 kPa vacuum was applied to the Buchner flask attached to each CC. This drew water through the CC and up the tube into the Buchner flask. Samples were taken weekly from October to June 1994/95 and 1995/96. During the 1993/1994 drainage season monitoring began in January 1994. Plate 6.2 shows the experimental set up at borehole 5.

Laboratory N determination

Nitrate-nitrogen was analysed on a Chemlab system 4 autoanalyser. A set of standards was analysed with each batch of samples and a calibration graph was constructed of peak height versus standard concentration for each analyte. The concentration of each analyte was determined from the calibration curve using a peak height analyser system. Quality control was carried out by the analyses of a drift and blank sample after every ten unknown samples. (The details of each analytical methodology may be seen in Appendix I)

6.5.3 Soil solution NO_3-N Results

The results of the nitrate movement through the unsaturated zone in the vicinity of the boreholes, as determined from soil solution nitrate concentrations from CC samples, will be presented in two different forms. Firstly, the concentration of nitrate (mg l^{-1}) moving through the unsaturated zone will be presented and discussed for the five plots which contain boreholes. Secondly, the data will be presented as load of nitrate leached from each plot and presented as kg N ha^{-1}.

Concentrations of nitrate moving through the unsaturated zone

Soil solution from the same depth below the soil surface will be presented for all plots which contained boreholes and discussed in terms of how the concentrations relate to the EU MAC concentration of 11.3 mg N l^{-1}.

For all plots and at all depths it is likely that the samples taken between January 1994 and June 1994 are unrepresentative due to the soil disturbance caused when installing the CC samplers. The results for 1993/94 are included but they will be treated with caution due to the unknown effect which installation has on the soil N dynamics.

Soil Solution NO_3-N sampled at 50 cm

A summary of soil solution NO_3-N concentrations which were measured at the 50 cm depth below the soil surface is presented in Table 6.4. The 5 plot mean presented in the table is the mean concentration of NO_3-N for all soil solution samples extracted on a particular date.

Table 6.4 Summary of soil solution NO_3-N concentrations (mg l^{-1}) measured at 50 cm depth.

Drainage Period		Plot No. (Borehole No.)					5 Plot
		12 (1)	5 (2)	16 (3)	3a (4)	7 (5)	Mean
Jan-June	Range†	1 - 22	3 - 17	0 - 20	1 - 6	1 - 43	3 - 28
94	Mean	7	8	4	3	10	8
Oct 94	Range	5 - 33	1 - 168	0 - 12	6 - 21	3 - 16	6 - 54
to Jun 95	Mean	26	42	8	12	14	20
Oct 95 to	Range	11 - 174	11 - 69	3 - 52	3 - 33	7 - 74	10 - 73
Feb 96	Mean	51	37	20	14	25	31

† The range is the minimum and maximum observed concentration.

Samples taken in 1993/94 had generally lower mean NO_3-N concentrations for all plots when compared to 1994/95 and 1995/96. This is in part due to sampling beginning in January 1994, and thus it is likely that the peak NO_3-N concentration in the soil solution percolating through the soil, after the start of autumn leaching, had already passed this sampling depth of 50 cm. Another factor which could have affected the NO_3-N concentrations was that the cups were newly installed and thus, as already stated, the effect of installation on NO_3-N leaching is unknown. Nitrate concentrations in excess of the EU MAC occurred in all plots except plot 3a and this is likely to be due to the fact that the CCs did not sample soil solution for the first 2 weeks, which corresponds to the time of peak NO_3-N concentrations in the other plots (Figure 6.8).

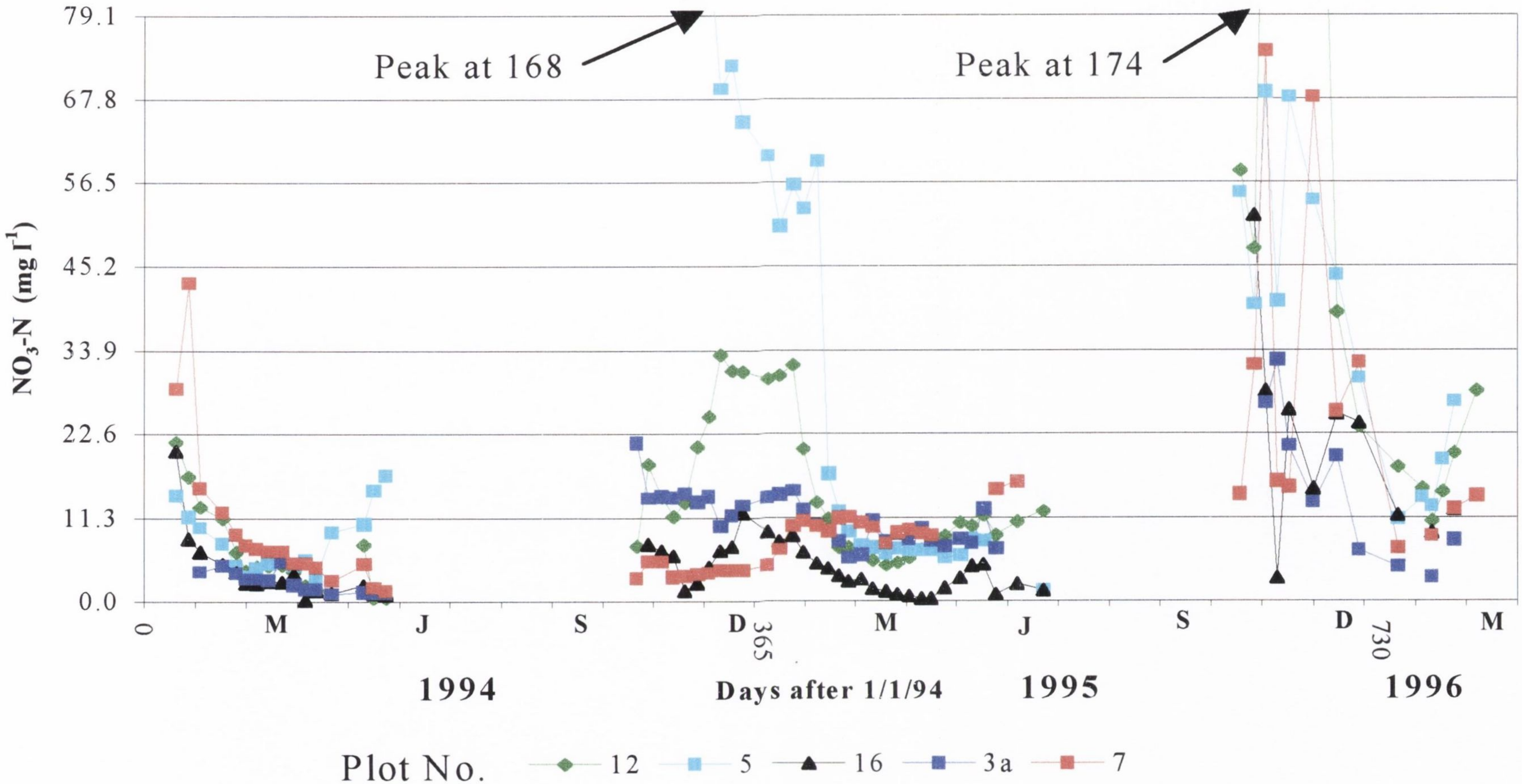


Figure 6.8 Soil solution NO_3-N concentrations sampled at a depth of 50 cm, in plots 12, 5, 16, 3a, and 7.

In the 1994/95 drainage season, all plots, except 16, had mean NO_3-N concentrations greater than the EU MAC (Table 6.4). The lowest mean NO_3-N concentration of 8 mg l^{-1} was observed in plot 16, but on one occasion the soil solution from this plot had NO_3-N greater than 11.3 mg l^{-1}. Plot 5 had the highest mean NO_3-N concentration of 42 mg l^{1} and the highest peak concentration of 168 mg l^{-1} at the 50 cm sampling depth. The average NO_3-N concentration of all CC samples taken during the 1994/95 drainage period at the 50 cm depth was 20 mg l^{-1}, nearly twice the EU MAC for drinking water.

Concentrations of NO_3-N in the soil solution in 1995/96 were the highest of all the years at the 50 cm sampling depth. The average NO_3-N concentration of the 5 plots was 31 mg l^{-1}, which is significantly higher than the average of 20 mg l^{-1}, measured during 1994/95.

The mean nitrate concentrations during 1995/96, in plots 12, 16, and 7, increased when compared to 1994/95 whereas the mean concentrations in plots 5 and 3a decreased slightly. Peak NO_3-N concentrations in all plots in 95/96 exceeded the EU MAC and ranged from 33 to 174 mg l^{-1}. The mean peak NO_3-N concentration of 174 mg l^{-1}, was the highest NO_3-N concentration measured at any depth during the entire monitoring period and occurred on plot 12. A further concern about the increased NO_3-N concentrations in 1995/96, was that the minimum concentration measured was 11 mg l^{-1} in plots 12 and 5, slightly lower than the EU MAC.

The mean nitrate leaching concentrations for the three winter drainage periods can be seen in Figure 6.8. The peak NO_3-N concentrations of plot 5 in 1994/95 and in plot 12 in 1995/96 is not shown in the diagram but in Table 6.4 the NO_3-N peaks are shown to be 168 and 174 mg l^{-1}, respectively, for plots 5 and 12.

When the first soil solution samples were taken on 19/1/94 (day no. 19), plots 12, 5, 16 and 7 had high NO_3-N concentrations of between 14 and 29 mg l^{-1}, which then decreased with time. Plot 3a had an initial NO_3-N concentration of 4 mg l^{-1} when the first sample was retrieved on 3/2/94 (day no. 33) and this also decreased with time.

Towards the end of sampling in 1993/94, plot 5 had a significant increase in NO_3-N concentration from a low of 3.4 mg l^{-1} on 12/4/94 (day no. 101) to a second high of 17 mg l^{-1} on 23/5/94 (day no. 142). There were also slight increases in NO_3-N concentrations in plots 12 and 7, which both occurred on 10/5/94 (day no. 129), a week before the increase in plot 5.

Between 21/4/94 (day no.110, week 16) and 13/5/94 (day no. 132 , week 19) a total of 66 mm of effective rainfall fell which decreased the soil moisture deficit (SMD) (Appendix C.2). This quantity of effective rainfall appears to have been sufficient to move soil NO_3-N to the sampling depth of 50 cm in plot 5.

In 1994/95 the temporal variation of soil solution NO_3-N increased from a low concentration, which ranged from 3.1 mg l^{-1} (plot 7) to 132 mg l^{-1} (plot 5), to peaks which ranged from 10.8 to 168 mg l^{-1} for plots 7 and 5, respectively, then decreasing in spring. Plot 3a had a different NO_3-N pattern of leaching, the NO_3-N concentration decreased from a high of 21.4 mg l^{-1} at the start of sampling (day no. 290) to a low of 5.8 mg l^{-1} before increasing once more to a high of 12.5 mg l^{-1} on 11/5/95 (day no. 496).

Peak NO_3-N concentrations occurred on different dates in each plot, varying from 17/10/94(day no. 290) in plot 3a to 20/2/95 (day no. 416) in plot 7. After the occurrence of NO_3-N peaks, the concentrations decreased in all plots, except plot 7 where they remained relatively static.

As in 1993/94, the NO_3-N concentrations increased at the end of April 1995(day no. 482) and the beginning of May 1995 (day no. 496) in all plots, the increases in plots 12, 16 and 7 were the most pronounced. As in 1993/94 these increases in NO_3-N concentrations in late April and early May occurred after a number of effective rainfall events (Appendix C.3) and a slight decrease in soil moisture deficit.

Temporal variation of soil solution NO_3-N during 1995/96 was very similar to that observed in 1994/95, initially low NO_3-N concentrations increased to peak concentrations which ranged from 174 mg l^{-1} in plot 12 to 33 mg l^{-1} in plot 3a. The peak NO_3-N concentrations occurred in late October 1995 (day no. 662) and early November 1995 (day no. 676), a much shorter period than during the 1994/95 drainage season. All plots exceeded the EU MAC of 11.3 mg l^{-1} NO_3-N.

During February 1996 (day no. 773) the NO_3-N concentrations measured at 50 cm increased in all plots, with the exception of plot 3a. The increased NO_3-N concentrations occurred after an extremely wet week during which there was 77 mm of effective rainfall (Appendix C.4).

Soil Solution NO_3-N sampled at 100 cm

A summary of soil solution NO_3-N which was sampled at a depth of 100 cm below the soil surface, from 1994 to 1996, can be see in Table 6.5.

Table 6.5 Summary of soil solution NO_3-N concentrations (mg l^{-1}) measured at 100 cm depth.

Drainage period		Plot No. (Borehole No.) 5 (2)	16 (3)	3a (4)	7 (5)	Plot Mean
1993/94	Range†		3 - 30		5 - 33	4 - 33
	Mean		9		16	12
1994/95	Range	0- 46	3 - 10	7 - 69	8 - 61	5 - 32
	Mean	19	9	26	28	21
1995/96	Range	7 - 41	0 - 32	27 - 43	10 - 25	11 - 34
	Mean	27	19	37	18	24

† Range refers to the minimum and maximum observed concentrations.

During the drainage period 1993/94 only CCs in plots 16 and 7 yielded soil solution samples. As stated earlier these results are probably influenced by the installation process and this should be considered when interpreting the data from this period. Both plots had soil solution samples >11.3 mg l^{-1}, although plot 16 had a mean concentration < 11.3 mg l^{-1} NO_3-N, whereas plot 7 had a mean > 11.3 mg l^{-1}.

In all plots during 1994/95 apart from plot 16 maximum soil solution NO_3-N concentrations were >11.3 mg l^{-1}; the maximum concentration observed was 69 mg l^{-1} (plot 3a). The mean NO_3-N concentration at the 100 cm sampling depth was >11.3 mg l^{-1} for all plots, with the exception of plot 16 which had a mean of 9 mg l^{-1}.

During the 1995/96 all plots had mean NO_3-N concentrations > 11.3 mg l^{-1}; the four plot mean at 100 cm was 24 mg l^{-1}, which was more than double the EU MAC. The highest mean NO_3-N concentration of 37 mg l^{-1} was measured in plot 3a. All soil solution samples taken in plot 3a had NO_3-N concentrations >25 mg l^{-1}, which is more than double the EU MAC.

Temporal variation of soil solution NO_3-N concentrations sampled at 100 cm during the study can be seen in Figure 6.9.

Similar temporal variation of NO_3-N concentrations were observed at 50 and 100 cm sampling depths (Figures 6.8 and 6.9), whereby the NO_3-N concentrations increased from initially low concentrations to a peak before decreasing again with time.

The soil solution samples taken at the end of the 1993/94 drainage season (days 19 to 142) had peak concentrations when the first samples were taken (day no. 19), which decreased with time until sampling ceased at the end of May 1994 (day no. 142). Drainage water NO_3-N concentrations in plot 7 took longer to decrease to < 5 mg l^{-1}, compared to plot 16 which decreased more rapidly to this level.

During the 1994/95 drainage season peak concentrations occurred between January and February 1995 (days 368 to 397), except for plot 3a which had high initial NO_3-N concentrations on day no. 290 which decreased with time. The NO_3-N concentration increase in plot 5 from 22 to 42 mg l^{-1} was due to the fact that only one CC was sampling soil water at this depth and when a second CC began sampling, the average NO_3-N concentration increased. There was a significant increase in NO_3-N concentration in late April and early May 1995 (day no. 482 to 489) in all plots; this was also observed at the 50 cm sampling depth.

In 1994/95 plot 5 had a significantly lower peak NO_3-N concentrations of 46 mg l^{-1} at the 100 cm depth compared to 168 mg l^{-1} at the 50 cm depth. The likely cause of this is the fact that dirty water was irrigated on the area which contained only CCs at the 50 cm depth, thus the 100 cm soil solution samples do not reflect the effect of dirty water.

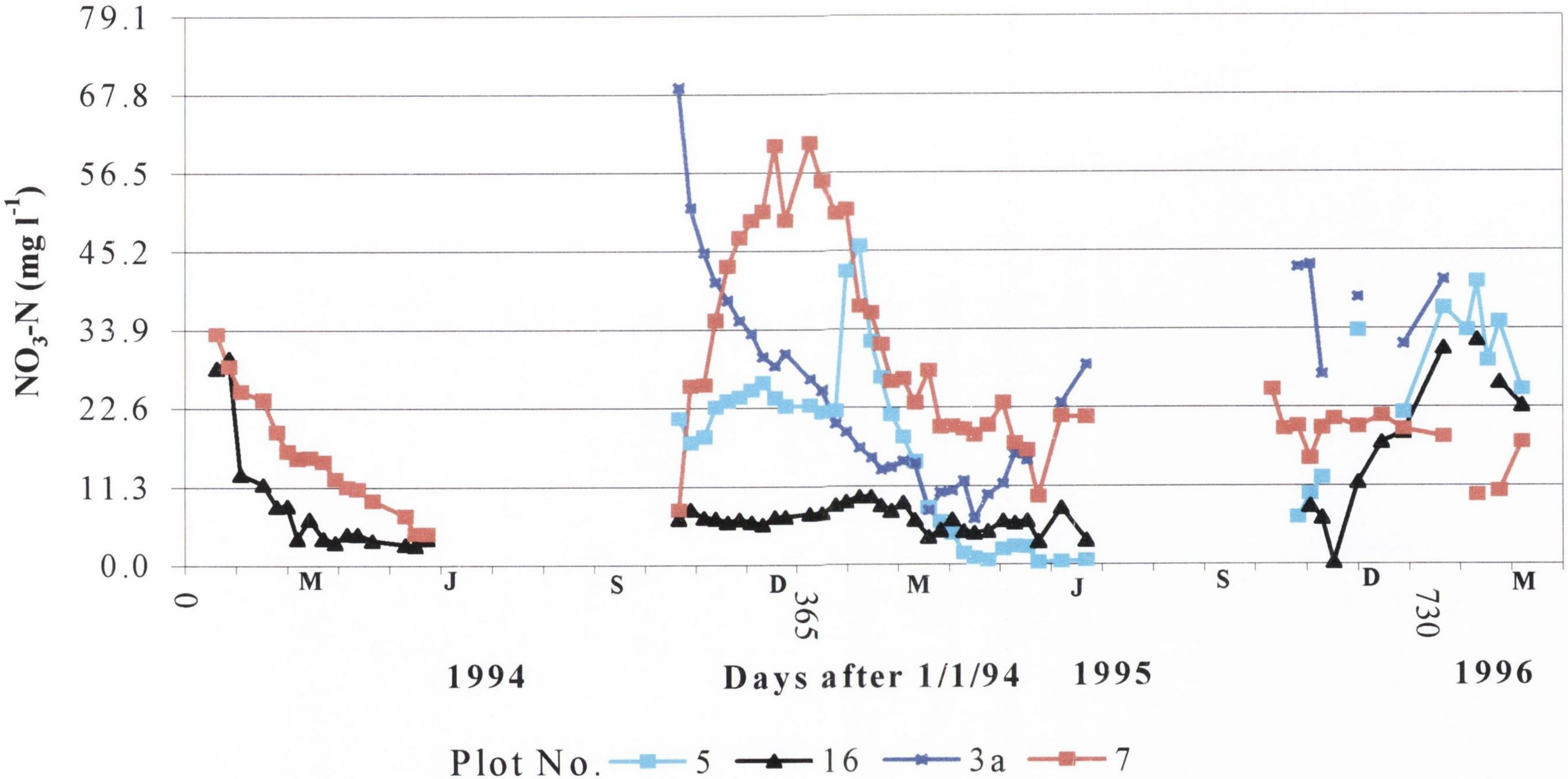


Figure 6.9 Soil solution NO_3-N concentrations sampled at a depth of 100 cm, in plots 5, 16, 3a, and 7.

Plots 3a and 7 had higher peak NO_3-N concentrations at the 100 cm depth of 69 and 61 mg l^{-1}, respectively, compared to 21 and 16 mg l^{-1} at the 50 cm depth. The differences between the peak concentrations measured in these plots at different depths could be caused by the deeper CCs sampling soil solution which had already passed the 50 cm sampling depth.

During the 1995/96 drainage season clear peaks in soil solution NO_3-N can be seen in plots 5 and 16 which both peaked on 30/1/96 (day no. 760). The NO_3-N peak in plot 5 was similar to the peak observed in 1994/95 whereas during the 1995/96 drainage season in plot 16 the NO_3-N peak was much greater than in 1994/95. The soil solution samples from plots 3a and 7 did not show any clear peak with the greatest NO_3-N concentrations observed during the first sampling on 17/10/95 and 2/10/95 (day no 655 and 640) for plots 3a and 7, respectively.

Soil solution samples from plot 3a were not as comprehensive as the other plots due to the CCs not returning samples for unknown reasons.

Soil Solution NO_3-N sampled at 150 cm

A summary of the soil solution NO_3-N concentrations is presented in Table 6.6.

Table 6.6 Summary of soil solution NO_3-N concentrations (mg l^{-1}) measured at 150 cm depth.

Drainage period		Plot No. (Borehole No.) 5 (2)	16 (3)	3a (4)	7 (5)	4 Plot Mean
1993/94	Range †				8 - 113	8 - 113
	Mean				48	51
1994/95	Range	8 - 41	4 - 62	7 - 37	12 - 64	13 - 51
	Mean	27	23	24	31	27
1995/96	Range	13 - 49	5 - 81	21 - 44	15 - 43	14 - 53
	Mean	30	24	31	25	30

† Range refers to the minimum and maximum observed concentrations.

During the 1993/94 drainage period, only CCs in plot 7 yielded soil solution samples. The maximum NO_3-N concentration observed was 113 mg l^{-1}, with a mean concentration of 48 mg l^{-1}.

All plots produced samples at the 150 cm depth during the 1994/95 drainage period. The EU MAC was breached by all the plots and the mean soil solution concentration in each plot sampled at 150 cm depth was also >11.3 mg l^{-1}, the four plot mean being 27 mg l^{-1}. Plots 16 and 3a had the lowest mean NO_3-N concentrations at the 150 cm depth but even these were double the EU MAC.

During the 1995/96 drainage period all borehole plots had mean NO_3-N concentrations > 11.3 mg l^{-1}, maximum concentrations ranged from 43 to 81 mg l^{-1}. The highest peak NO_3-N concentration of 81 mg l^{-1} was measured in plot 16, even though this plot had the lowest mean concentration of NO_3-N for the 1995/96 period.

Temporal variation of soil solution NO_3-N concentrations can be seen in Figure 6.10.

The NO_3-N variations during the 1993/94 period increased after the initial sample peaked at 113 mg l^{-1} on 3/2/94 (day no. 33). Whereas at the shallower depths of 50 and 100 cm maximum concentrations of NO_3-N were observed when sampling began.

Maximum and mean soil solution NO_3-N concentrations, sampled at 150 cm during the 1994/95 drainage period breached the EU MAC concentration of 11.3 mg l^{-1} in all plots. As at the shallower sampling depths, soil solution NO_3-N concentrations increased from low levels, ranging from 6 to 35 mg l^{-1}, to peak levels at the beginning of December 1994. Increases of soil solution NO_3-N concentrations during May 1995 were observed in all plots, although in plot 5 the increase was only about 1 mg l^{-1}, whereas in the other plots the increase ranged between 4 and 10 mg l^{-1}. When sampling ceased on 15/6/95, plots 3a and 7 had NO_3-N concentrations >11.3 mg l^{-1} whereas in the other two plots the concentrations had decreased to <11.3 mg l^{-1}.

Temporal variation of soil solution NO_3-N concentrations in 95/96 were similar to those observed in 1994/95, maximum concentrations occurred during December 1995, except in plot 5 where the peak concentration occurred in late January 1995. In plot 5 the soil solution NO_3-N remained >40 mg l^{-1} for two months, which is considerably longer than peak concentrations observed in other plots. When sampling was completed at the end of 2/96, all plots had soil

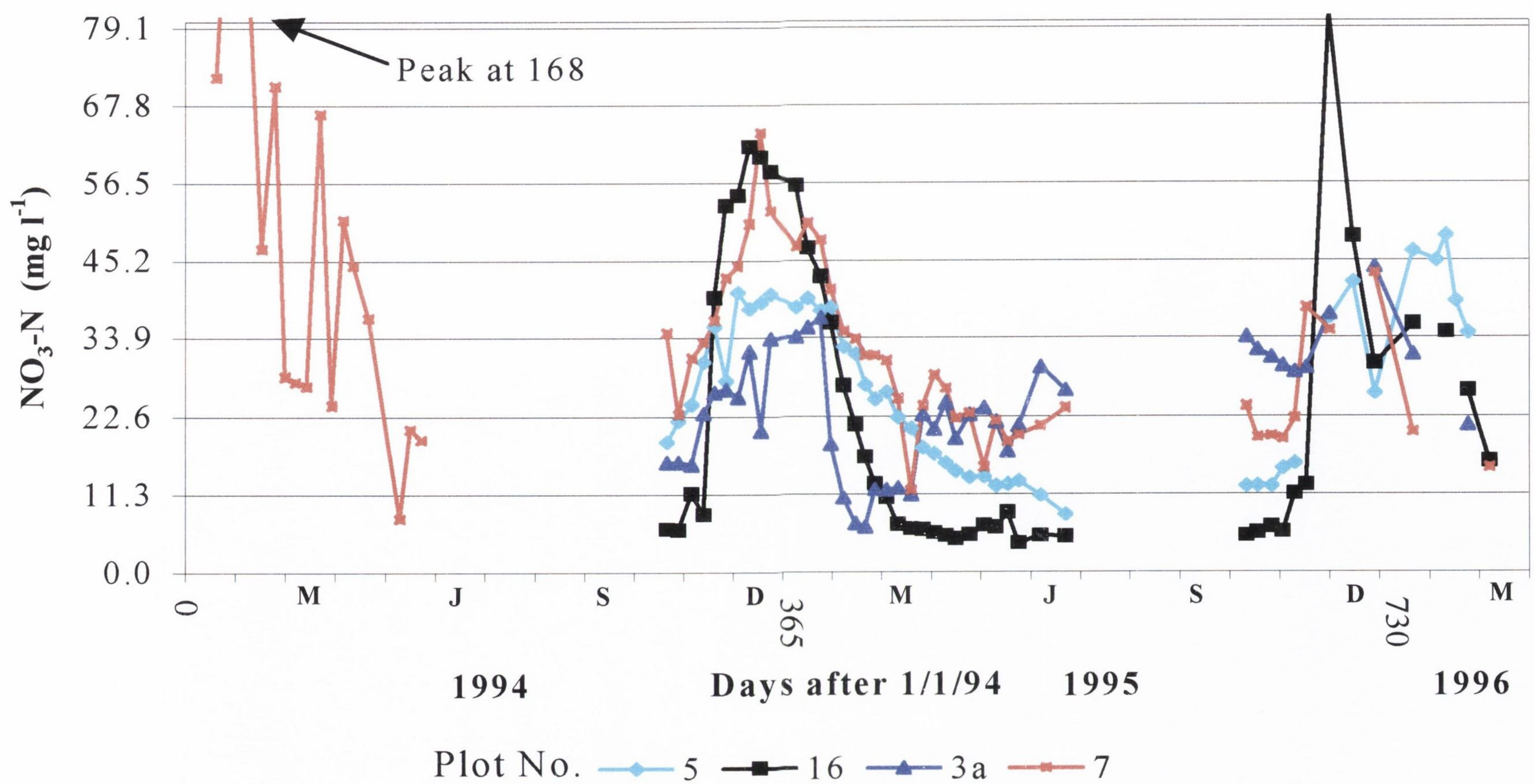


Figure 6.10 Soil solution NO_3-N concentrations sampled at a depth of 150 cm, in plots 5, 16, 3a, and 7.

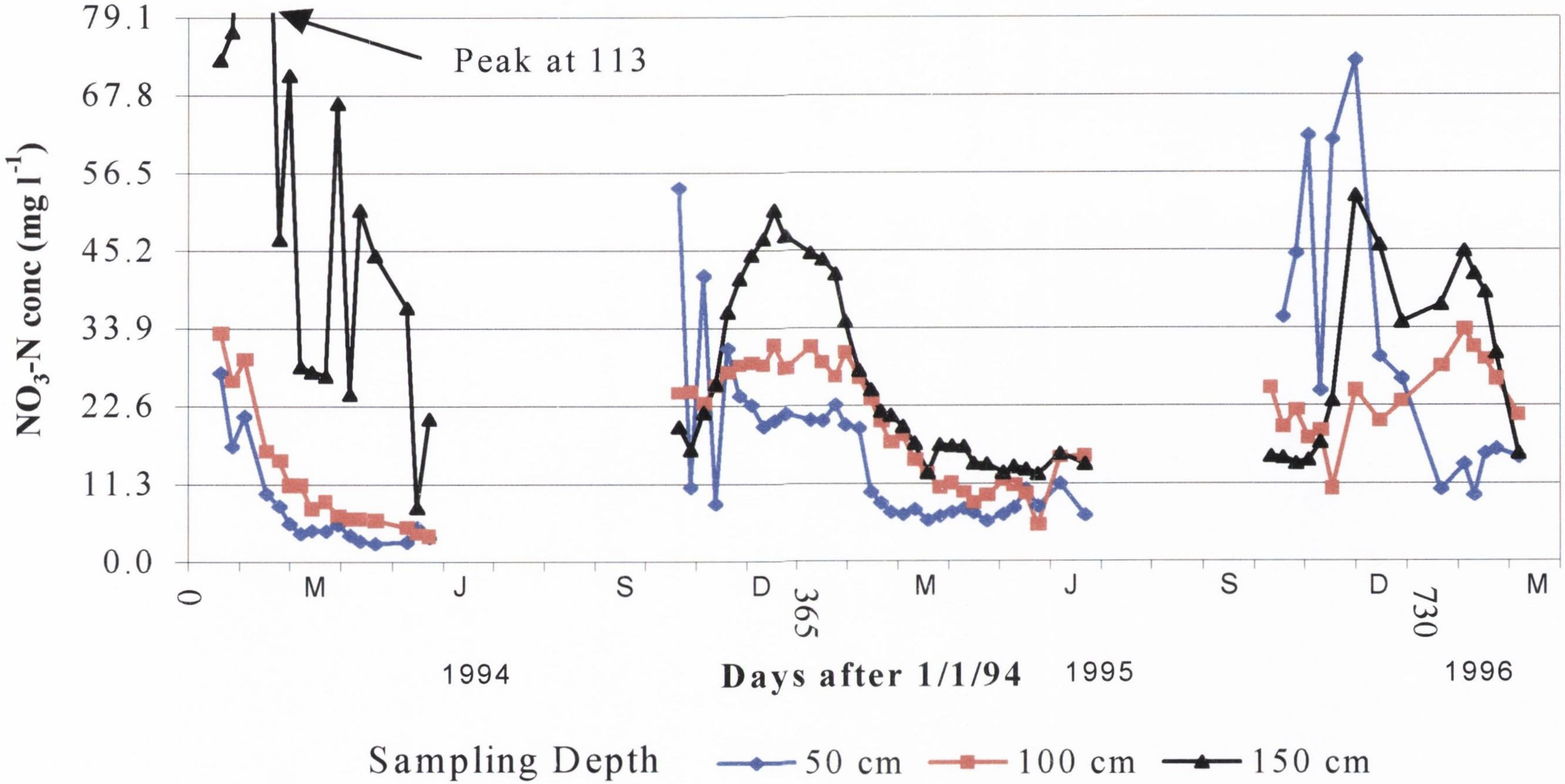


Figure 6.11 Mean soil solution NO_3-N concentrations measured at 50, 100 and 150 cm depths.

solution NO_3-N concentrations >11.3 mg l^{-1}.

6.5.4 Discussion of Mean Soil Solution NO_3-N concentrations

The mean of all plots taken at each depth below the soil surface was calculated for the purpose of visualising average leaching (Figure 6.11).

Regarding temporal variation of soil solution NO_3-N concentrations, at all sampling depths in most plots during 1994/95 and 1995/96 monitoring periods, the concentration of NO_3-N increases from an initially low concentration to a peak and then decreases again. This characteristic breakthrough curve of soil solution NO_3-N is reported by many workers (MacDuff *et al.*, 1992; Bergstrom, 1995; Ledgard *et al.*, 1996a; Ryan and Fanning, 1996).

Secondary NO_3-N peaks, after the maximum peak, have been attributed to application of N (fertiliser, slurry or mineralised) after leaching has already begun. Ryan and Fanning (1996) observed secondary peaks of nitrate leaching and attributed these to application of slurry in November and February. In the present study, increases of NO_3-N concentrations were observed in May/early June in most plots and this is likely to be due to fertiliser applications between January and April. Tyson *et al.* (1997) also observed increases in March and April, based on the mean leaching for a 13 year period, which were attributed to the first spring application of fertiliser.

Increases in the concentration of soil solution NO_3-N in May 1995 (day no. 485 to 516) observed in all plots, corresponded to week 21 which received 188 mm of effective rainfall (section 4.5.5). The effective rainfall caused an increase in soil moisture at between 0 and 140 cm deep as measured with the neutron probe. The rainfall in May was sufficiently high to cause leaching through the soil at a time of increasing inorganic soil N concentrations. It is possible to observe further increases in soil moisture (Figure 4.5, section 4.5.5) in June and August 1995, when the soil solution samples were not taken, thus leaching of NO_3-N may have also occurred during the summer.

6.5.5 Load of Nitrate leached

The estimated loads of N leached were calculated as the sum of using the soil solution NO_3-N concentrations and the estimated drainage volume, as presented in section 4.5.3.

Table 6.7 Estimated nitrate leaching loads (kg ha^{-1}) from 50, 100, 150 cm depths and estimated drainage volume sampled.

Plot no. and borehole (no.)	sampling depth (cm)	Sampling year 1993/94	1994/95	1995/96
plot 12 (1)	50	38	114	319
plot 5 (2)	50	33	421	194
	100		163	174
	150		206	225
plot 16 (3)	50	24	34	98
	100	43	51	131
	150		193	211
plot 3a (4)	50	10	78	58
	100		174	210
	150		137	196
plot 7 (5)	50	51	53	129
	100	78	254	109
	150	255	246	147

The load of N estimated to have been leached generally increases from the 50 to 150 cm sampling depths, such as in plot 16 where the estimated leached N load increases from 34 kg ha^{-1} at 50 cm to 193 kg ha^{-1} at 100 cm in 1994. The reason for increasing N load deeper down the soil profile is that at the shallower depths the start of leaching may have been missed, as hypothesised from the soil solution NO_3-N leaching curves which did not exhibit the characteristic breakthrough curves seen at deeper depths (section 6.5.3).

In plots 5 and 3a the N load leached did not increase with increasing sample depth each year. In 1994 the highest N load measured in plot 5 was sampled at 50 cm and this was due to dirty water being irrigated over the area containing the 50 cm CCs and not over the area containing the CCs at deeper depths.

The average load of N leached from Ballyderown can be seen in Table 6.8 which shows that the load of N leached increases with sampling depth.

Table 6.8 Average loads of nitrate leached (kg N ha^{-1}) from Ballyderown (mean of all plots).

Year	Drainage vol (mm)	Sample depth 50	100	150	s.e. mean (±) 50	100	150
93/94	387	31	60	255	7		
94/95	667	140	161	196	71	42	23
95/96	626	160	156	195	46	22	17

The mean loads of N leached from Ballyderown were similar for 1994 and 1995 at all sampling depths.

The relationship between NO_3-N leaching, as measured in soil solution samples at each depth, and TN and AN loads applied to each plot (section 3.9.3) was determined. No significant relationship existed between the load of N applied to each plot and the amount of N estimated to have been leached at any sampling depth through the soil, using CCs, whereas a significant relationship was shown to exist between inorganic soil N available for leaching, as shown by soil sampling in autumn, and TN and AN loads applied to each plot (section 6.3.3). A possible reason for no significant relationship being found between N leaching, as determined from soil solution samples and N loads applied, could be the small sample sizes. As only data collected in 1994/95 and 1995/96 was used; the sample sizes were 10 measurements for soil solution sampled at 50 cm and 8 samples for soil solution sampled at the deeper depths, whereas the sample size for comparison of N load applied and inorganic soil N in autumn was slightly larger.

The loads of NO_3-N leaching from the soils in Ballyderown are high. In a lysimeter study, Ryan (Pers. Com., 1998a) reported maximum leaching of 87 kg N ha^{-1} from a freely draining Elton (Co. Limerick) soil which had received 300 kg N as fertiliser and 124 kg N as slurry. Barraclough *et al.* (1983) reported losses of 8 to 54 kg N ha^{-1} from a sandy clay loam receiving 500 kg N ha^{-1} as fertiliser.

6.6 Nitrate leaching from dirty water applications at Ballyderown

6.6.1 Introduction to the effect of dirty water irrigation on nitrate leaching

A separate experiment was designed to determine the effect of dirty water application on nitrate leaching due to the observations made that when dirty water was applied to plot 5 high soil solution NO_3-N was observed in 1994/95 at the 50 cm sampling depth (6.4.3).

6.6.2 Methodology for determining the effect of dirty water irrigation on nitrate leaching

Between 11/4/95 and 11/2/96 dirty water was irrigated on plots 6 and 6a to simulate farming practice which was observed on the farm where dirty water was irrigated on one plot for a long period such as in plot 4a in 1994 and plot 3a in late 1994/early 1995 (see section 3.5.4).

The amount of nitrate leaching below the two plots (6 and 6a) was measured by both soil analyses and soil solution analyses from CCs. Soil samples were taken in November 1995 as described in section 6.3.2 and CCs were installed as described in section 6.5.2. Each plot had 12 CCs installed, which were located in groups of three in four areas of each plot. Each CC was installed at a depth of 50 cm below the soil surface and at a distance of 7 metres from the plot boundaries. The ceramic cups were installed in March 1995, and dirty water was applied to the plots as outlined in section 3.5.4.

6.6.3 Nitrate leaching from dirty water irrigation

The effect of excessive dirty water irrigation on soil inorganic N during 1995 can be seen in Figure 6.12.

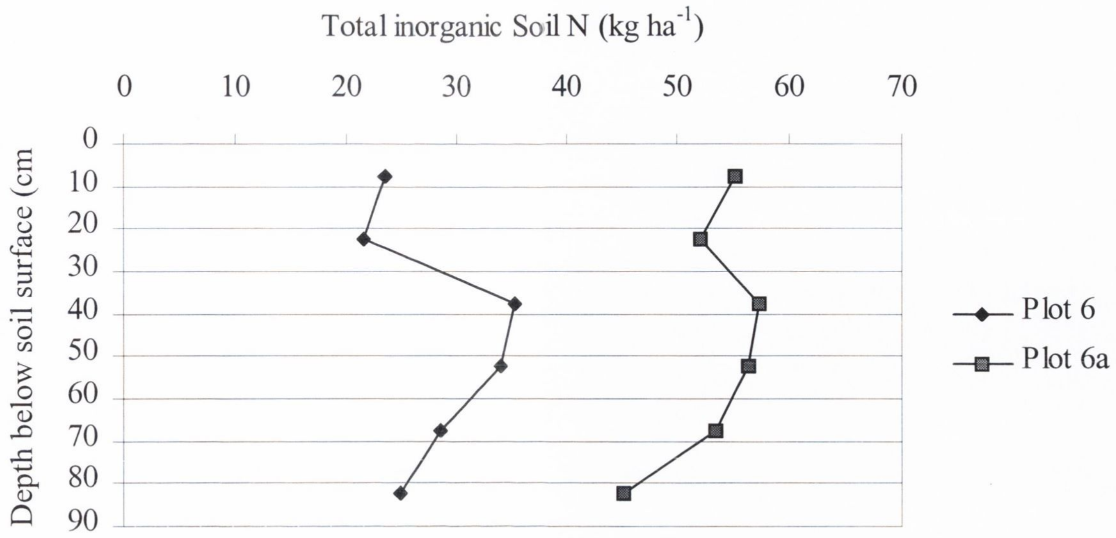


Figure 6.12 Soil inorganic N profiles from plots 6 and 6a, in November 1995 which had dirty water applied during 1995.

The two plots affected by excessive dirty water irrigation exhibit similar inorganic soil N distribution patterns down the soil profile. The peak inorganic soil N quantity occurs at the 30 to 45 cm sampling depth, which is more pronounced in plot 6 than 6a. After the peak soil N quantity, there is a decrease in soil inorganic N contents. The increase in soil N appears to be related to the soil solute leaching front.

There is a large difference in the quantity of N available for leaching between the two plots. Plot 6a has a much higher total inorganic soil N quantity, reflecting the higher N load applied to the plot (Table 6.9).

Table 6.9 N loads applied during 1995 to plots 6 and 6a (kg N ha^{-1}).

Plot	Dirty water TN	Dirty water AN	Total N applied
6	437	189	922
6a	756	346	1204

TN= Total Kjeldahl Nitrogen AN= Available Nitrogen

Temporal variation of soil solution NO_3-N concentrations, sampled at 50 cm deep in plots 6 and 6a, can be seen in Figures 6.13 and 6.14, respectively.

The temporal variation of soil solution NO_3-N concentrations were very similar to those observed in section 6.5.3. Due to greater replication of soil solution sampling standard errors of the mean are shown; the coefficients of variation (CV) ranged from 7 to 44% and 8 to 50% with mean CV of 26 and 21% for plots 6 and 6a, respectively.

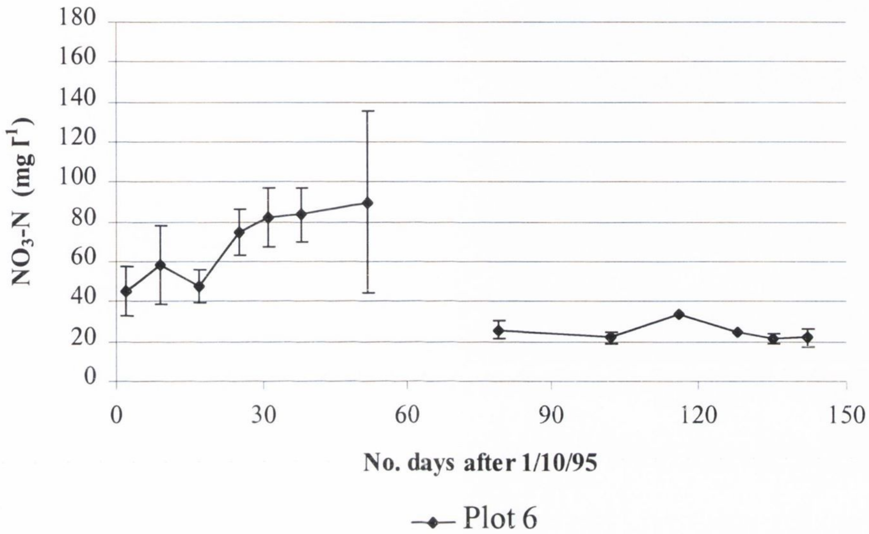


Figure 6.13 Mean soil solution NO_3-N concentrations sampled at 0.5 m b.g.l. measured in plot 6, vertical bars are 1 standard error of the mean.

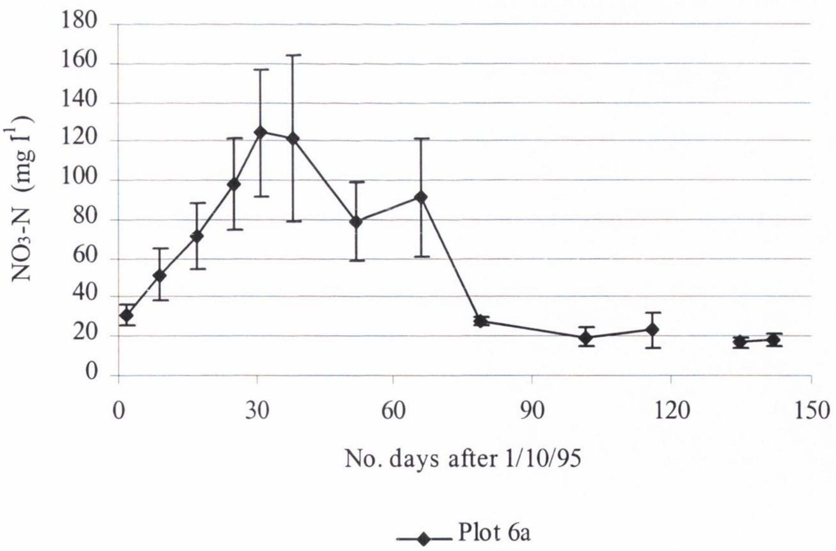


Figure 6.14 Mean soil solution NO_3-N concentrations sampled at 0.5 m b.g.l. measured in plot 6a, vertical bars are 1 standard error of the mean.

Plot 6 had a less well defined peak than plot 6a due to the CCs not taking samples on day 66 (5/12/95). The maximum observed concentration in plot 6 of 90 mg l^{-1} occurred on day 52 (21/11/95) whereas the maximum concentration observed in plot 6a of 124 mg l^{-1} was well defined and occurred on day 31 (31/10/95). The mean NO_3-N concentrations observed in plots 6 and 6a during the monitoring period were 49 and 59 mg l^{-1}, respectively. The greater loads of TN and AN applied to plot 6a caused higher mean and maximum NO_3-N concentrations to be observed when compared to plot 6.

Amounts of NO_3-N leached from each plot were calculated for the soil solution samples taken in the four areas within each plot. The amounts of N leached varied considerably within each plot ranging from 164 to 264 kg N ha^{-1} and 95 to 323 kg N ha^{-1} for plots 6 and 6a, respectively (Table 6.10).

Table 6.10 Amount of N leached from dirty water irrigated plots October 95 to April 96 (kg N ha^{-1}).

	Replicate Number				Plot	Standard
Plot	1	2	3	4	Mean	Error
6	264	199	164	212	210	21
6a	323	288	307	95	253	53

Although every effort was made to ensure even irrigation of dirty water to each plot, the low N leaching as measured in plot 6a, replicate 4, may have been due to the soil in this area receiving less dirty water than the other replicate areas. The high TN and AN loads applied to plots 6 and 6a caused high amounts of N to be leached from each plot, although the difference in leaching rates was only 43 kg ha^{-1}, compared to the difference of TN and AN loads of 319 and 157 kg N ha^{-1}.

The effect of over application of dirty water in plot 6 during June 1995 can be seen in Plate 6.3. The area of grass was effected by dirty water which contained significant amounts of silage effluent from recently cut silage. The weather during this period was hot and dry. Following these observations it was recommended that the dirty water be diluted during the first few days after silage harvesting and that the Roto Rainer be set at the fastest advancement speed to prevent further scouring.

6.7 Conclusions

Inorganic soil N levels in soil samples taken from selected plots on the farm had elevated N concentrations. The effect of dirty water application significantly increased the quantity of inorganic soil N for example in November 1992 plot 5 had 112 kg N ha^{-1} of inorganic soil N compared with a mean of 41 kg N ha^{-1} for plots which did not receive dirty water.

Inorganic soil N analyses carried out in November 1994 and 1995 do not clearly show the effect of dirty water irrigation. Plot 5 had dirty water irrigation in 1994 with 139 kg N ha^{-1} available from 0 to 75 cm deep. The mean levels in non irrigated plots was 98 kg N ha^{-1} although plot 7 had a similar N content to plot 5. Dirty water irrigation also increased inorganic soil N contents in 1995 with plots 6 and 6a having 143 and 275 kg N ha^{-1} in the top 75 cm of soil compared to a mean of 79 kg N ha^{-1} in non irrigated plots.

The irrigation of dirty water under the management outlined in section 3.5 clearly caused a significant increase in the quantity of inorganic N available for leaching. A significant relationship was found between inorganic soil N contents for the 0 to 75 cm soil depth and the quantity of TN and AN applied to each plot.

The annual soil mineral N levels, was clearly described in section 6.4. A significant increase of soil inorganic N contents from 0 to 10 cm in September to October 1995 was due to the peak soil organic N mineralisation occurring at this time (section 3.6). The increases of inorganic soil N in plots 5, 3a, 16 and 7 are extremely important as this period was also a time of soil re-wetting and leaching began soon after the inorganic soil N peaks which prevented significant uptake by the grass. The mineralisation of soil organic N appears to have been a dominant source of N for nitrate leaching during the winter period.

Soil solution NO_3-N was measured in 1993/94, 1994/95 and 1995/96. The results from 1993/94 are likely to be influenced strongly by the recent installation of the ceramic cups. During the 1994/95 and 1995/96 drainage season soil solution sampled at 50 cm in all plots breached the EU MAC.

While these results relate only to the 50 cm depth they are indicative of the potential for contamination of the groundwater. The results from the 100 and 150 cm sampling depths are more indicative of the risk to groundwater. These show that for the 1994/95 and the 1995/96 drainage seasons the mean NO_3-N concentrations in the soil drainage water exceeded the EU MAC in plots 5, 3a, 16 and 7.

Mean concentrations of NO_3-N leached from all samples taken at each depth clearly indicates that the farming practices occurring on Ballyderown was causing extremely high NO_3-N concentrations in the soil solution.

There were higher mean NO_3-N concentrations at the 150 cm depth compared with the 100 cm depth in all three drainage seasons. All plots exceeded the EU MAC and during the 1995/96 drainage season.

The amounts of N leached from the soils in plots 5, 16, 3a and 7 on the farm, based on the 150 cm sampling depth were high ranging from 137 to 255 kg N ha^{-1}. Clearly, the influence of soil texture, depth, weather, and treatment play an enormous role in the amount of N leached.

These results illustrate the effect which the intensive grassland agriculture on this farm has on elevating the concentrations of NO_3-N that leach through the soil and subsoil to recharge groundwater. Where such practices are occurring on farms with similar soils the risk to groundwater will be high. Such practices are unsustainable in the longer term and a nutrient management plan would be necessary to reduce the N load.

A separate experiment quantifying the effect of dirty water applications on nitrate leaching showed significant increases in soil inorganic N. The high levels of inorganic soil N were conducive to nitrate leaching to groundwater as was observed from soil solution samples. The levels of NO_3-N in both plots receiving dirty water were well above the EU MAC and they illustrate the high risk to water supplies from such practices on shallow, light textured soils.

If such practices were common on an area of similar soils there is little doubt that contamination of groundwater with nitrate would occur. If excessive irrigation of dirty water alone can cause such elevated NO_3-N levels in soil solution it is clear that late fertiliser N and slurry applications plus extended grazing can only make matters worse.

It is estimated from the soil solution sampling that a safe total N application quantity should be based on the N budget of plot 16. Although this plot breached the EU MAC on some occasions it had the lowest levels of N leaching measured on the farm due to it receiving fertiliser N ranging 160 to 287 kg N ha^{-1} with a mean of 233 kg N ha^{-1} and no slurry or dirty water.

From the observations made during this study we can say that fertiliser N applications of 233 kg N ha^{-1} to grassland plots which were grazed by dairy cows cause NO_3-N greater than the EU MAC on some sampling dates. It is difficult to speculate further than this as the lowest N application still breached the EU MAC. Where fertiliser applications in excess of 230 kg N ha^{-1} are applied to grazed grassland (at similar stocking rates) on similar soils to the study farm it is likely that nitrate pollution can occur.

CHAPTER 7 SATURATED ZONE CHEMISTRY

7.1 Introduction to nitrate in the saturated zone

Factors which control and influence the quantity of nitrate leached to groundwater were presented in section 6.2. The reader is referred to this section for literature review material on the occurrence of nitrate in the saturated zone.

To further ascertain the source of the high NO_3-N concentrations measured in the groundwater beneath the farm, N isotope analysis was carried out. Other groundwater chemical parameters were analysed as part of the standard analytical suite. Coliform counts (total and faecal), potassium, sodium, potassium/sodium ratio and chlorides were analysed in order to characterised the nitrate contamination source. Concentrations of these parameters are often used as indices of point source versus diffuse water pollution in groundwater supplies.

7.2 Methodology

7.2.1 Field sample collection and analysis

Groundwater samples were taken from the five monitoring boreholes, the farm supply (canteen) (see Figure 2.2 for borehole and plot locations) and occasional samples from the rising stream. Samples from the five monitoring boreholes were taken using a hand bailer which was lowered down the borehole using builder's line. In August 1994 the aluminium bailer was replaced with a PVC bailer, which filled from the base; samples were removed from 15 m below the standing water table level. Each borehole had 12 l of water removed before a 50 ml sample was taken for analyses. These samples were stored in a cool box at 4 °C for transport to the laboratory where they were analysed within 24 hours. The farm supply was sampled from a tap, which was turned on for five minutes before sampling. The spring was sampled by submersing a bottle in the flowing spring.

Weekly sampling of the groundwater was carried out from January 1994 to February 1996. Samples were analysed for NO_3-N, NH_4-N and MRP on a Chemlab Continuous Flow Auto Analyser (Nitrate results are presented for each borehole in Appendix K). Only the NO_3-N results are presented as both NH_4-N and MRP concentrations were normally below the detection limits of 0.1 and 0.005 mg l^{-1}, respectively. Weekly groundwater samples were also analysed for K^+ and Na^+ by atomic absorption spectrophotometry and Cl^- by potentiometric titration as described in Appendix I.

7.2.2 Data analysis

Groundwater nitrate concentrations were compared to numerous parameters. Statistical comparisons were carried out using a computerised statistical package data desk (Velleman, 1993). Simple linear regression (regression) was used to compare nitrate concentrations with other parameters. When regression analysis was carried out the model assumptions of normality were firstly investigated and if the data appeared to be skewed then transformation to the log scale was carried out to normalise the data. After regression analysis was carried out, plots of residuals and normal quantile plots of residuals were examined to ascertain if there were anomalous observations and whether there was any underlying trend apparent in the residuals. Only regressions which had intercept slopes which were significantly different from 0 (at $P<0.05$) are presented.

7.3 Nitrate in the saturated zone

7.3.1 Introduction

Occurrence and variation of groundwater nitrate concentrations in the saturated zone is presented in this section. Groundwater nitrate concentrations were examined over the monitoring period 1993 to 1996 and compared to groundwater recharge and soil solution nitrate which was determined beside each borehole, as presented in section 6.5 and 6.6.

Other saturated zone chemical and biological parameters are presented to aid in the identification of nitrate sources and in the characterisation of the form of pollution which is affecting the groundwater and which is thought to be diffuse in nature.

7.3.2 Methodology

This has been presented in section 7.2.1. The data used in this section was collected between 1993 and 1996. Historical data has been supplied by Teagasc from 1988 to 1993, inclusive. Soil moisture deficit was calculated from meteorological data collected from Teagasc, Moorepark by W. Murphy in Teagasc, Johnstown Castle.

The canteen supply and spring are presented later in this section for the comparison of NO_3-N concentrations to other chemical and biological parameters. This is due to the data not being as temporally continuous as the five monitoring boreholes on the study farm.

7.3.3 Nitrate Results and Discussion From the Five Monitoring Boreholes

Borehole 1

Temporal variation of groundwater NO_3-N sampled in borehole 1 between January 1993 and June 1996 can be seen in Figure 7.1. Groundwater NO_3-N concentrations followed the general pattern of being lowest in October and beginning to increase after the lowest observed concentration to peak in January/February of the next calendar year after leaching began.

Groundwater NO_3-N fluctuations after the summer of 1993 and 1995 followed this general pattern of temporal variation with very pronounced minimum concentrations observed in October of each year (days 292 and 1020 for 1993 and 1995, respectively). Sharp increases in NO_3-N concentration were observed after the minimum NO_3-N concentration of 15.7 and 11.1 mg l^{-1} to peak concentrations of 42.1 and 39.2 mg l^{-1} in 1993 and 1995, respectively. The peak concentrations after leaching began in the autumn of 1993 and 1995 were observed in February 1994 (day 399) and January 1996 (day 1125) after which dates concentrations began to decrease again.

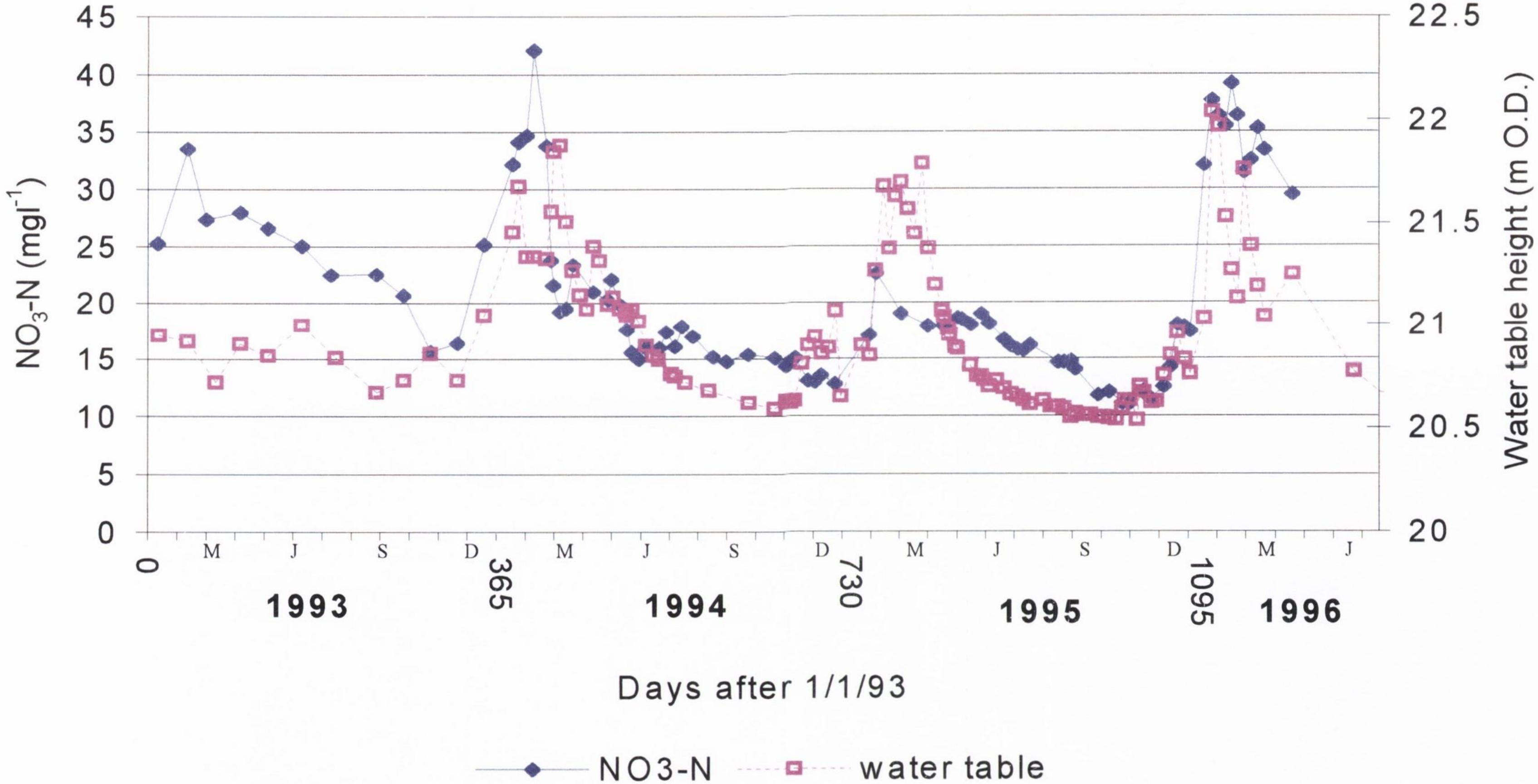


Figure 7.1 Temporal variation of groundwater NO_3-N and water table height in borehole 1 from January 1993 to June 1996.

The temporal variation of groundwater NO_3-N sampled in borehole 1 during 1994 was not as distinctive as in 1993 and 1995 but none the less did follow the same general pattern (Figure 7.1). The lowest concentration of 12.8 mg l^{-1} was observed in December 1994 after which there was a slight increase in concentration peaking at 22.6 mg l^{-1} in late January 1995 (day 755).

On average there was a 2.7 fold difference between the minimum and maximum NO_3-N concentration observed during each winter recharge period; the increase was greatest in 1995 (3.5 fold) and lowest in 1994 (1.8 fold).

The increase in groundwater NO_3-N, sampled in borehole 1 during the winter recharge period of 1993/94 from 15.7 to 42.1 mg l^{-1}, is likely to be due to the ploughing and re-seeding of this plot in September 1993. The process of killing the grass on the plot and then ploughing and re-seeding released a large amount of N from the soil which was then moved downward as winter recharge began. In section 6.3.3 a dramatic increase in the amount of soil N available for leaching during 1993 (84 kg N ha^{-1}) was seen compared to 1990-1992 (41 kg N ha^{-1}). Soil inorganic N was not measured regularly during autumn 1993 when plot 12 (which contains borehole 1) was ploughed. However when plot 5 (which contains borehole 5) was ploughed in September 1995 a 10 fold increase in the level of soil inorganic N was observed (section 6.4.3).

Borehole 2

The temporal variation of both groundwater NO_3-N concentrations and water table height observed in borehole 2 can be seen in Figure 7.2.

Temporal variation of groundwater NO_3-N concentrations in borehole 2 follow similar patterns to borehole 1 with one major difference which occurred in 1993/94. When recharge occurred during the 1993/94 recharge period the NO_3-N concentrations decreased from 35.3 mg l^{-1} in November 1993 (day 320) to 22.1 mg l^{-1} in January 1994 (day 383). During 1994 there was a gradually decreasing trend in groundwater NO_3-N concentrations with some fluctuation.

The characteristic groundwater NO_3-N temporal fluctuations observed in borehole 1 can

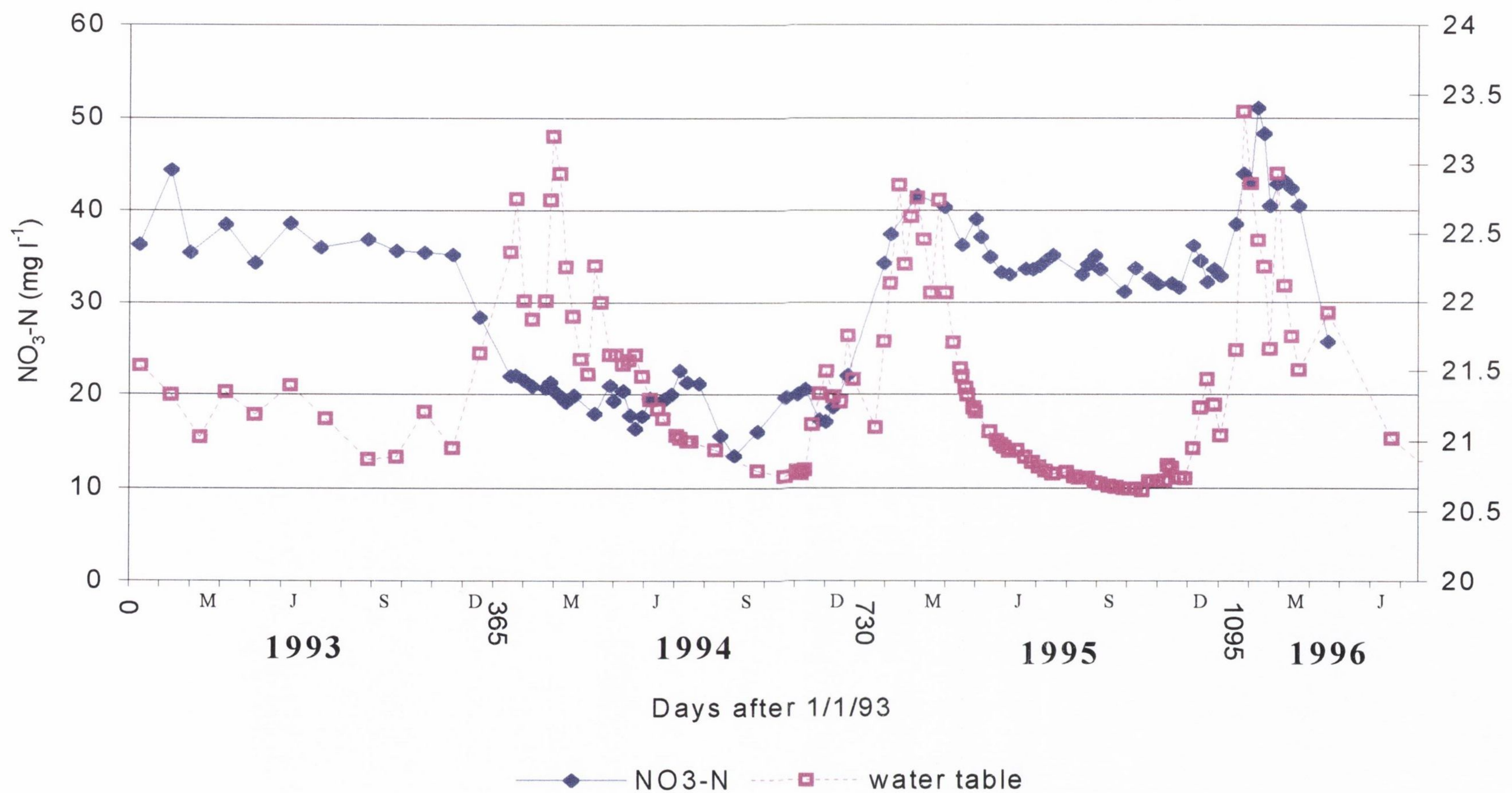


Figure 7.2 Temporal variation of groundwater NO_3-N and water table height in borehole 2 from January 1993 to June 1996.

clearly be seen in borehole 2 during the 1994/95 winter recharge period. Groundwater NO_3-N concentrations increased from 17.1 mg l^{-1} in November 1994 (day 691) to peak at 41.6 mg l^{-1} in February 1995 (day 781). As with the increases in NO_3-N concentrations observed in borehole 1 there was a 2.4 fold increase in concentrations during the 1994/95 winter recharge period. The marked increase in groundwater NO_3-N concentrations during the 1994/95 recharge period was due to the irrigation of dirty water during the summer of 1994.

A further dramatic increase in groundwater NO_3-N concentrations can be observed during the 1995/96 winter recharge period which also followed the characteristic groundwater temporal fluctuation model observed in borehole 1. Groundwater NO_3-N concentrations increased from a low of 32.9 mg l^{-1} in December 1995 (day 1082) to a peak of 51.1 mg l^{-1} in January 1996 (day 1119) , a 1.6 fold increase. Although dirty water was not irrigated in plot 5 during 1995 the increase in groundwater NO_3-N was due to the ploughing and re-seeding of this plot in September 1995 which caused a flush of N to be released from the soil. A dramatic increase in the concentration of soil inorganic N was described in section 6.4.3 when the level increased from ~20 to 233 μg N g dry soil^{-1} after the plot was sprayed with herbicide to kill the grass before the plot was ploughed. This 11 fold increase in the level of inorganic soil N caused the groundwater NO_3-N concentrations to increase for the second successive year.

Borehole 3

The temporal variation of groundwater NO_3-N and water table height observed in borehole 3 can be seen in Figure 7.3.

The NO_3-N concentrations observed in borehole 3 do not appear to follow the pattern as described for boreholes 1 and 2. Considerable temporal variation can be observed with changes in groundwater NO_3-N concentrations over small time periods such as during 1994. During this period a double peak of NO_3-N concentrations can be observed on days 553 and 670 (arrows 1 and 2, respectively) which correspond to July and November. Thus NO_3-N leaching to groundwater could be observed during the summer of 1994 which increased NO_3-N concentrations from a low of 15.3 mg l^{-1} in March 1994 (day 426) to a peak of 27.8 mg l^{-1} in July (day 553) after which date concentrations decreased again. This increase in groundwater NO_3-N was not associated with a corresponding increase in water table height which possibly

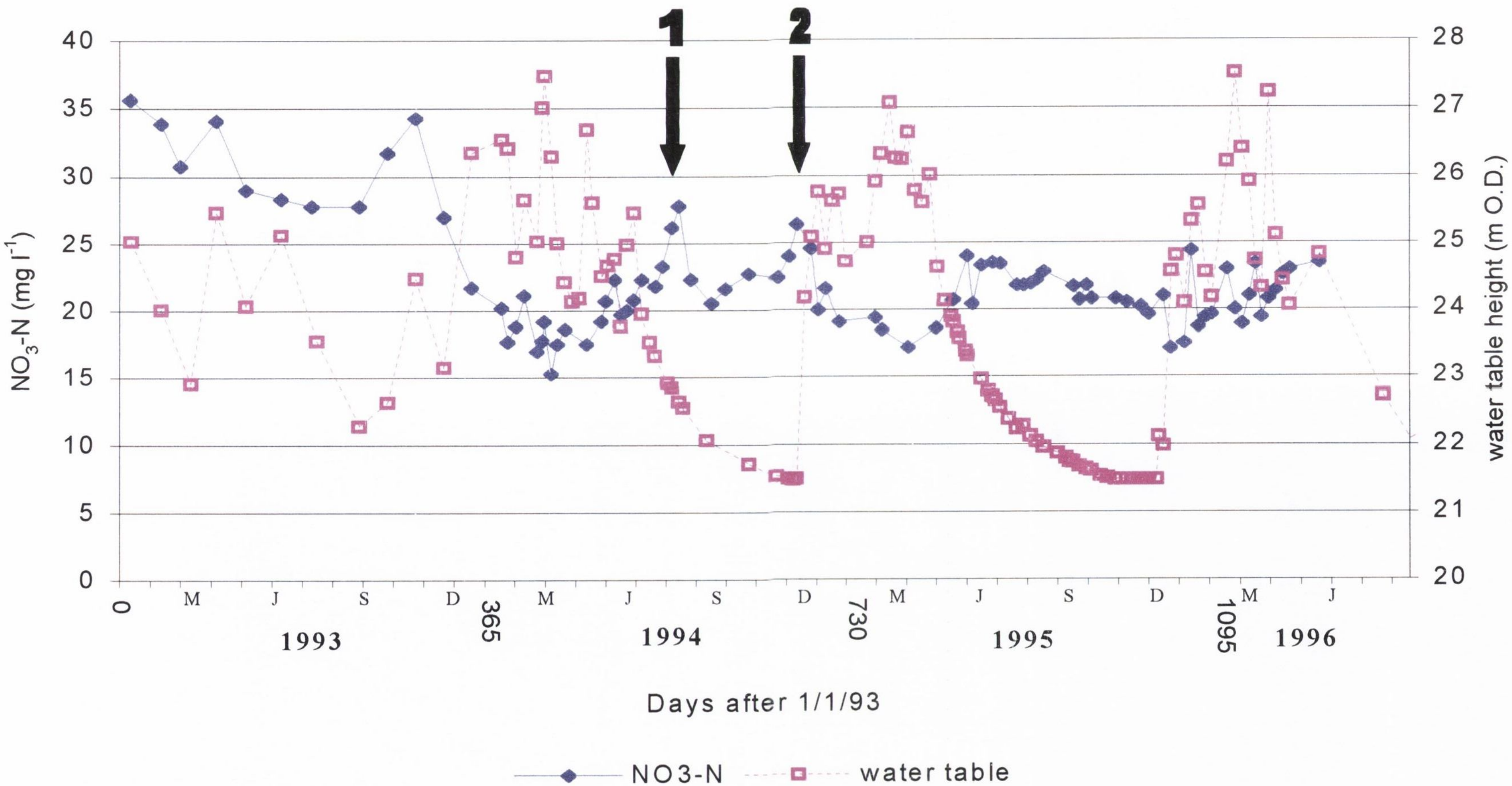


Figure 7.3 Temporal variation of groundwater NO_3-N and water table height in borehole 3 from January 1993 to June 1996.

could indicate that this NO_3-N was leached from a neighbouring plot which had a thinner soil.

As recharge occurred in October 1993 there was an initial increase in the groundwater NO_3-N concentration from a low of 27.8 mg l^{-1} in August (day 236) to a peak of 34.3 mg l^{-1} in October (day 292). After October 1993, when peak NO_3-N was observed, the concentration decreased significantly from 34.3 mg l^{-1} to 20.2 mg l^{-1} in January 1994 (day 377). Between January (day 377) and April (day 461) there was a decreasing trend of groundwater NO_3-N from 20.2 mg l^{-1} to 17.5 mg l^{-1} although there was some fluctuation around the trend.

The NO_3-N peak in November 1994 occurred earlier than peak concentrations observed in other boreholes such as borehole 1 and 2 which occurred in December 1994 and February 1995, respectively. Although NO_3-N concentrations began to increase from October 1994 (day 651) peaking at 26.4 mg l^{-1} in November (day 670), which corresponded to the lowest water table height measured that year. When recharge occurred and the water table increased in height there was a corresponding decrease in the groundwater NO_3-N concentration from November 1994 to the lowest observed concentrations of 17.2 mg l^{-1} in February 1995 (day 781). After February 1995 (day 781) the groundwater NO_3-N concentrations began to increase once more peaking at 24 mg l^{-1} in April 1995. After this date there was a generally decreasing trend in groundwater NO_3-N concentrations with some variations.

As recharge occurred in Autumn 1995 there was a lot of variation in NO_3-N concentrations over short periods of time which appeared to be related to changes in the borehole water table level. Increases in groundwater NO_3-N are associated with increases in water table height and *vice versa*.

Borehole 4

The results of NO_3-N and water table temporal variation can be seen in Figure 7.4 .

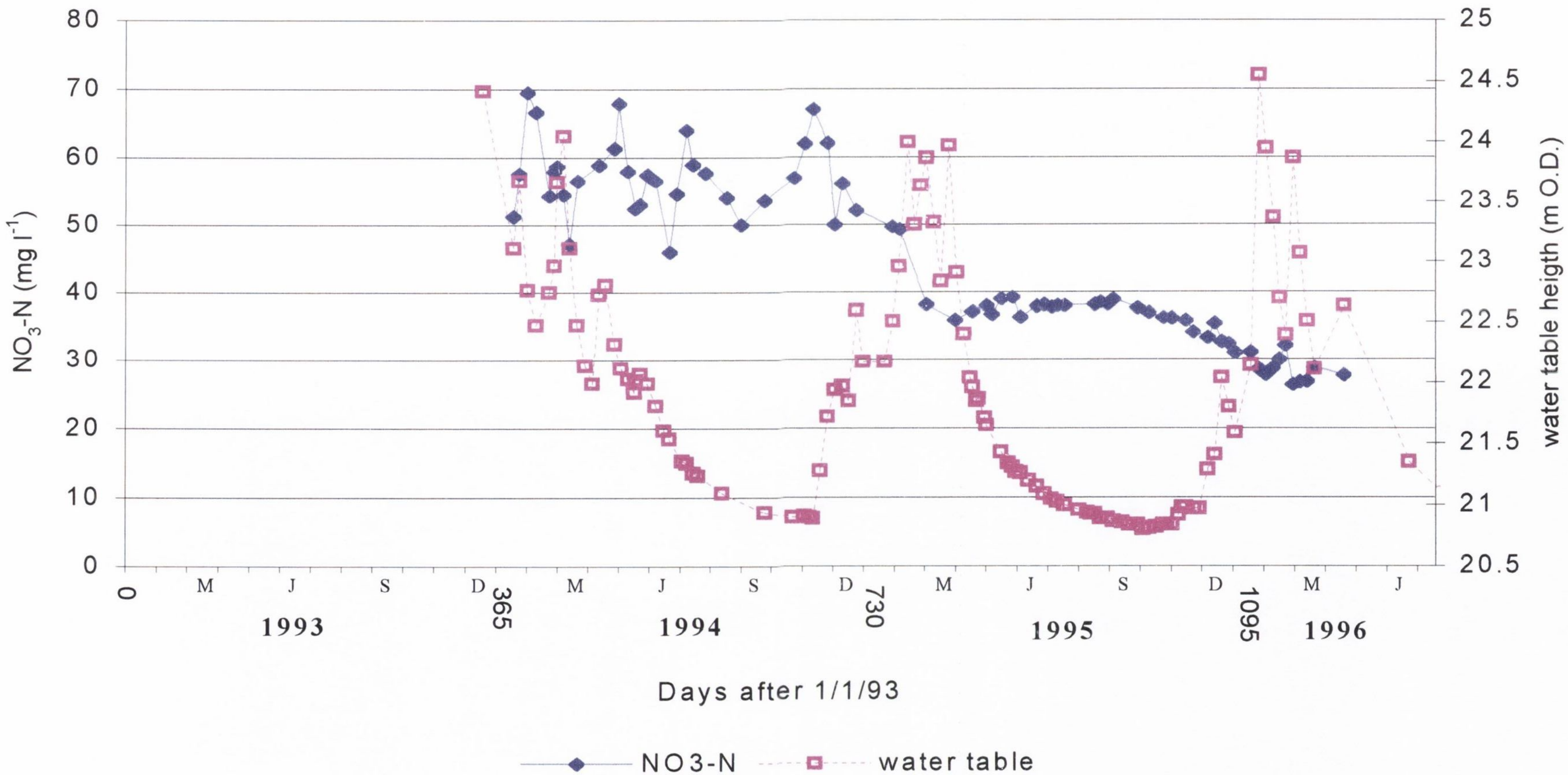


Figure 7.4 Temporal variation of groundwater NO_3-N and water table height in borehole 4 from January 1993 to June 1996.

Between January 1994 (day 377) and January 1995 (day 755) NO_3-N concentrations fluctuated generally between 50 and 70 mg l^{-1} except on two sampling dates which had concentrations of 47 and 46 mg l^{-1} in March 1994 (day 432) and June 1994 (day 530). During 1994 four NO_3-N peaks >60 mg l^{-1} occurred January, April, June and November. As in borehole 3 it is possible to observe increased groundwater NO_3-N concentrations in spring/summer indicating N leaching from N applied at the start of the growing season.

Groundwater NO_3-N peaks in January and April 1994 (days 391 and 480) occurred 8 and 27 days after observed increases in the water table height in borehole 4. The NO_3-N peak which occurred in June (day 546) did not follow any observed increases in the water table height.

As observed in borehole 3, increased groundwater NO_3-N in November 1994 (day 670) occurred in conjunction with the lowest observed water table height measurement. When recharge occurred one week later in November 1994 the groundwater NO_3-N concentration began to decrease. The most notable decrease in groundwater NO_3-N concentrations occurred between January and March 1995 when it decreased from 49.3 (day 755) to 35.9 mg l^{-1} (day 809).

During 1995 the groundwater NO_3-N concentrations were much more stable with very little variation in concentration observed. As recharge occurred in October 1995 (day 1020) groundwater NO_3-N concentrations decreased from 36.1 mg l^{-1} in October 1995 (day 1020) to 27.7 mg l^{-1} in April 1996 (day 1188).

Borehole 5

The NO_3-N concentrations and water table height fluctuations observed in borehole 5 can be seen in Figure 7.5.

Borehole 5 had the lowest annual groundwater NO_3-N concentrations observed on the farm during the monitoring period varying from 12.8 in August 1994 (day 586) to a maximum of 21.5 mg l^{-1} observed on both February 1995 and March 1996 (days 781 and 1159), respectively.

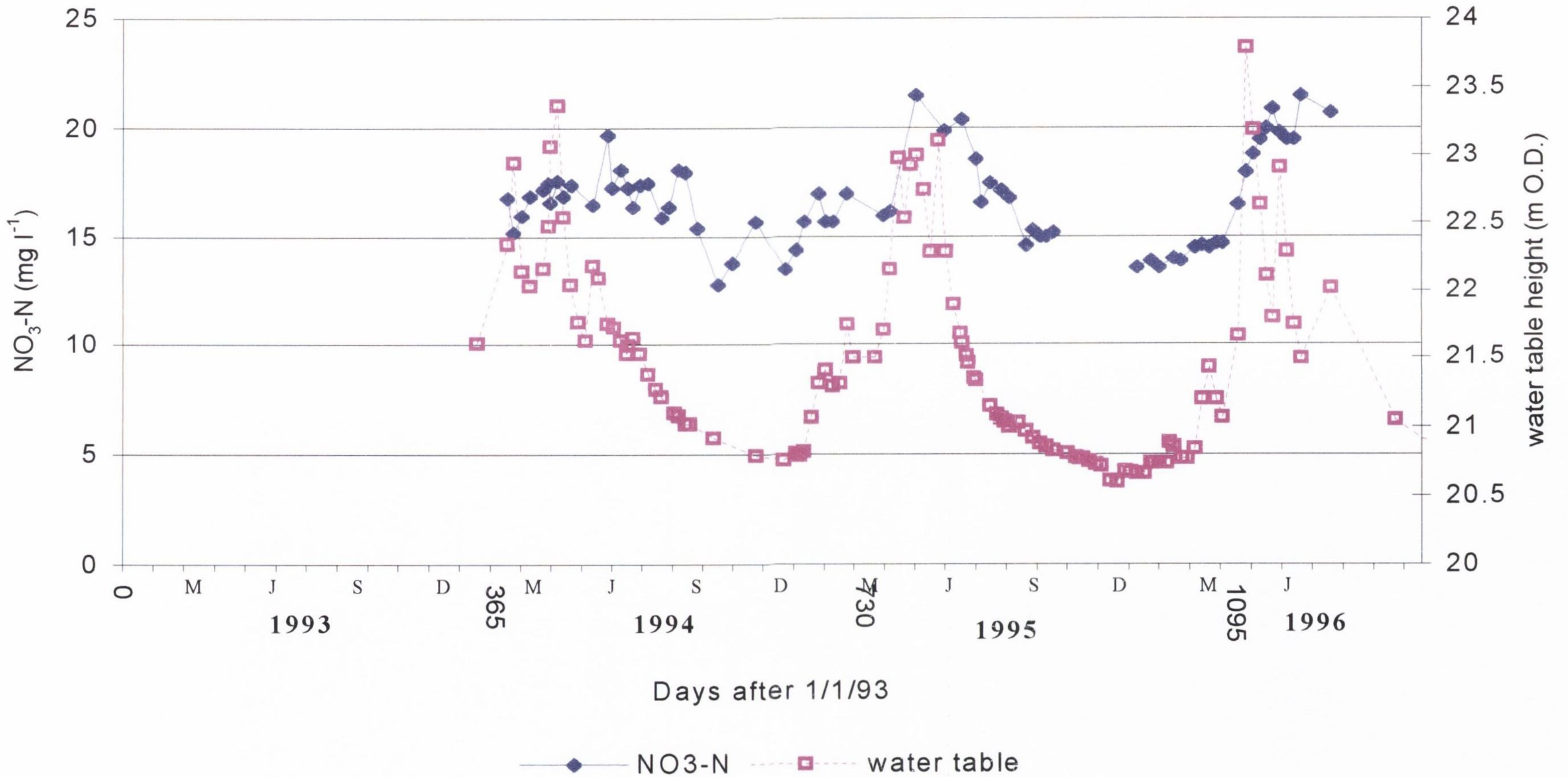


Figure 7.5 Temporal variation of groundwater NO_3-N and water table height in borehole 5 from January 1993 to June 1996.

In general the NO_3-N concentrations in borehole 5 followed the same pattern as observed in boreholes 1 and 2. As recharge occurred in autumn 1994 (day 670) groundwater NO_3-N concentrations increased slowly at first until the water table height increased to the winter maximum, the nitrates then increased from 16.2 mg l^{-1} in January 1995 (day 755) to a maximum of 21.5 mg l^{-1} in February 1995 (day 781). During the autumn recharge in 1995, groundwater NO_3-N concentrations increased from a low of 14.7 mg l^{-1} in December 1995 (day 1082) to peaks in February and March 1996 of 20.9 and 21.5 mg l^{-1} (days 1131 and 1159), respectively.

To summarise, the groundwater NO_3-N concentrations in boreholes 1, 2 and 5 generally increased from low concentrations in November/December of each year to peaks in January/February of each year after which date the concentrations decreased again although one notable exception occurred in borehole 2 during the 1993/94 recharge period when groundwater NO_3-N concentrations decreased due to lower amounts of N available for leaching from this plot.

During 1994, boreholes 3 and 4 had similar temporal variation of groundwater NO_3-N concentrations with increases in both boreholes occurring independent of changes in water table levels. Increases in groundwater NO_3-N concentrations were observed during the summer in both boreholes and both had peaks in November 1994 before the water table height increased due to winter recharge. Thus both appear to be influenced by NO_3-N leaching from other plots which migrates to both boreholes before recharge occurs at those plots. Possible sources of the NO_3-N leaching which could affect both boreholes would be plots 13 and 14 which have depth to bedrock of <1 m (Map 4.1).

When high groundwater nitrate concentrations were observed on the farm such as in borehole 1 during the 1993/94 recharge period and borehole 4 in January 1993 the concentrations quickly decreased to similar levels as observed in the other boreholes on the farm, when the source of the elevated nitrate concentration was removed. The groundwater nitrate concentrations in borehole 1 decreased from a peak of greater than 40 mg l^{-1} in early 1994 to less than 20 mg l^{-1} later in the spring of 1994. Nitrate concentrations in borehole 4 decreased from 50 to 70 mg l^{-1} in 1994 to less than 30 mg l^{-1} in 1996.

7.3.4 Comparison between soil solution and groundwater NO_3-N

Temporal variation of NO_3-N concentration in the ceramic cup samplers (at each sampling depth) as presented in section 6.5 and groundwater were compared to examine the relationship between both estimates of NO_3-N loss from the monitored plots. Comparisons are made from 1/1/94 until 6/4/96, no results were compared for 1993 as the suction cups were first sampled in January 1994.

The comparison is made more difficult due to the nature of soil solution samples which sample a small block of soil and thus may be influenced by localised high NO_3-N concentrations due to dung and urine patches. Groundwater NO_3-N is more likely to reflect the N leaching from a much larger area than soil solution samples. Thus if soil solution samples are influenced by dung and urine patches N leaching is over estimated making the comparison with groundwater NO_3-N difficult.

The comparison of soil solution at 50 cm depth and groundwater NO_3-N concentrations observed at borehole 1 (plot 12) are presented in Figure 7.6 . At this site suction cups were only installed at 50 cm due to the thin depth to bedrock of less than 1 metre. The suction cup results presented are the mean of the three cups at the 50 cm depth beside the borehole.

During early 1994 the soil solution had lower NO_3-N concentrations than the groundwater which was probably due to the major part of the leaching already having occurred in autumn 1993. During the 1994/95 recharge period the soil solution NO_3-N concentrations peaked at 33.3 mg l^{-1} on 6/12/94 (day 340) whereas peak groundwater NO_3-N concentration was 22.6 mg l^{-1} on 25/1/95 (day 390).

Although the concentrations of NO_3-N were different in the soil solution and the groundwater, a relationship exists between them whereby the soil solution NO_3-N peaked 50 days before the corresponding peak in the groundwater. Thus in the 1994/95 recharge period there was a lag time of 50 days between peak soil solution and groundwater NO_3-N concentrations. The water table in this borehole varied between 22 and 23 m below ground level or 20 to 22 m O.D. (Section 5.3.3).

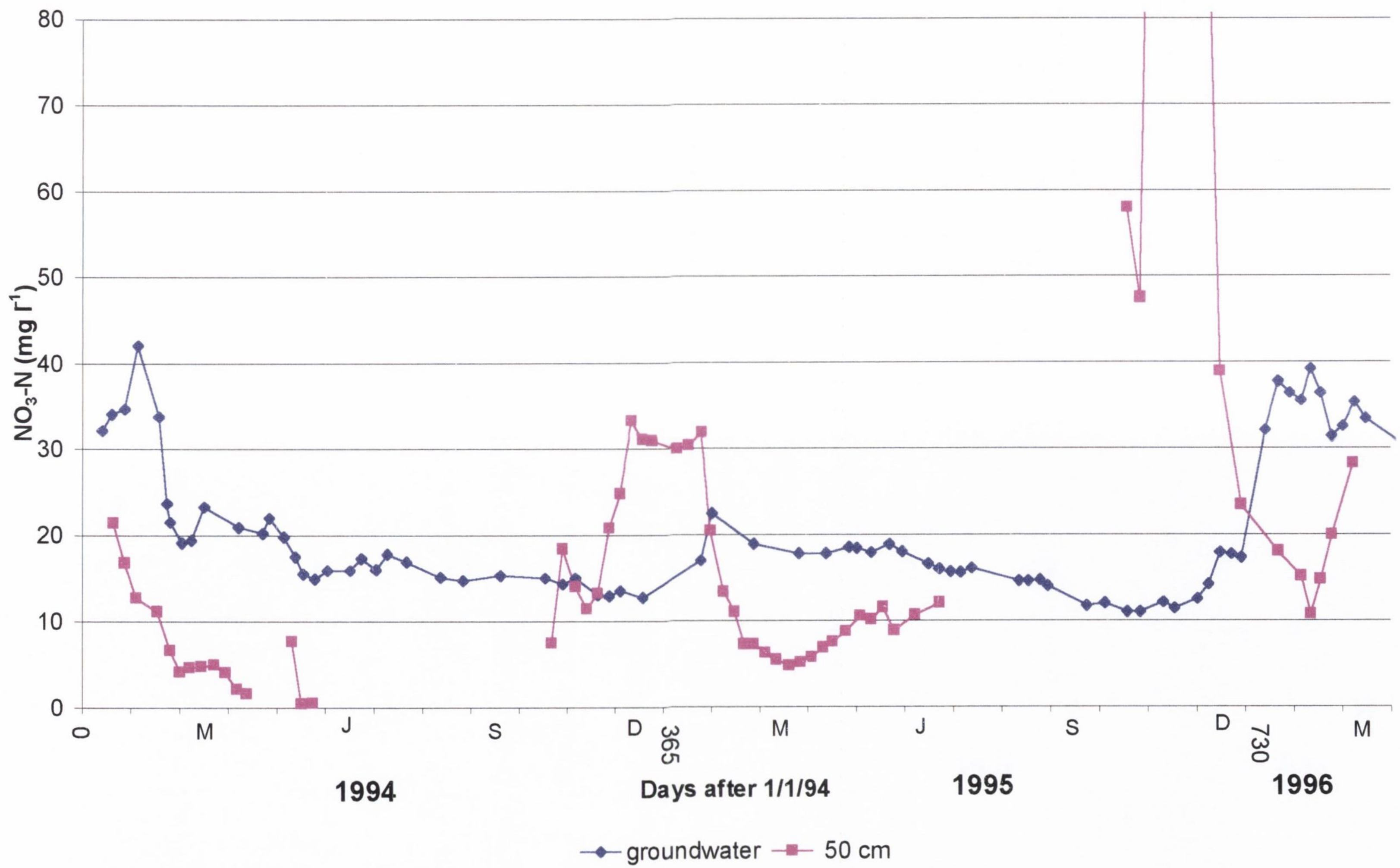


Figure 7.6 Borehole 1 groundwater and soil solution NO_3-N (sampled at 50 cm depth).

During the 1995/96 recharge period the only relationship between soil solution and groundwater NO_3-N concentrations was that there was a 64 day lag period between peak soil solution and groundwater NO_3-N concentrations. The concentration of NO_3-N peaked at 174 mg l^{-1} and 37.7 mg l^{-1} in the soil solution and groundwater, respectively. The large concentration difference is likely to be due to the soil solution samplers reflecting localised contamination on the soil above the ceramic cups due to a dung or urine patch, whereas the groundwater is reflecting NO_3-N leaching over a larger area than is sampled by ceramic cups.

The relationship between groundwater and soil solution NO_3-N concentrations in plot 5, which contains borehole 2, can be seen in Figure 7.7. Peak soil solution NO_3-N concentrations at the 150 cm sampling depth appear to be very similar to the groundwater NO_3-N in borehole 2 when a time lag is accounted for.

During the 1994/95 recharge both soil solution at 150 cm and groundwater NO_3-N concentrations peaked at 40.6 and 41.6 mg l^{-1}, respectively. There was a 93 day lag between peak NO_3-N concentrations in the soil solution at 150 cm and groundwater. The relationship between groundwater and soil solution NO_3-N concentrations at 50 and 100 cm was not as good for a number of reasons. Soil solution NO_3-N at 50 cm was influenced by dirty water irrigation which occurred during the summer of 1994 which elevated the concentration of NO_3-N leached, as measured at this depth. Soil solution sampled at 100 cm was lower than groundwater NO_3-N at day 365 onward until a further ceramic cup began to sample on 24/1/95 (day 389) which doubled the NO_3-N concentration. This was due to sampling problems with the ceramic cups.

During the 1995/96 recharge period soil solution samples, at 100 and 150 cm, had similar NO_3-N concentrations to the groundwater although a better relationship appears to exist between samples at 150 cm, which peaked at 49 mg l^{-1}, and the groundwater which peaked at 51 mg l^{-1}. There was no lag time between peak groundwater and soil solution NO_3-N concentrations at the 100 and 150 cm sampling depths.

The temporal NO_3-N concentration variations in the groundwater and soil solution in plot 16, which contains borehole 3, are compared in Figure 7.8.

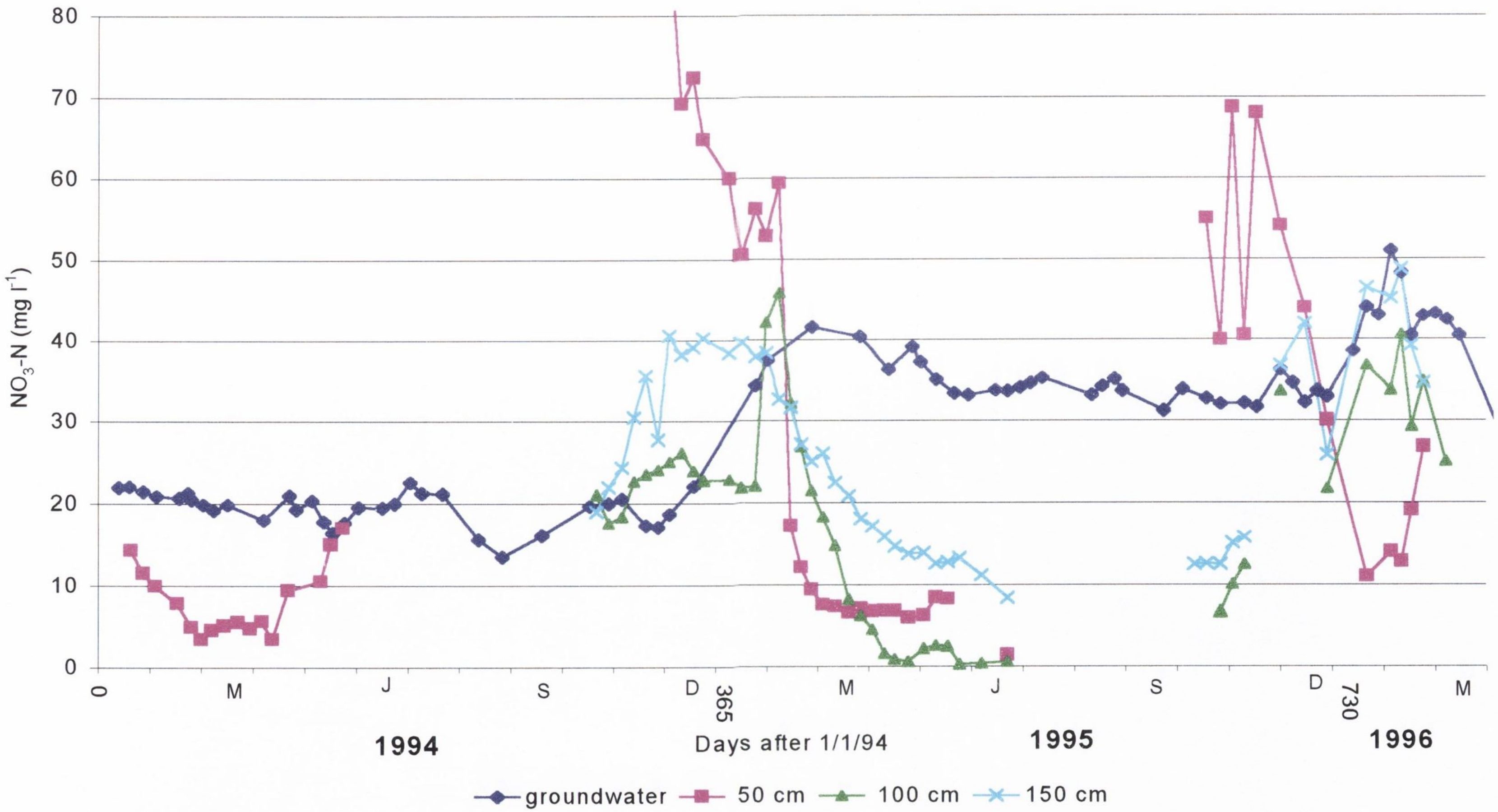


Figure 7.7 Borehole 2 groundwater and soil solution NO_3-N (sampled at 50, 100, and 150 cm depths).

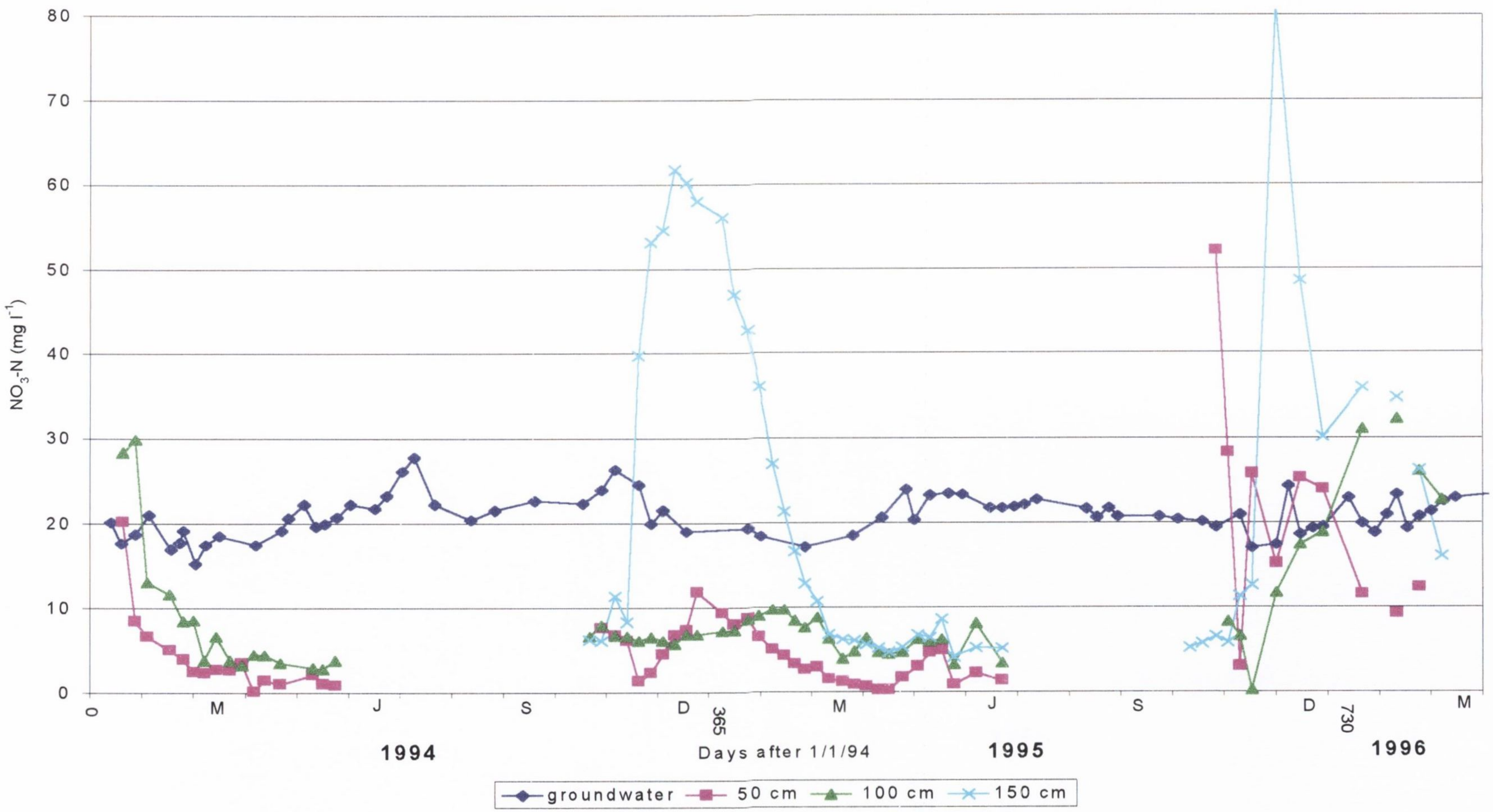


Figure 7.8 Borehole 3 groundwater and soil solution NO_3-N (sampled at 50, 100 and 150 cm depths).

The relationship between groundwater and soil solution NO_3-N concentrations at borehole 3 does not appear to be clear. Groundwater NO_3-N concentration is more constant than at the other boreholes and variation in groundwater NO_3-N appears to be independent of the soil solution NO_3-N concentration. In June 1994 (day 188) there is a peak in the groundwater NO_3-N concentration and although there was no soil solution sampling in this period a short lag time would be expected as observed at boreholes 1 and 2. The soil is deeper in this area of the farm (>3 m) and thus the lag period would be expected to be greater than at the other borehole locations. The NO_3-N concentrations in the soil solution samples at the 100 and 150 cm sampling depths peaked in December 1994 which coincided with a decrease in the groundwater NO_3-N concentration after a peak the previous month.

The groundwater NO_3-N concentration peak in April 1995 (day 475) again preceded the soil solution NO_3-N increase in this plot, which occurred on day 496. This again indicates that the source of the NO_3-N in the groundwater is another plot with a faster travel time although this peak may be due to the soil solution peak seen in December 1994. This is considered to be unlikely however, as the soil solution peak was lower at 50 and 100 cm than the groundwater NO_3-N concentration. The high soil solution NO_3-N concentration peak at the 150 cm depth is likely to be due to a localised source such as a dung or urine patch above the ceramic cups. A total of three ceramic cups were installed at the 150 cm depth and they were located relatively close at a distance of 50 cm. There was an average standard deviation for this winter recharge period of 9.3 mg l^{-1} which illustrates the similar NO_3-N concentrations observed from samples from each cup. Thus the source of the higher NO_3-N concentrations at this depth influenced the concentrations observed from samples from each cup.

During the 1994/95 recharge period, with the exception of the 150 cm sampling depth, the soil solution had significantly lower NO_3-N concentrations than the groundwater. In the 1995/96 recharge period the relationship between concentrations is not so clear due to rapid changes in NO_3-N concentrations, which occurred both in the soil solution and the groundwater.

From the comparison between groundwater and soil solution NO_3-N concentration variation it appears that the groundwater chemistry of plot 16 (which contains borehole 3) is influenced by other plots from which NO_3-N enters the groundwater more quickly. This is shown by the groundwater NO_3-N concentration peaks occurring before soil solution peaks. Plots 13 and

14, which are close to plot 16, have thin soils (<1 m (Figure 4.1)) and thus would have faster travel times from soil surface to groundwater. This may explain why the groundwater beneath plot 16, which contains borehole 3, has high NO_3-N concentrations although it receives the lowest N applications on the farm.

The temporal variation of groundwater and soil solution NO_3-N concentrations in plot 3a, which contains borehole 4, are compared in Figure 7.9.

When sampling began in 1994 the soil solution had NO_3-N concentrations <10 mg l^{-1} whereas the groundwater concentration varied between 50 and 70 mg l^{-1}. The soil solution was only sampled at 50 cm and thus higher NO_3-N concentrations may have already passed this sampling depth when sampling began in early 1994.

Soil solution samples collected during the 1994/95 recharge period had higher NO_3-N concentrations than these collected in early 1994 and yet they were still generally considerably lower than the groundwater NO_3-N concentrations. One exception was at the 100 cm sampling depth which had similar NO_3-N concentrations to the groundwater when sampling began but this decreased rapidly as sampling progressed. Groundwater NO_3-N concentrations during the 1994/95 period decreased significantly to ~38 mg l^{-1} but the soil solution was <30 mg l^{-1} at all depths during the same period.

During the 1995/96 recharge period NO_3-N concentrations in the soil solution at 100 and 150 cm depths fluctuated around and near to the groundwater concentrations. Some sampling dates had higher NO_3-N concentrations and some had lower.

When the groundwater at borehole 4 was first sampled during 1994, the NO_3-N concentrations were extremely high at >50 mg l^{-1} and these were occurring independently of the soil solution in this plot. Thus it would appear that the source of the high NO_3-N concentrations in the groundwater was not occurring within plot 3a, in which borehole 4 was located. The source of the high NO_3-N could be attributed to either dirty water irrigation in plot 4 and 4a or from the application of slurry before ploughing of plots 13, 13a, 15 and 15a.

Recharge in plot 3a had lower NO_3-N concentrations than the groundwater during the 1994/95

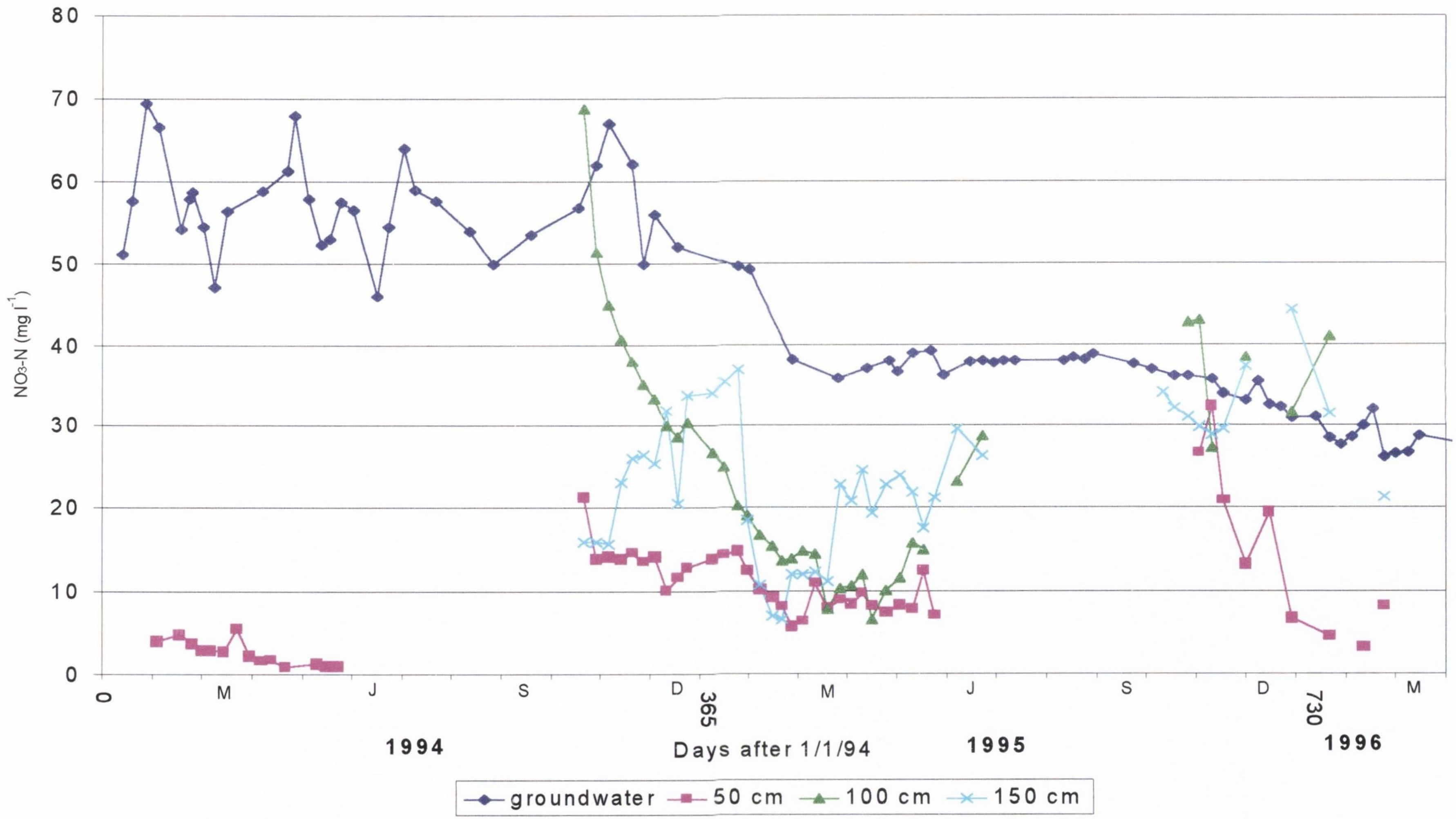


Figure 7.9 Borehole 4 groundwater and soil solution NO_3-N (sampled at 50, 100, 150 cm depths).

period and this reduced the groundwater NO_3-N concentration. When recharge occurred during the 1995/96 period the NO_3-N concentrations in the recharge were similar to the groundwater, as observed in the soil solution samples. To reduce the groundwater concentrations even further it would be necessary to reduce the concentration of NO_3-N in the recharge from plot 3 and also the neighbouring plots 4 and 4a which have been shown to influence the groundwater quality in borehole 4.

In boreholes 3 and 4 the groundwater NO_3-N concentrations tended to be greater than the soil solution concentrations and this was attributed to N leaching from other plots which may have received larger N application rates, such as dirty water irrigation or slurry application before ploughing in neighbouring plots.

The opposite was observed in borehole 5 whereby higher NO_3-N concentrations were observed in the soil solution samples than in the groundwater (Figure 7.10).

During the 1994/95 and 1995/96 recharge periods the soil solution had higher NO_3-N concentrations than the groundwater (with the exception of the 50 cm depth in 1994/95). Peak NO_3-N concentrations in the 1994/95 recharge period were >60 mg l^{-1} in the soil solution at 100 and 150 cm depths whereas the groundwater peak was 21.5 mg l^{-1}. In 1995/96 the soil solution NO_3-N concentration peaks were 74, 25, and 43 mg l^{-1} for the 50, 100 and 150 cm sampling depths, respectively, whereas the groundwater peaked at 21 mg l^{-1} NO_3-N.

Thus it would appear that the groundwater which flowed beneath plot 7, which contains borehole 5, had NO_3-N concentrations which were lower than those leaching from plot 7. It would appear that agricultural practices close to plot 7 are not causing N leaching to the same extent as measured in plot 7. Thus it is unlikely that a neighbouring farm is causing the elevated groundwater NO_3-N concentrations if recharge from plot 7 had higher concentrations than were present in the groundwater. The practices occurring in the plot are likely to have increased the groundwater NO_3-N concentrations.

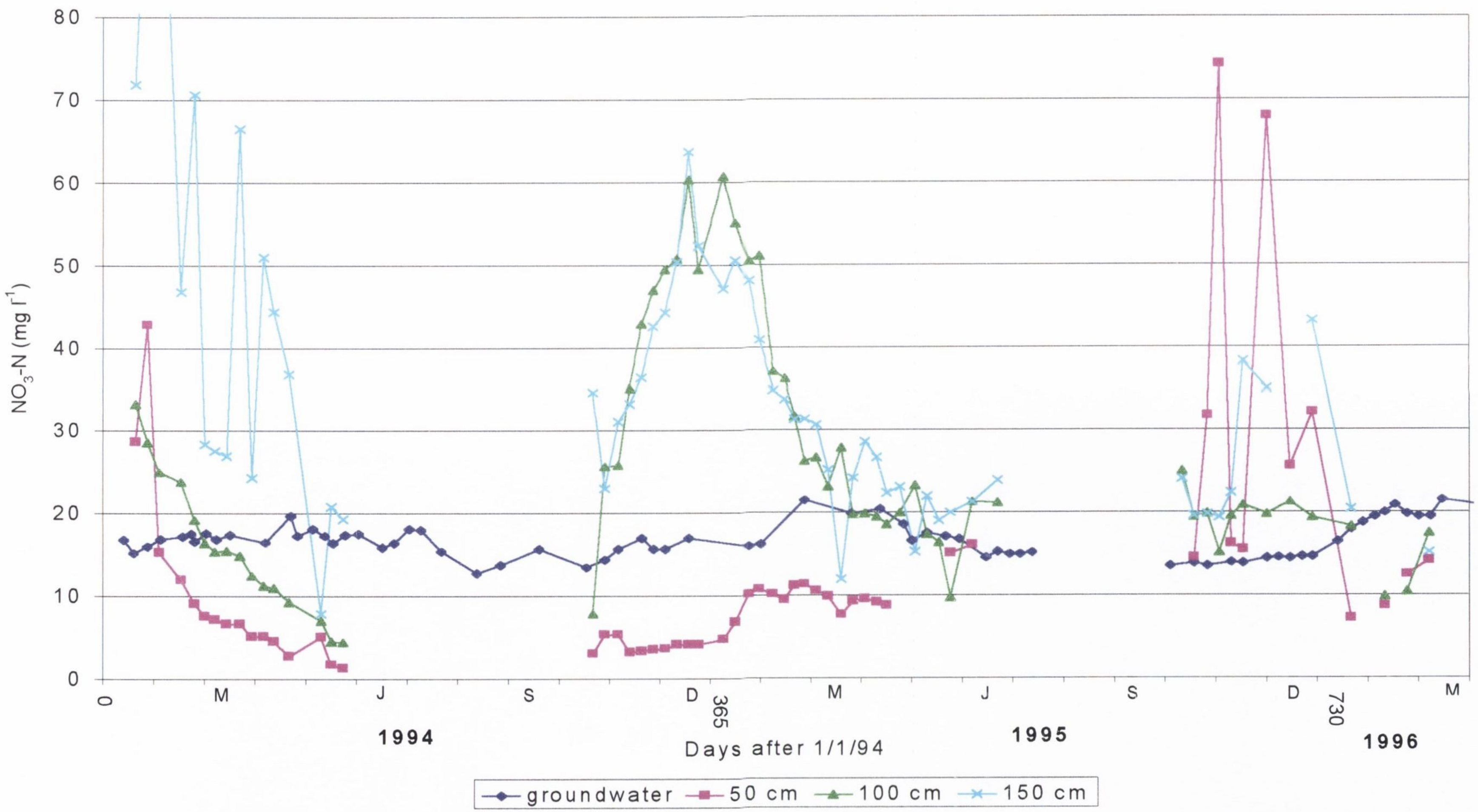


Figure 7.10 Borehole 5 groundwater and soil solution NO_3-N (sampled at 50, 100, 150 cm).

Summary:- By comparing groundwater and soil solution NO_3-N concentrations it was possible to observe three trends.

Firstly, groundwater NO_3-N was similar to soil solution NO_3-N concentrations e.g., borehole 2, located in plot 5. Soil solution samples at the 150 cm depth were similar to the groundwater.

Secondly, groundwater NO_3-N concentrations greater than soil solution concentrations. This indicates that the groundwater was influenced by activities occurring in other plots e.g., boreholes 3 and 4 where the extremely high groundwater NO_3-N concentrations were caused by excessive dirty water irrigation in plots 4 and 4a or by slurry application before ploughing and re-seeding of plots 13, 13a, 15 and 15a.

Thirdly groundwater NO_3-N concentrations less than soil solution concentrations, indicating that groundwater NO_3-N is not representative of the agricultural practices within the plot containing the borehole e.g., borehole 5, in plot 7 where the soil solution had considerably higher NO_3-N concentrations than observed in the groundwater.

7.3.5 Long-term groundwater NO_3-N variation

The data used in this section are from both historical data (collected monthly by Teagasc from 1985 to 1993) and from the current study from late 1993 until 1996. Historical data existed for boreholes 1, 2 and 3 as boreholes 4 and 5 were only installed in late 1993. Long term NO_3-N variation in boreholes 1, 2 and 3 from 1/1/85 to 6/4/96 can be seen in Figure 7.11.

In general there is a good relationship between the variation in each of the boreholes: as the NO_3-N concentration in one borehole increases the NO_3-N concentrations in the other boreholes also increase. An interesting point to note is the increase in NO_3-N concentration in borehole 3 from ~10 mg l^{-1} at the start of sampling to >20 mg l^{-1} during the 1988/89 recharge period. This increase in groundwater NO_3-N concentration is not thought to be due to any change in farm managerial practices but is likely to be a result of borehole development during the two pumping tests which were carried out during the summer of 1988 as described

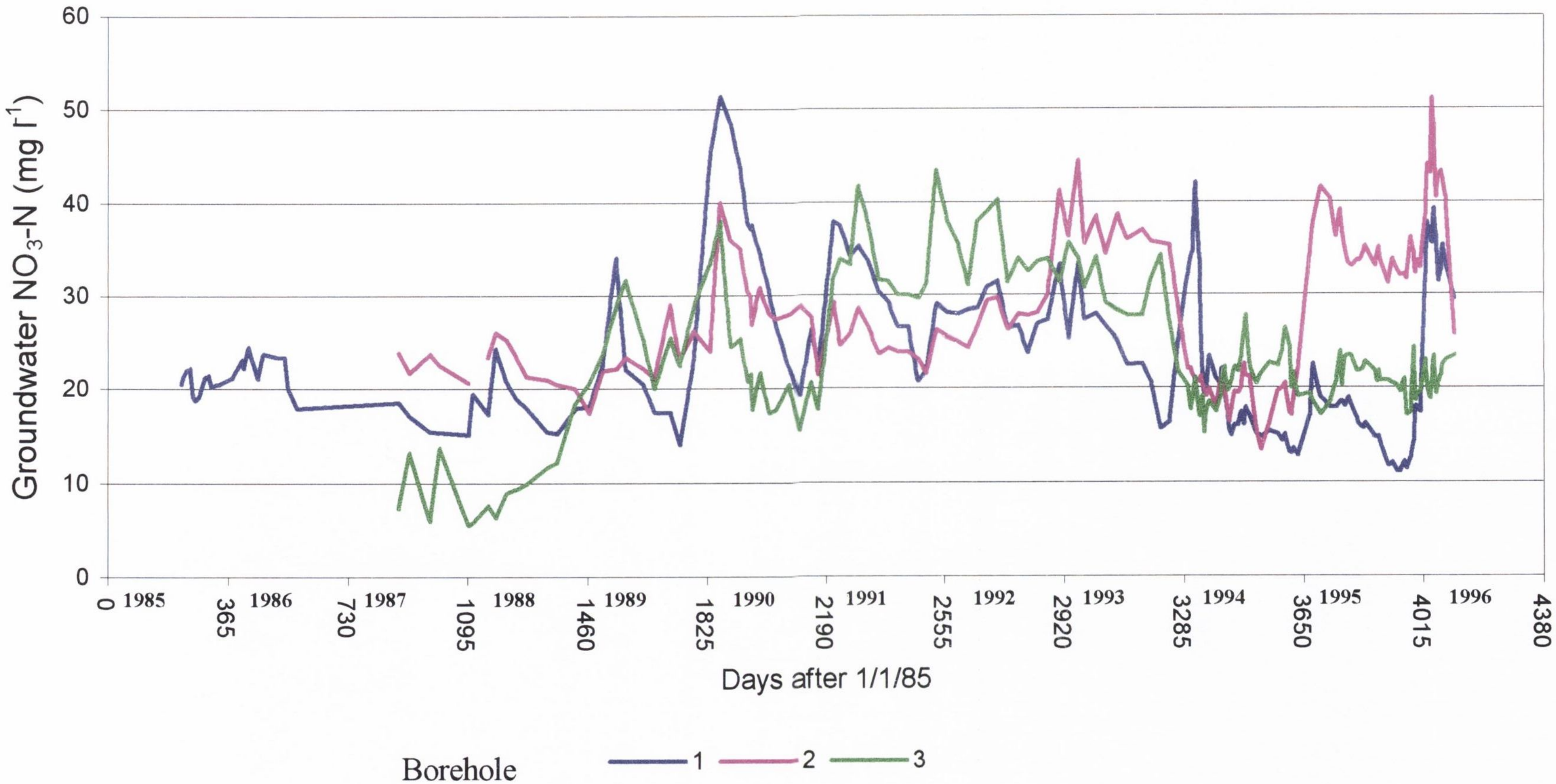


Figure 7.11 Temporal variation of groundwater NO_3-N sampled in boreholes 1, 2 and 3 from 1/1/85 to 06/04/96.

in section 5.4. The development of flow paths into the borehole is likely to have caused the groundwater in the borehole to sample a larger area than when first drilled. It is suggested that the groundwater chemistry in borehole 3 became a mixture of what was occurring within the immediate area of the borehole and also other plots such as 13 and 14.

The recharge period 1989/90 is interesting as the NO_3-N concentration in each borehole increased significantly to 51, 40 and 38 mg l^{-1} for boreholes 1, 2 and 3, respectively. The NO_3-N concentrations in borehole 1 during this period is the highest concentrations ever recorded from this borehole which indicates a large increase in N leaching in the autumn of 1989.

During the 1989 growing season there were no changes to the farm managerial practices and the plot received average fertiliser and slurry applications and no dirty water. It seems likely that the elevated NO_3-N in borehole 1 during the 1989/90 recharge period was due to meteorological factors. McGuire (1991) reported low summer rainfall in 1989 of 320 mm (March to October, inclusive) and a substantial soil moisture deficit prevailed from April to September, inclusive. Calculated effective rainfall for 1989 was 345 mm which is about 50% of the mean annual effective rainfall. Thus it appears that restriction of plant growth during the summer of 1989 caused a flush of NO_3-N leaching upon soil re-wetting in the autumn of 1989. Plot 12, which contains borehole 1, has the thinnest depth of soil to bedrock and would be the most susceptible to drought, such as occurred during the summer of 1989.

The long-term temporal trend of groundwater NO_3-N concentrations in borehole 2 fluctuates generally between 20 and 30 mg l^{-1}, except under exceptional circumstances which include dirty water irrigation and ploughing and re-seeding. In 1992/93 groundwater NO_3-N in borehole 2 increased significantly from <30 mg l^{-1} to a peak of >40 mg l^{-1} after which point it remained ~35 mg l^{-1} before decreasing again with recharge in 1993/94. Dirty water was irrigated in this plot in 1992 but no information was available to quantify the amount of nutrients applied to the plot or the length of time of the irrigation. Dirty water irrigation increased the groundwater NO_3-N concentrations during the 1994/95 recharge period as shown in Figure 7.2. Ploughing in September 1995 again increased the groundwater NO_3-N concentration during the 1995/96 recharge period.

7.3.6 Comparison of groundwater NO_3-N and soil moisture deficit

The concentration of NO_3-N in groundwater was compared to soil moisture deficit (s.m.d.) from the preceding year to examine if a relationship existed between the two. Groundwater NO_3-N concentrations at borehole 1 were used in the comparison as the area around borehole 1 never had dirty water applied to it and application of slurry was moderate. Groundwater NO_3-N observations from 1988 to 1996 (with the exception of 1994 due to the ploughing and re-seeding of the plot in September 1993, Figure 7.11) were compared with calculated S.m.d. from 1987 to 1995.

A lag period of one year between s.m.d. and groundwater NO_3-N was used as increased NO_3-N concentrations were observed at the beginning of the following year after s.m.d. measurements i.e., increased s.m.d. during the summer of 1995 was shown to increase groundwater NO_3-N concentrations in January 1996. Regression analysis was used to compare groundwater maximum and mean NO_3-N concentrations to maximum and mean summer (June to August inclusive) s.m.d.

Highly significant relationships were found between groundwater NO_3-N concentrations and calculated s.m.d. from the previous year. Mean annual groundwater NO_3-N concentration was significantly related to the maximum s.m.d. ($P=0.0001$, $R^2=0.9242$) and mean summer s.m.d. ($P=0.0013$, $R^2=0.8434$) (Figure 7.12). The maximum observed groundwater NO_3-N concentration was also significantly related to both maximum s.m.d. ($P=0.0076$, $R^2=0.7226$) and mean summer s.m.d. ($P=0.0107$, $R^2=0.6904$) (Figure 7.13). Both maximum and mean observed NO_3-N concentrations were best explained by maximum s.m.d. rather than the mean summer s.m.d. as comparisons with maximum s.m.d. had lower P values and higher R^2 values (Figures 7.12 and 7.13).

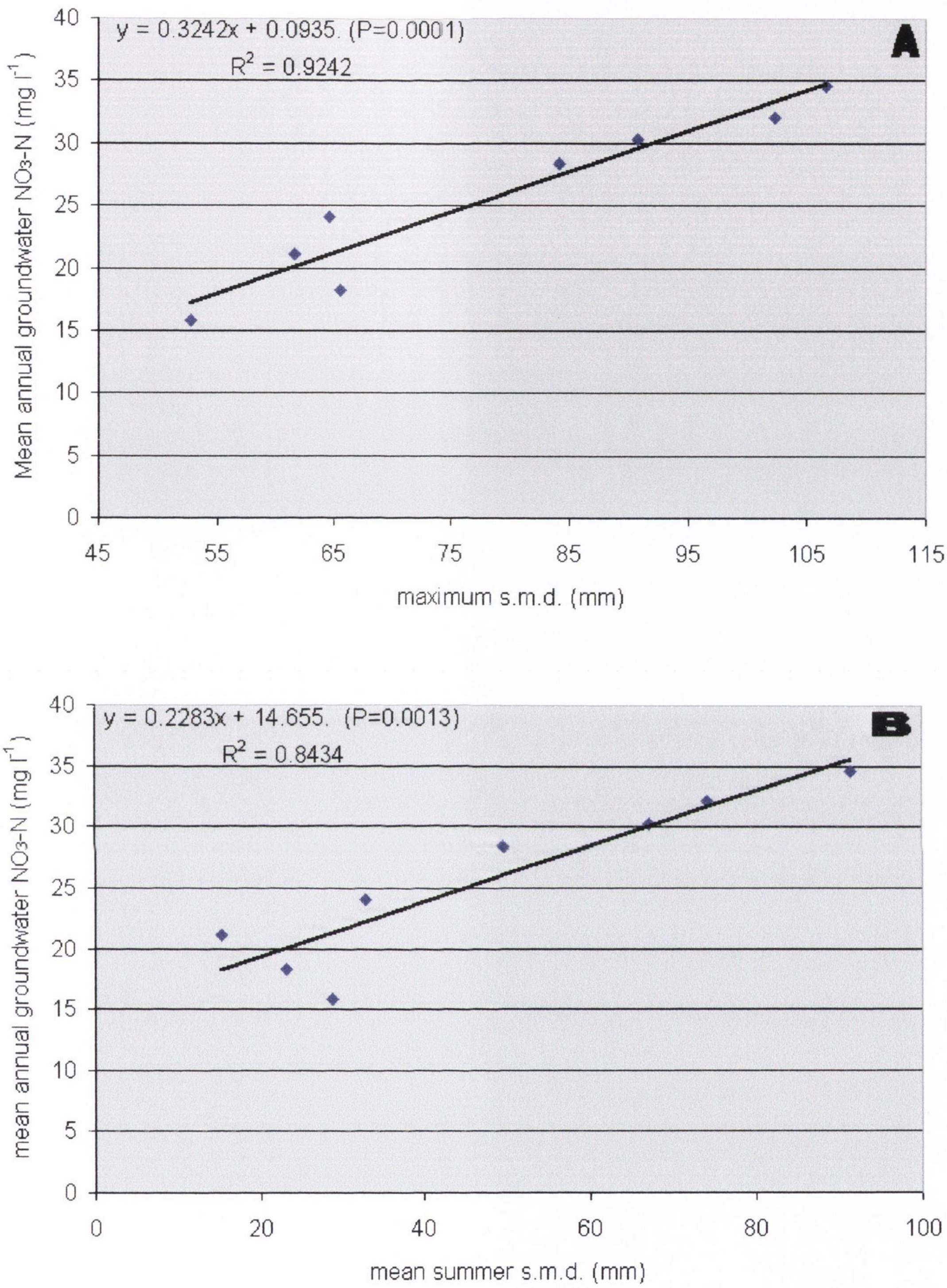


Figure 7.12 Mean annual groundwater NO_3-N in borehole 1 compared to the previous year's (A) maximum s.m.d. (B) mean summer s.m.d..

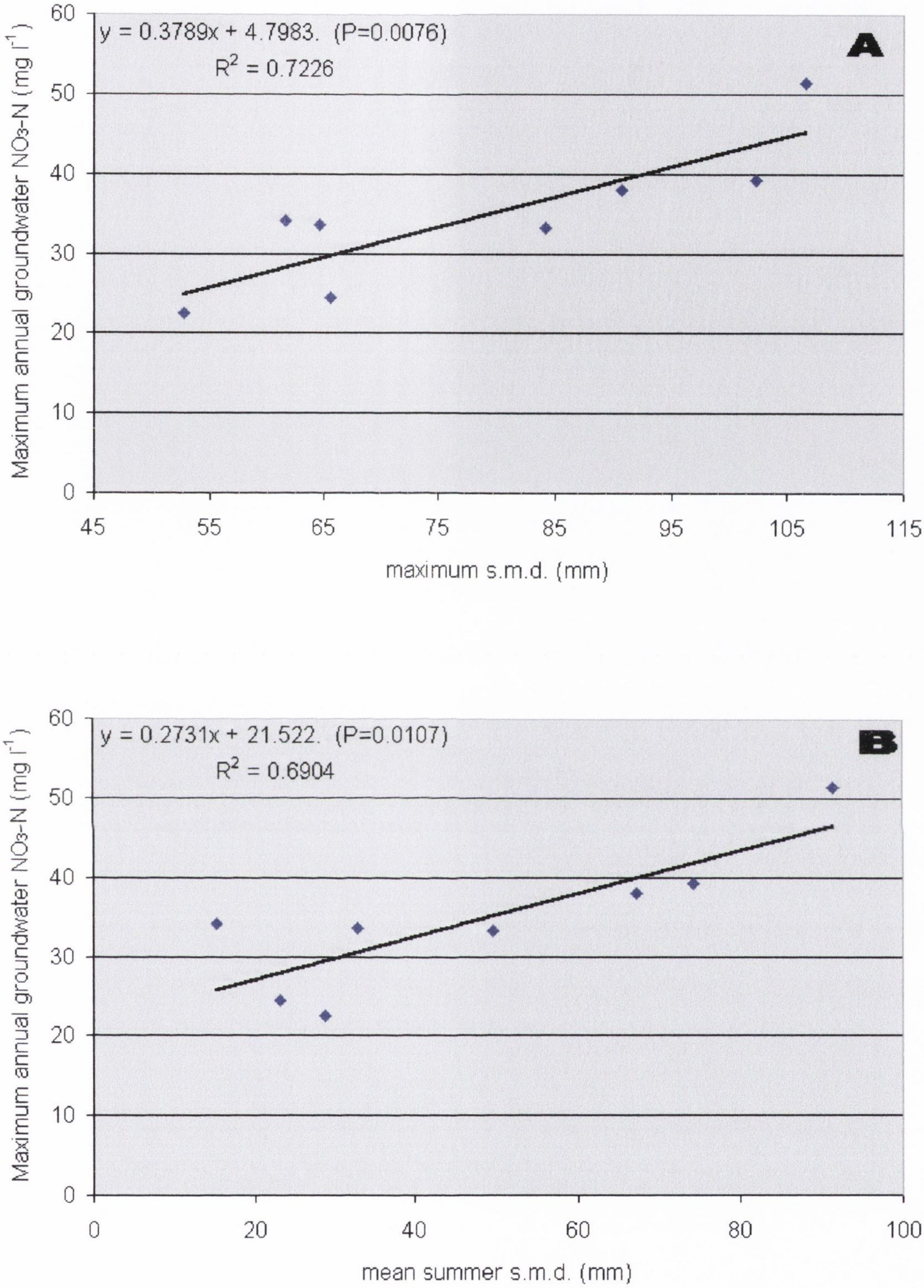


Figure 7.13 Maximum annual groundwater NO_3-N concentration in borehole 1 compared to the previous year's (A) maximum s.m.d. and (B) mean summer s.m.d..

Increased nitrate leaching after summer droughts has been reported in the literature. Sherwood (1988) reports that concentrations of NO_3-N in soil solution beneath an old pasture in Ireland receiving 240 kg N ha^{-1} were dependent on the conditions of grass growth during summer months and highest NO_3-N concentrations were observed in autumn/winter after a summer drought. Garwood and Ryden (1986) also report elevated nitrate leaching after a drought where NO_3-N losses increased from an average of 15 to 145 kg N ha^{-1} $year^{-1}$ in a drought year, with a fertiliser application rate of 250 kg N ha^{-1}. Webster and Dowdell (1984) observed a doubling of NO_3-N concentration in drainage water from cut grass lysimeters when a drought was imposed. Tyson *et al.* (1997) reported a significant correlation between winter NO_3-N leaching and the preceding summer maximum soil moisture deficit over a 13 year period, with the highest losses following dry summers.

Increased nitrate leaching after drought periods can be a result of two factors. Restriction of grass growth limits N uptake by grass; thus an accumulation of unused fertiliser N could build up in the soil which is then leached by subsequent soil re-wetting. Soil re-wetting can also lead to increased mineralisation of soil organic matter. Whitehead (1995) notes that although grass uptake of soil available N is restricted during drought periods there is also a subsequent increase in soil organic N mineralisation upon soil re-wetting.

Through the measurement of soil organic matter mineralisation, which was presented in section 3.6.4, and the variation of soil inorganic N in section 6.4.3, it was possible to observe both a build-up of soil inorganic N during the summer period and increased mineralisation upon soil re-wetting. The source of increased soil inorganic N during the summer drought period of 1995 is unclear and could be due to both non-utilised fertiliser N and N released by either grass or microbial biomass. Garwood and Williams (1967) found a decrease in the quantity of fine grass roots during drought periods, a process which can release large quantities of N. The decrease of fine grass roots both releases N into the soil and also further restricts plant growth although upon re-wetting the roots grew again but not to the same extent as before the drought. Ryan *et al.* (1998) also observed an increase in soil inorganic N in an Irish forest soil after a drought in 1992 which was attributed to both the restriction in plant uptake and also an increase in mineralisation after soil re-wetting. Herlihy (1979) observed that drought increased the amount of N mineralised on a number of Irish soils compared to when the soil moisture was maintained at a constant level.

The observed relationship between groundwater NO_3-N concentrations and soil moisture deficit can thus be attributed to a mixture of both restricted plant uptake of available soil N during drought periods and subsequent mineralisation upon soil re-wetting after the drought. The more severe the drought the more restricted grass growth becomes causing fine grass roots to die releasing more N into the soil and further restricting grass growth.

7.4 N isotope analysis of groundwater samples from Ballyderown

7.4.1 Introduction to the natural abundance of ^{15}N

The isotopic form of an element has an increase number of neutrons compared to the common form of an element. The common form of an element has a proton:neutron ratio of 1 (or up to 1.5 for heavy elements) whereas the isotopic form has a lower ratio such as 0.875 for ^{15}N. The dominant common form of N is ^{14}N (99.67%) which has 7 protons and 7 neutrons compared to the rarer isotopic form which is ^{15}N (0.37%) which has 7 protons and 8 neutrons (Letolle, 1980).

The unit used to express ^{15}N abundance at the naturally occurring level is $\delta^{15}N$, measured as the per mil ^{15}N excess (‰ ^{15}N).

$$\delta^{15}N = \frac{R(sample) - R(standard)}{R(standard)} * 1000‰$$

The usual practice for stable-isotope notation defines R as the atomic $^{15}N/^{14}N$ ratio. The standard used is atmospheric N_2, as the isotopic composition is considered globally uniform, with ^{15}N abundance of 0.3663% (Junk and Svec, 1958).

Many of the important processes involving N in the hydrosphere are performed by bacteria and result in kinetic fractionations associated with unidirectional reactions. Some of the processes result in little isotopic separation, for example N fixation has an isotopic separation of~ 0‰, but many chemical reactions form a product which is significantly ^{15}N depleted compared to the reactant. The isotopic fractionation factor($\in$) for a reaction is:

$$\in = \frac{R_{product}}{R_{reactant}} - 1 * 10^3$$

Inorganic fertilisers

Fertilisers have generally low ^{15}N values. Freyer and Aly (1974) analysed a range of inorganic fertilisers for $^{15}NH_4$ and $^{15}NO_3$. The $\delta^{15}NH_4$ ranged from -3.5 to +1.6‰, the $^{15}NO_3$ ranged from -22.7 to +5.7‰. Of the ten NO_3 fertilisers analysed in their experiment, there were only two values less than 0 ‰.

Nitrate and NH_4 fertilisers are usually derived from atmospheric N by industrial fixation, resulting in little overall isotopic fractionation and therefore have δ ^{15}N-values close to zero (Heaton, 1986). Nitrogenous fertilisers in South Africa had δ ^{15}N values in the range -4.4 to +1.8‰ and this is due to the low ^{15}N abundance of 0.3663‰.

Animal manure and slurry

Nitrogen is mainly excreted in the urea form and thus must be hydrolysed to NH_4 and then nitrified to NO_3 as discussed in section 3.4.2. Ammonia which is volatilised is strongly depleted in ^{15}N and thus NO_3 which is formed from the remaining ammonium is ^{15}N enriched. Volatilised NH_3 is depleted in ^{15}N by ~33‰ compared to the original urea-N (Heaton, 1984). The degree of ^{15}N enrichment depends on a variety of environmental conditions which control volatilisation.

If 16% of the urea N (~+4‰) is volatilised the remaining 84% of N would have δ ^{15}N = +10‰; whilst a loss of 37% of the urea N would leave the remaining 63% of N with δ ^{15}N =+20‰ (calculations assume an equilibrium fractionation of 1.034). Ammonia volatilisation from landspread animal manures makes it difficult to assign a precise value for δ ^{15}N of animal NO_3 in a particular study area.

Komor and Anderson (1993) observed $\delta\,^{15}N$ between +22 and +45‰ beneath cattle feedlots in seven borehole supplies, exceeding the majority of published work.

Soil organic matter mineralisation

The formation of NH_4^+ from organic N, which normally occurs slowly, has a separation factor of 0‰ (ϵNH_4^+ from organic N) (Heaton, 1986; Wilson *et al.*, 1994). Subsequent nitrification of the NH_4^+ causes a large kinetic fractionation of between -35 to -5‰ (ϵNO_3 from NH_4^+) (Delwiche and Steyn, 1970; Freyer and Aly, 1975; Wilson *et al.*, 1994).

$$\text{organic-N} \rightarrow NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \qquad \text{Equation 1}$$

Thus due to different isotopic fractionations with different steps in the formation of NO_3^- from soil organic N (equation 1) the average $\delta\,^{15}N$ of NO_3^- in the N leached to groundwater depends on the step which is rate-limiting for the processes. Typically mineralisation of soil organic matter has $\delta\,^{15}N$ values in the range +4 to +9‰ (Kreitler, 1975; Heaton, 1985; Exner and Spalding, 1994; Gellenbeck, 1994). In a study of groundwater beneath the Springbok flats, South Africa, Heaton (1985) found $\delta\,^{15}N$ in the range of +1.8 and +8.4‰ in the groundwater; these were very similar to the range found in a soil incubation study i.e., NO_3-N (+3.8 to 10‰) and organic soil N (+5 to +6.2‰). Heaton (1984) showed soil ^{15}N -values in the range +3 to +12‰ and the isotopic composition of water from this is in the range +4 to +8‰. In the U.K., Wilson *et al.* (1994) reported NO_3 from soil organic matter mineralisation in the range +5.4 to +9.3‰. Fogg *et al.* (1998) found a mean $\delta\,^{15}N$ value of 2.62 ± 0.89‰ for soil water extracts from a soil which had not received fertiliser N for 30 years.

Denitrification

Denitrification in general has an isotopic separation factor of $\epsilon N_2\text{-}NO_3^- \sim$ -35‰. Similar values of -40 to -30 ‰ were calculated for oceanic denitrification, and laboratory experiments have produced values from -33 to -10 depending on the experimental conditions.

As the NO_3 concentration decreases due to denitrification the $\delta^{15}N(NO_3)$ increases, becoming heavier. Denitrification of 20% of the NO_3-N in groundwater may increase the ^{15}N content by ~+8‰ compared with its original value (Heaton, 1984). Wilson *et al.* (1994) describe the $\delta^{15}N$ fractionation due to denitrification. Vibrant ^{14}N bonds are weaker than the heavier ^{15}N, so denitrification would be expected to fractionate the ^{15}N relative to ^{14}N in the products and reactants owing to the greater reactivity of the $^{14}NO_3$. Consequently denitrification is treated as a unidirectional reaction ($NO_3 \rightarrow N_2$) so that the changes in the isotopic composition of NO_3 and N gas can be modelled by Rayleigh fractionation based on isotopic measurements of these two N species alone.

$\delta^{15}N(NO_3)$ greater than +10‰ are interpreted as representing localised pollution from animal or sewage waste. Values from +4 to +9 ‰ are characterised by N sourcing from soil organic N. Values from -4 to +4 ‰ are indicative of fertiliser source as they lie close to $\delta^{15}N$ for atmospheric N which is 0 ‰. Heaton (1986) observed groundwater nitrate $\delta^{15}N$ ranging from -15.7 to -5.8 ‰ which were attributed to isotopically light rainwaters. Isotopically light NO_3 observed by Heaton (1986) may reflect the leaching of nitrified ammonium fertilisers.

Sewage effluent

Sewage effluent was shown by Gellenbeck (1994) to have a low $\delta\,^{15}N$ of +1.4 to +3.2‰ with N in the ammoniacal form. Upon subsequent nitrification and leaching to shallow groundwater the isotopic content of N had changed from +13.3 to +14‰ (Gellenbeck, 1994). In another study $\delta\,^{15}N$ in a septic tank plume had concentrations ranging from +8.1 to +13.9‰ (mean+9.1‰); at the edge of the plume the $\delta\,^{15}N$ ranged from +3.4 to +6.2‰ with a mean of 4.6‰ (Aravena *et al.,* 1993).

Mixed sources of contamination

One problem of isotopic studies in determining the N source is that fertiliser derived N becomes an integral part of the soil organic matter thus losing its $\delta\,^{15}N$ identity (Kohl *et al.*, 1973; Mentis *et al.*, 1975). Thus the groundwater $\delta\,^{15}N$ value could indicate that mineralised

N is the source of N in the groundwater but will not show that this is due to excessive fertiliser applications. Surface water is more subject to runoff, allowing fertilisers to enter directly in to the water body. Thus N isotope studies may be able to differentiate fertiliser N in this situation.

In many cases $\delta\ ^{15}N$ values >10‰ are generally interpreted as representing point source pollution based on location of potentially polluting activities or general water chemistry (eg. high K^+ or Cl^- concentrations) or the presence of faecal bacteria (Mariotti *et al.*, 1984).

Exner and Spalding (1994) concluded that groundwater in the Sydney study area was being affected by a mixed N source i.e., from fertilisers, soil organic matter and spread manures; the $\delta\ ^{15}N$ ranged from +5.8 to +8.8‰. The study also showed that $\delta\ ^{15}N$ became lighter with increasing distance from the feedlot at the centre of the study. This was due to animal manures from the feedlot being applied nearby due to the expense of haulage, thus inorganic fertilisers become more important with increasing distance from the feedlot.

Berndt (1990) also showed N contamination from a mixed source. Of the two sites which were studied, one had only sewage effluent applied and the other site had both sewage and fertilisers applied. The $\delta\ ^{15}N$ ranged from +8.9 to 16.7‰ and +5.4 to 12.2‰ for sewage and sewage plus fertiliser, respectively, and the treatments had statistically different $\delta\ ^{15}N$ values.

Samples which have $\delta\ ^{15}N$ values in the range +4 to +8‰ are typical for fertiliser sources N (Townsend *et al.*, 1996) which are slightly higher than the accepted range for fertilisers of -4 to +4‰ (Heaton, 1986). $\delta\ ^{15}N$ values in the range +4 to +9‰ are typical for mineralised soil organic matter.

Fertilisers generally have very low values and are typically found in the aquatic system in the range -4 to +4 ‰ (Heaton, 1986) These authors found that samples which had $\delta\ ^{15}N$ values of +10 to +20 ‰ were indicative of the effects of denitrification which causes enrichment of ^{15}N. Kreitler (1975) reports that $\delta\ ^{15}N$ ranging from +2 to +8‰ are indicative of either artificial fertilisers or the mineralisation of soil organic N. $\delta\ ^{15}N$ in the range +10 to + 22‰ is indicative of N from the decomposition of animal waste.

Temporal variation of δ ^{15}N

In residential areas (Komor and Anderson, 1993) found δ ^{15}N between 1.5 and 11.7‰ with a mean of 6‰. A total of 12 wells were sampled in the US from June to August 1986 and again in May 1987. Eight of the wells had changes in the δ ^{15}N exceeding 1‰. These temporal changes may be due to changes in the proportions of N sources or to variable amounts of fractionation of a single source, e.g., a decrease from +7.8‰ to +1.5‰ could indicate that the proportion of fertiliser N was greater in the second sample than the first or that more denitrification occurred in the first sample. There was also an increase in δ ^{15}N with groundwater depth.

7.4.2 ^{15}N Methodology

Nitrogen 15 analyses were carried out on groundwater samples taken from Ballyderown during 1993 and 1994. The groundwater samples were taken monthly from boreholes on the farm which were preserved with 4 ml of chloroform per litre of sample and stored at 4°C until analysis. Three samples were selected for analysis, October 1993 and February and August 1994. Two commonly used fertilisers were also taken for ^{15}N determination. The samples were sent to the Institute of Nuclear Research of the Hungarian Academy of Sciences for δ ^{15}N determination.

Determination of δ ^{15}N was carried out using the methodology described by Ross and Martin (1970). The sample was contained in a screw capped vial which was coupled with a neoprene O-ring to a special assembly, evacuated, and the sample oxidised with air-free hypobromite solution from a reservoir in the assembly. Isotope analyses were then carried out on the N gas liberated.

7.4.3 ^{15}N Results and Discussion

Two fertilisers which are commonly used on the farm were isotopically analysed for N and they had values of δ ^{15}N +0.5 and +1.1‰ for ammonia sulphate and calcium ammonium nitrate, respectively. Thus the fertilisers had very low and positive δ ^{15}N values.

The results of groundwater δ ^{15}N determinations can be seen presented as a frequency histogram (Figure 7.14).

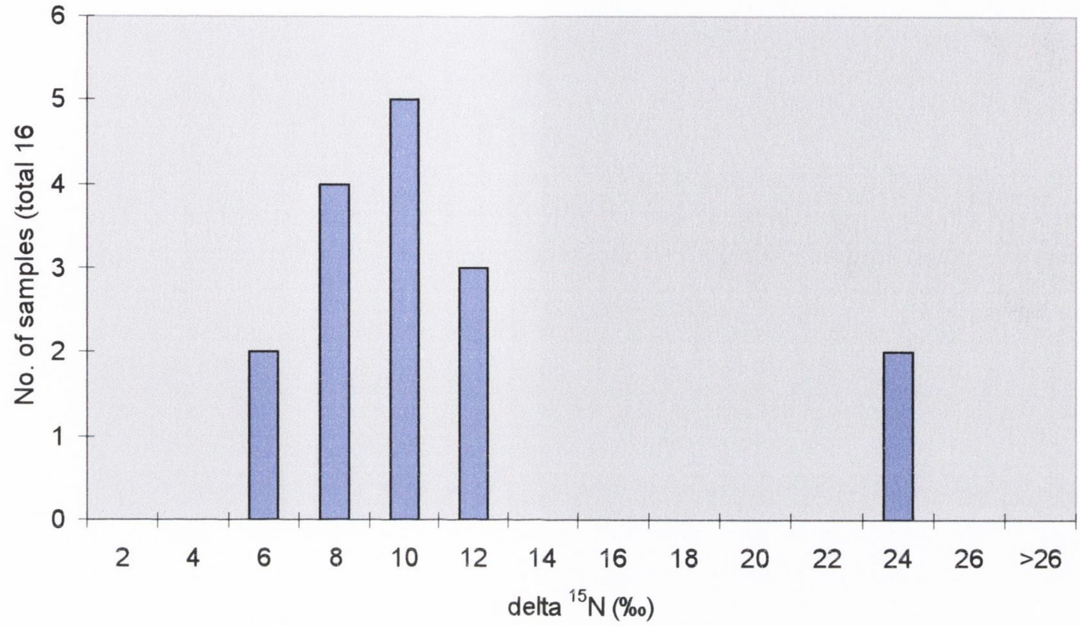


Figure 7.14 Frequency histogram of all groundwater δ ^{15}N ratios from Ballyderown. The category marked 6‰, for example, encompasses the δ ^{15}N from 4.1 to 6‰.

The δ ^{15}N results from the groundwater samples at Ballyderown varied from +5 to +24‰. The majority (87.5%) of δ ^{15}N ratios were in the range from +4.1 to +12‰ (Figure 7.14). There were only two determinations which were greater than +12‰ which were in the range +22 to +24 ‰. The mean δ ^{15}N ratio of the results between +4.1 to +12‰ was +8.4‰ with a standard error of 0.52‰.

The results of the δ ^{15}N determination of groundwater samples, taken on the three sampling dates, 19/10/93, 21/2/94 and 23/8/94 are shown in Table 7.1.

Table 7.1 Temporal variation of δ ^{15}N (‰) ratios observed at Ballyderown.

	Borehole						
Date	1	2	3	4	5	Canteen	Spring
19/10/93	6.9	5.1	24.0	-	-	11.0	-
21/02/94	10.5	6.2	5.6	22.6	-	9.6	-
23/08/94	9.0	9.4	7.4	11.0	8.8	9.4	7.7

There appears to be considerable temporal variation in the results of δ ^{15}N values for each groundwater source. Groundwater samples from borehole 3 over the sampling period decreased from +24‰, when the first sample was taken on 19/10/93, to +5.6‰ on 21/2/94 before increasing again to +7.4‰ on 23/8/94. Whereas δ ^{15}N in borehole 2 increased over the sampling period from +5.1 to +9.4‰ thus indicating that a N source with heavier δ ^{15}N ratio was starting to dominate over the lighter N source. In borehole 1 δ ^{15}N increased from a low of +6.9‰ on 19/10/93 peaking at +10.5‰ on 21/2/94 before decreasing again to +9.0‰ on 23/8/94.

The high δ ^{15}N observed in borehole 3 on the first sampling date corresponded to both increased groundwater NO_3-N concentration and water table height (day 292 in Figure 7.3) indicating that leaching had occurred or was occurring: the increase in groundwater NO_3-N concentration in borehole 3 on day 292 (Figure 7.3) was not observed in either boreholes 1 or 2 although slight increases in water table height were observed. Thus the source of the increased NO_3-N was not present at boreholes 1 or 2. The high δ ^{15}N value of 24‰ was in the range of +22 to +45‰ from cattle feedlots (Komor and Anderson, 1993) and thus the increased NO_3-N concentrations at this time in borehole 3 are likely to be from an animal manure source. As no animal manure was applied to plot 16, which contains borehole 3, the likely source of the NO_3-N is another nearby plot. Plots 13, 13a, 15 and 15a had slurry applied to them at the start of September 1993 just before the plots were ploughed for re-seeding. The source of the high NO_3-N concentration and δ ^{15}N value in October 1993 is likely to be slurry applied to plots 13, 13a, 15 and 15a. The decreased δ ^{15}N in 1994 was due to the N from the slurry having been lost and N from a lighter source, such as soil organic N mineralisation, dominating the δ ^{15}N values.

The other high $\delta\ ^{15}N$ value of +22.6‰ observed in borehole 4, when sampled on 21/02/94, again indicates that the groundwater NO_3-N source is animal manure. The groundwater NO_3-N source at this time in borehole 4 has been attributed to dirty water irrigation occurring in plots surrounding plot 3a, which contains borehole 4. There may also be some influence of slurry applied to plots 13 and 13a which are also located close to plot 3a. The $\delta\ ^{15}N$ decreased from +22.6 to +11‰ between 21/2/94 (day 417) and 23/8/94 (day 600) (Figure 7.4). The decrease of $\delta\ ^{15}N$ occurred simultaneously with a decrease of groundwater NO_3-N concentration from 58 to 50 mg l^{-1} (Figure 7.4).

The remaining $\delta\ ^{15}N$ observed in all the boreholes indicates a mixed source of groundwater NO_3-N. It is difficult to separate the effect of fertiliser which has a low $\delta\ ^{15}N$ range of 0 to +4‰, from slurry applications and grazing dung and urine deposits which have high $\delta\ ^{15}N$ values due to all sources being applied to plots at the same time. Mineralised soil organic N has a $\delta\ ^{15}N$ somewhere between fertiliser and animal manures. The $\delta\ ^{15}N$ from mineralisation on the farm may be higher due to the high organic N content of the soil which is made up of slurry organic N which is mineralised over time. Thus N mineralisation in the field corresponds to both native soil organic N and also any remaining slurry organic N and thus mineralised N may have a higher $\delta\ ^{15}N$ than other reported ranges due to the source of organic soil N being a mixture of native and remaining slurry N.

The relationship between groundwater NO_3-N and the $\delta\ ^{15}N$ ratio of the NO_3-N (from Table 7.1) can be seen in Figure 7.15.

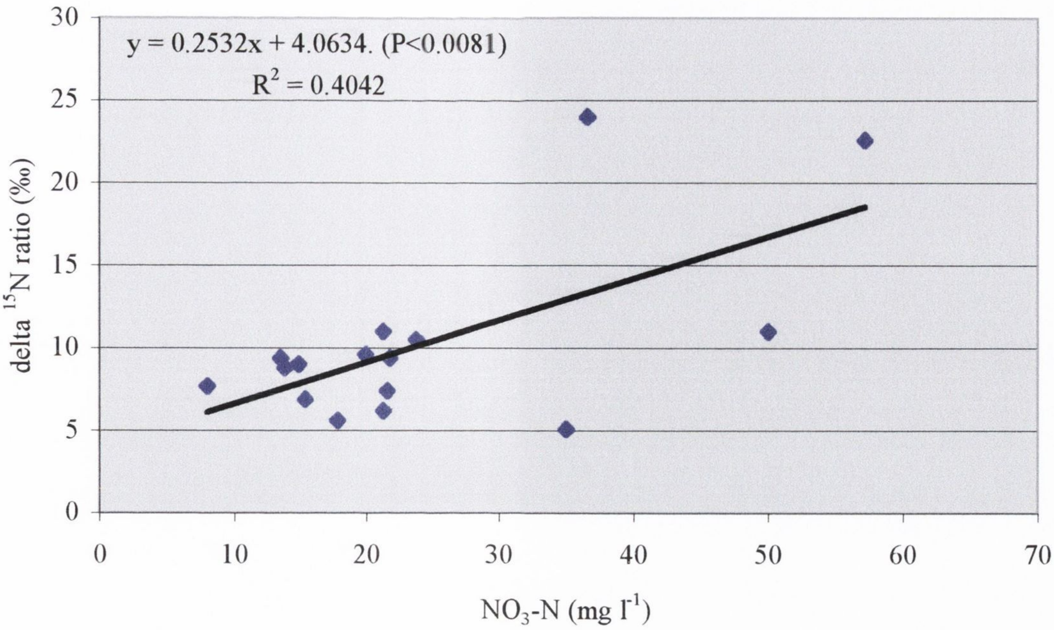


Figure 7.15 The relationship between δ ^{15}N ratios and NO_3-N concentrations for all boreholes on the three sampling dates.

There appears to be a significant ($P<0.0081$, $R^2=0.4042$) relationship between groundwater NO_3-N concentration and the δ ^{15}N ratio measured. Although the relationship between δ ^{15}N and groundwater NO_3-N concentration is not strong and is being influenced by the two high δ ^{15}N values it none the less raises the point that on the farm extremely high NO_3-N concentrations are associated with application of slurry and/or dirty water, whereas the lower δ ^{15}N concentrations are reflecting the general source of the groundwater NO_3-N being either a mixed source or being due to mineralisation of organic N.

A further interesting finding is that the NO_3-N in the canteen supply has δ ^{15}N values similar to the rest of the farm which ranged from +9.4 to +11‰ which are on the border of the mineralisation and animal manure values although the source was thought to be influenced by a point source such as the farm yard due to the presence of coliforms in the supply (section 7.5.3). The NO_3-N concentrations in the canteen supply do not appear to be dominated by N from the farmyard. Thus it is possible to have indications of localised pollution (such as coliforms or elevated K^+ or Cl^- concentrations) although associated N may not be from the same source as the other indicators as suggested by the δ ^{15}N .

From the $\delta\ ^{15}N$ determinations on groundwater NO_3-N from Ballyderown it is clear that animal manures greatly increase the $\delta\ ^{15}N$ to >+20‰ and this was only observed in two boreholes. The rest of the farm had $\delta\ ^{15}N$ in the range +4 to +12‰ which indicates mixed N sources of fertiliser, animal slurry and excretions while grazing and soil organic N mineralisation which may also be influenced by historical slurry applications. From this work it is clear that attributing sources of groundwater NO_3-N by determining $\delta\ ^{15}N$ is complicated due to the large number of N sources and pathways which occur on a grassland farm.

7.5 Saturated zone coliform monitoring

7.5.1 Introduction

From the perspective of human consumption the greatest threat is the presence or absence of pathogens which are capable of infecting or transmitting disease to humans (Lucey *et al.*, 1999). Although coliforms are not pathogenic they do act as indicators of the possibility of pathogenic micro-organisms occurrence. The main purpose of the current study for determination of groundwater faecal coliforms was to examine if the groundwater nitrate was associated with indicators of an organic N source. The presence of faecal coliforms indicates pollution from a warm blooded animal as these bacteria typically die within a relatively short time period (up to 100 days) after leaving the host organism. In order to examine if NO_3-N in the saturated zone was related to the application of farm yard slurries and dirty water, the groundwater was monitored for faecal coliforms on 4 occasions from November 1994 to February 1995.

High nitrate concentrations associated with faecal coliform concentrations was observed by Spalding (1991) in Nebraska, USA which was attributed to poor well design making boreholes vulnerable to surface contamination. Although Howell *et al.* (1995) observed faecal coliform contamination of shallow groundwater and stream water in agricultural areas affected by intensive grazing (ie diffuse contamination), which was attributed to rapid recharge.

Faecal colifroms are incubated at 44.5 °C as this represents a mammalian digestive system thus faecal coliforms are indicators of pollution by mammalian excreta. Whereas total coliforms includes common coliforms such as soil microbes which indicate that the groundwater has either travelled quickly through the unsaturated zone or due to inadequate borehole design.

7.5.2 Methodology for monitoring saturated zone coliforms

Boreholes were sterilised using 150 ml Milton Fluid which was then diluted in 1.5 litres of distilled water; this was left in the borehole until the following week when the boreholes had two well volumes removed. For the sampling procedure the equipment was sterilised using dilute Milton fluid. The bailer was lowered into the borehole using a fishing line which was wound around a plastic frame to prevent any possible sample contamination. The well was bailed in the usual manner. A sample was removed in a sterile jar and placed in a cool box awaiting analyses on return to the laboratory.

Analyses for coliforms were carried out using the membrane filtration technique, where 100 ml of sample was filtered through a selective membrane. This was then incubated at two different temperatures for 24 hours as outlined in Appendix 1.

7.5.3 Saturated zone coliform results

The results of the groundwater coliform monitoring on the four sampling dates is presented in Table 7.2.

Table 7.2 Results of groundwater coliform monitoring (counts 100 ml^{-1} of sample).

	15/11/94		13/12/94		18/1/95		20/2/95	
Borehole	Total	Faecal	Total	Faecal	Total	Faecal	Total	Faecal
1	0	0	0	0	0	0	0	0
2	130	0	22	0	0	0	0	0
3	0	0	1	0	0	0	0	0
4	0	0	1	0	0	0	0	0
5	0	0	0	0	0	0	0	0
Canteen	0	0	4	0	10	4	10	2
Spring	-	-	-	-	-	-	2	0

From the results in Table 7.2 it is possible to see that at no time was there contamination of boreholes 1 to 5 by faecal coliforms, although in November and December 1994 some total coliforms occurred in borehole 2 (on both sampling dates) and in borehole 3 and 4 in December. The total coliform count of one for boreholes 3 and 4 were <10 counts per 100 ml which is a level below which is regarded as of little sanitary significance (WHO, 1984).

The canteen supply had total coliform counts on three of the sampling dates and faecal coliforms present on two sampling dates. The presence of faecal coliforms in the canteen supply tends to suggest that this borehole was being affected by a point source of contamination such as the farm yard although the $\delta^{15}N$ suggests a mixed source of NO_3-N contamination (section 7.4.3). Thus although there appears to be point source contamination it does not appear to be the main cause of groundwater NO_3-N contamination. Thus the classification of a groundwater supply as being point source contaminated may hide the fact that NO_3-N concentrations in the supply may be due to diffuse pollution and not to the same point source which is causing biological pollution.

The results of the groundwater coliform monitoring shows that, with the exception of borehole 2 in November and December 1994, the groundwater sampled beneath the plots showed no presence of coliform contamination. The monitoring period selected for the coliform analysis was the period of maximum recharge. The water table in all boreholes rose in November 1994 and reached the maximum height in early February 1995.

7.6 Saturated zone potassium, sodium and chloride variation

7.6.1 Introduction

Other chemical parameters were monitored as part of the routine groundwater sampling and analysis as detailed in section 7.2.1. Potassium (K^+), sodium (Na^+) and chloride (Cl^-) were selected for laboratory determination due to these chemical parameters also being related to different sources of groundwater contamination. Concentrations of K, Cl^- and the ratio of K/Na have been used to characterise groundwater contamination as either point source pollution when these are elevated or general diffuse pollution if the concentrations are determined to be background.

The concentration of K^+ in groundwater can be used to identify point source contamination which can lead to elevated K^+ concentrations although background concentrations may be higher in sandstones and volcanics and a concentration of 4.5 mg l^{-1} has been suggested by Deakin (1994) to identify point source influenced groundwater. The ratio of K^+ (mg l^{-1}) to Na^+ (mg l^{-1}) has been used to identify potentially point source polluted supplies which generally have an elevated K^+ concentration in relation to the Na^+ concentration.

Daly and Daly (1982) proposed K^+ concentrations of greater than 5 mg l^{-1} and K/Na ratios of greater than 0.3 as indicating contamination from local sources such as farmyards, septic tanks and other organic vegetable waste. Potassium concentrations greater than 5 mg l^{-1} in groundwater would need 9 kg K ha^{-1} to be leached and as K^+ is preferentially absorbed on to clays compared with Na^+ the ratio of K/Na is also a useful relationship. A survey of the principal springs in Ireland showed that in Kerry springs had a mean K^+ concentration of 2.9 mg l^{-1} and five of the fifteen springs (33%) had K^+ concentrations >4 mg l^{-1} (Daly *et al.*, 1989).

Daly and Daly (1982) suggest that groundwater recharge from diffuse fields will have low K^+ and K/Na ratios due to K^+ absorption whereas organic matter point sources have higher K^+ and K/Na ratios.

Sodium concentrations in groundwater are generally determined by proximity to the sea as rainfall is the most common source of Na. Cation exchange is another process which accounts for significant amounts of Na^+ in groundwater. Clay minerals most often contribute significant quantities of Na^+ to water either in soil and quaternary deposits or from clay rich bedrock such as shales (Domenico and Schwartz, 1990).

High concentrations of Cl^- in groundwater has been associated with sewage effluent (Lucey *et al.*, 1999). Although Cl^- concentrations of 30 to 55 mg l^{-1} have been associated with localised pollution (Deakin, 1994; Lucey *et al.*, 1999). A study in Germany groundwater beneath landfills showed a linear association between NO_3-N and Cl^- concentrations (Zahn and Grimm, 1993). Diffuse contamination of groundwater by nitrate was observed to be associated with Chloride beneath agricultural areas in Wisconsin, USA (Saffina and Keeney, 1977). High chloride concentrations can be attributed to both point and diffuse sources of pollution.

Deakin (1994) observed mean groundwater Cl^- concentrations for contaminated and uncontaminated boreholes of 23.4 and 25.1 mg l^{-1}, respectively, which are close to the values observed in the Fermoy region. A total of 85% of 886 Irish groundwater samples had Cl^- concentrations less than 30 mg l^{-1} as reported by Lucey *et al.* (1999).

7.6.2 Methodology

Weekly groundwater samples taken for NO_3-N determination, from October 1993 to February 1996, as described in section 7.2.1, were also analysed for K^+ and Na^+ on a Varian Atomic Absorption spectrophotometer, and Cl^- using a Mettler DL21 titrimeter (Appendix I). Chloride data was not as complete as K^+ and Na^+ data due to unavoidable laboratory problems. No Cl^- determinations were carried out between 23/8/94 and 6/4/95.

7.6.3 Groundwater Potassium Results and Discussion

A summary of observed groundwater K^+ concentrations from 1/1/94 until 1/8/96 can be seen in Table 7.3.

Table 7.3 Summary of groundwater K^+ observations from Ballyderown (mg l^{-1}) between 1/1/94 and 1/8/96.

Summary	Borehole					
Statistics	1	2	3	4	5	Canteen
mean	1.8	2.5	3.8	1.6	1.0	4.1
median	1.5	2.2	3.6	1.6	0.9	4.7
standard deviation	0.8	0.8	0.8	0.3	0.3	1.6
standard error	0.094	0.1	0.097	0.031	0.047	0.21
maximum	4.9	4.7	8.3	2.3	2.7	6.9
minimum	1.0	1.5	2.8	1.0	0.4	0.2
range	3.9	3.2	5.5	1.3	2.3	6.7
Sample size	65	64	65	65	51	59

Mean observed K^+ concentrations during the sampling period ranged from 1 to 4.1 mg l^{-1} with the lowest mean concentration observed at borehole 5 and the highest mean level observed in the canteen supply. Borehole 3 and the canteen supply had mean K^+ concentrations >3 mg l^{-1} and the mean concentrations in the remaining boreholes varied between 1 and 2.5 mg l^{-1}. Maximum observed K^+ concentrations in each borehole ranged from 2.3 to 8.3 mg l^{-1} in boreholes 4 and 3, respectively. Boreholes 4 and 5 were the only boreholes which had maximum observed concentrations <4.5 mg l^{-1}, a concentration above which is sometimes used to indicate point source contamination.

The temporal variation of groundwater K^+ concentrations at Ballyderown can be seen in Figure 7.16.

There does not appear to be a clear temporal trend in the concentration of groundwater K^+ observed in Ballyderown, although during the 1995/96 recharge period there does appear to be a significant increase in groundwater K^+ concentration especially in boreholes 1 to 3 and the canteen supply. Deakin (1994) also observed increased groundwater K^+ concentrations during winter periods in Co. Limerick which suggests that some K^+ leaching through soil occurs.

Temporal variation of groundwater K^+ concentrations was statistically compared between the 6 different observation points using Pearson Product Moment Correlation. Where there appeared to be significant relationships regression analysis was carried out. Boreholes 1, 2 and

3 appeared to have similar temporal variation of K^+ concentrations during the study period. Due to the skewed nature of the K^+ observations and also to the appearance of pattern in the regression residuals it was decided to log transform the data. The log transformation improved the probability and the R^2 of each regression.

The relationship between the log K^+ concentration observed in borehole 1 and 2 is presented in Figure 7.17.

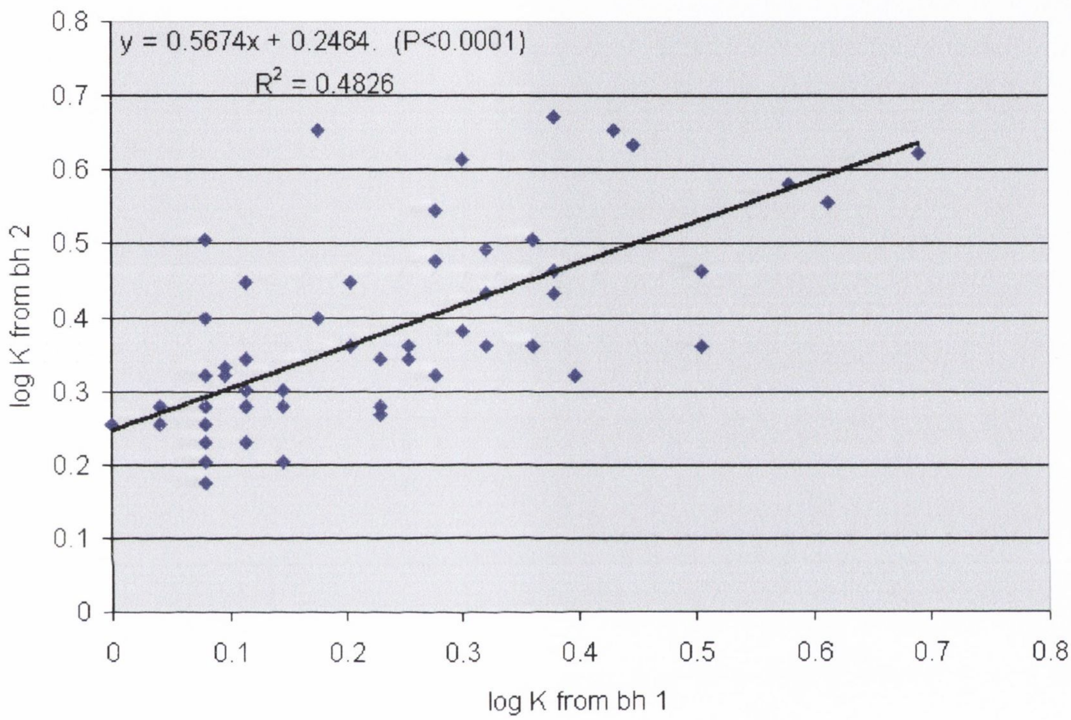


Figure 7.17 Relationship between log K^+ concentration in boreholes 1 and 2, between 1/1/94 and 1/8/96.

The log K^+ concentrations in borehole 1 were significantly ($P<0.0001$) related to the concentrations observed in borehole 2 with R^2=0.48. A slightly weaker, highly significant ($P<0.0001$) relationship was found between log K^+ observed in borehole 1 and borehole 3 with R^2=0.234. A weaker relationship (P=0.0002) was also found between boreholes 2 and 3, R^2=0.198.

Deakin (1994) reported groundwater K^+ concentrations, from public supply sources in Co. Limerick, ranging from 0.3 to 3.8 mg l^{-1} for non point source contaminated sites which is lower

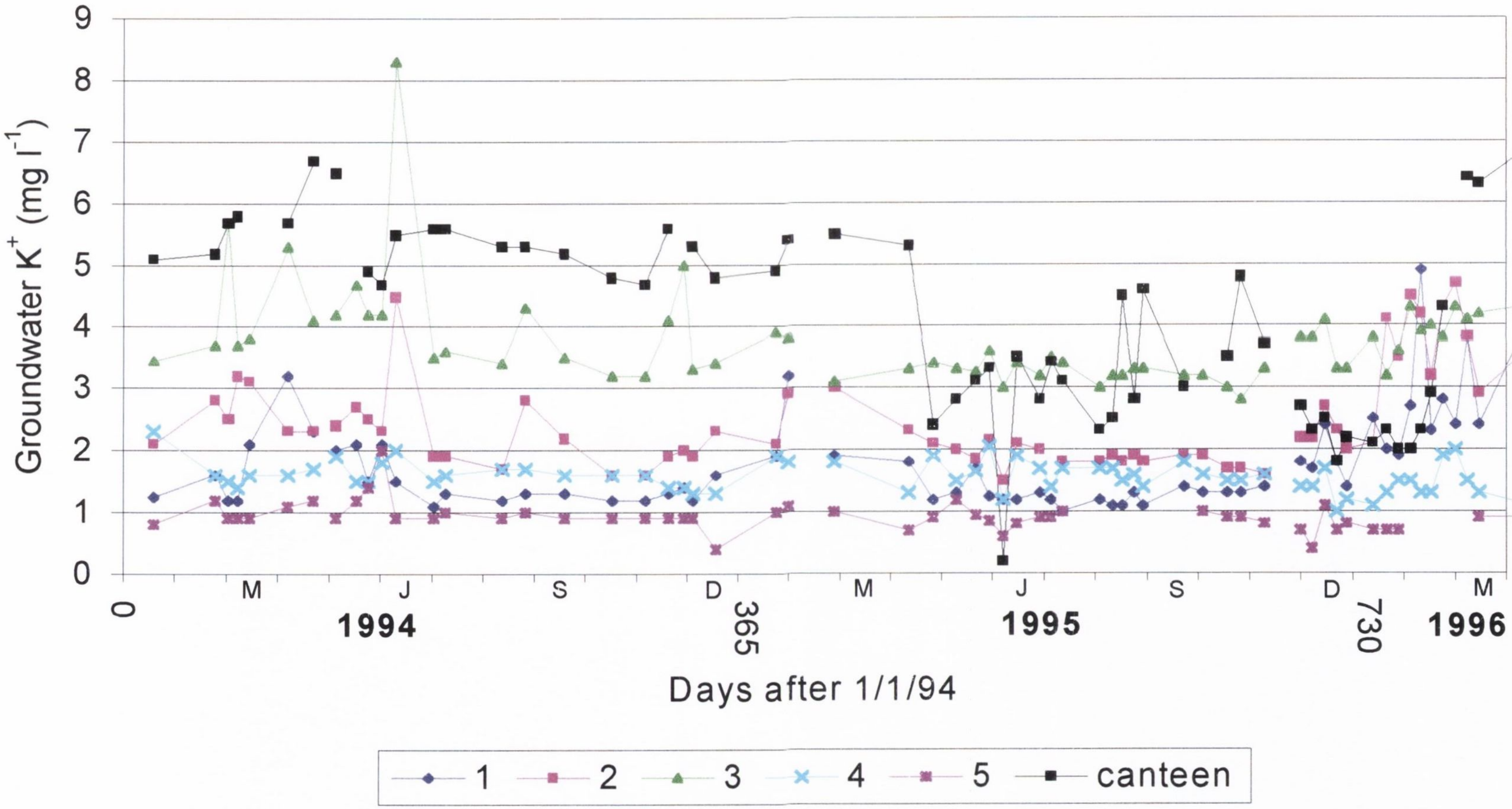


Figure 7.16 Temporal variation of groundwater K^+ concentrations (mg l^{-1})observed in boreholes at Ballyderown (1/1/94 to 1/8/96).

than the observed ranges in boreholes 1, 2, 3 and the canteen supply. The mean groundwater K^+ concentration of 1.5 mg l^{-1} for public supply sources in Co. Limerick was lower than the mean of all boreholes at Ballyderown, with the exception of borehole 5.

Potassium is applied to the plots at Ballyderown in the form of inorganic K^+ fertilisers and as animal manure either from direct excretion in a grazed plot or as landspread slurry. Potassium fertilisation occurred in conjunction with phosphorus application in March of each year in the N:P:K fertiliser form 0-7-30. Soil K^+ levels were determined from soil samples taken from 0 to 90 cm in autumn 1995.

Table 7.4 Soil and quaternary deposit K^+ concentrations in mg kg dry soil^{-1}, as sampled from certain plots at Ballyderown in Autumn 1995.

Depth	plot number (borehole identity)						
cm	12 (1)	5 (2)	16 (3)	3a (4)	7 (5)	6	6a
0 to 15	195	250	149	63	300	272	259
15 to 30	103	204	170	109	290	157	118
30 to 45	85	163	150	133	191	119	106
45 to 60	80	133	131	141	152	88	80
60 to 75	75	127	160	136	132	77	77
75 to 90	51		181	140	130	89	58

The soil K^+ concentrations observed in Ballyderown were high (Table 7.4). With the exception of plots 16 and 3a all boreholes had high top soil K^+ concentrations. Interestingly plots 16 and 3a have increasing soil K^+ concentrations with depth which may indicate net removal of K^+ from these plots due to the non application of K^+ fertilisers. The increasing soil K^+ concentrations with depth indicates that the soil is releasing K. The soil/quaternary deposits are developed from a red sandstone parent material (section 4.2). Thus the soil/quaternary deposits may also be acting as sources of K^+ for leaching to the groundwater.

7.6.4 Groundwater Sodium Results and Discussion

A summary of observed Na^+ concentrations in each borehole from 1/1/94 to 2/4/96 can be seen in Table 7.5.

Table 7.5 Summary of groundwater Na^+ concentrations (mg l^{-1}) from Ballyderown.

Summary Statistics	Borehole 1	2	3	4	5	Canteen
mean	8.6	14.2	10.4	15.5	8.4	12.0
median	8.4	13.4	10.2	14.7	8.0	12.0
standard deviation	1.7	3.3	0.9	4.1	3.4	1.0
Standard error	0.21	0.41	0.11	0.5	0.56	0.13
maximum	16.9	30.2	14.8	35.6	26.7	15.5
minimum	6.7	10.0	9.5	13.1	5.8	10.5
range	10.2	20.2	5.3	22.5	20.9	5.0
sample size	66	65	66	66	37	57

Mean groundwater Na^+ concentrations ranged from 8.4 to 15.5 mg l^{-1} in boreholes 5 and 4, respectively. Boreholes 1 and 5 had mean groundwater Na^+ concentrations <10 mg l^{-1} whereas the remaining boreholes had mean Na^+ concentrations of >10 mg l^{-1}. Borehole 4 had the highest mean and maximum observed Na^+ concentrations of 15.5 and 35.6 mg l^{-1}, respectively.

The temporal variation of groundwater Na^+ concentrations observed between 1/1/94 and 2/4/96, inclusive, can be seen in Figure 7.18. There does not appear to be any clear seasonal temporal variation of Na^+ concentrations suggesting that there is a constant supply of Na^+ or that Na^+ does not build up in the soil causing increased concentrations upon groundwater recharge.

Increased Na^+ concentrations observed in all boreholes on 29/11/94 (day 333) occurred 28 days after observed increases in borehole water table height increases (Figure 5.5). The increase was most dramatic in boreholes 2, 4 and 5 which all increased to >20 mg l^{-1}. A further marked increase of groundwater Na^+ concentration occurred on 21/2/95(day 417). This increase was more marked in boreholes 2 and 4 which increased from <15 mg l^{-1} to ~ 30 mg l^{-1} whereas in the other boreholes there was only a slight increase in concentration. This marked increase in concentration occurred in week 8 (Appendix C3) which had two very wet weeks preceding it during which there was 102.9 mm of effective rainfall which may have been the source of elevated Na^+ or could have moved Na^+ from the soil to the groundwater. After this date groundwater Na^+ concentrations in each borehole remained very uniform with no marked changes of concentrations observed.

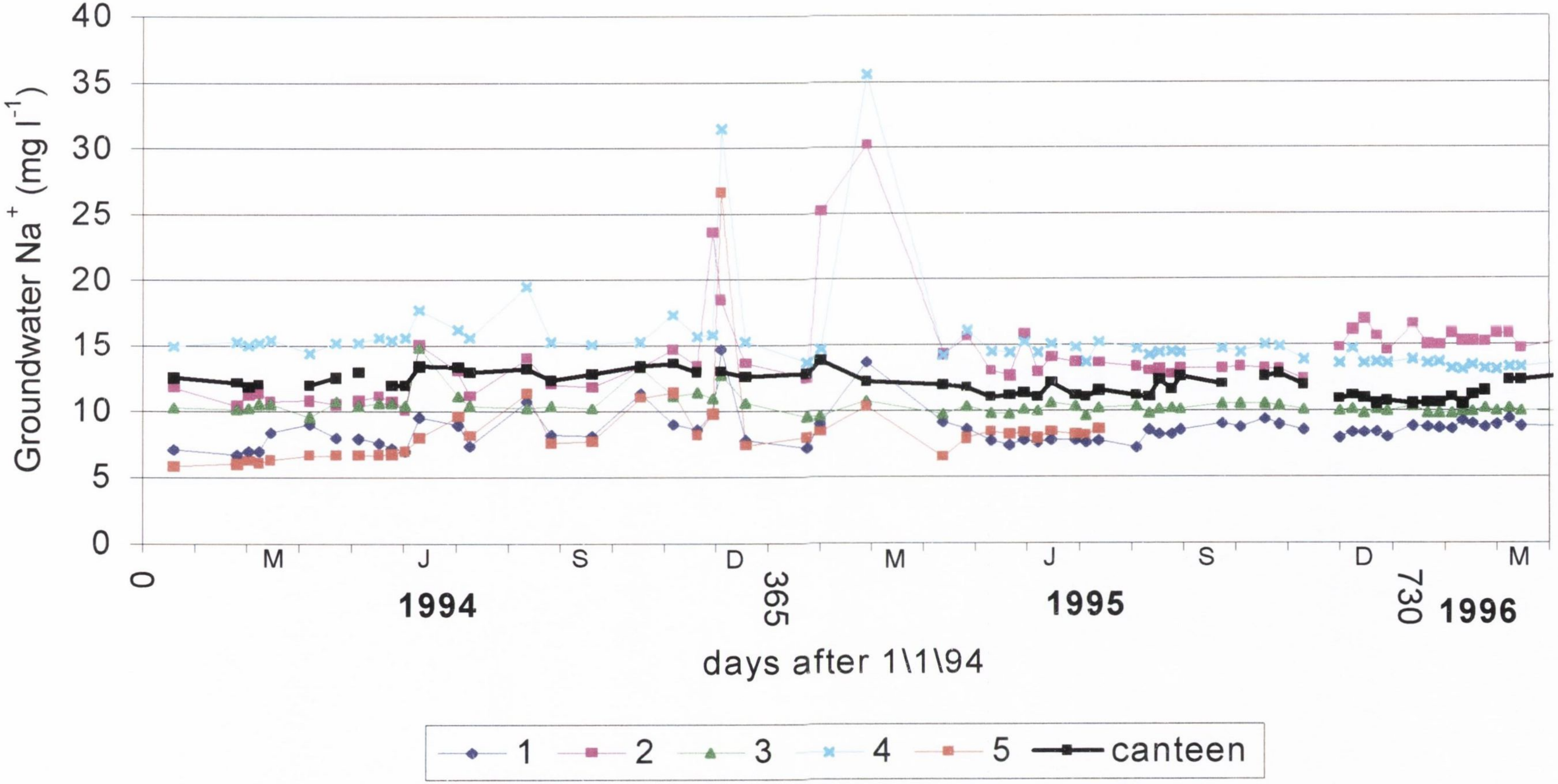


Figure 7.18 Temporal variation of groundwater Na^+ concentrations in boreholes observed at Ballyderown (1/1/94 to 1/8/96).

Correlations were carried out between Na^+ concentration observed in each borehole over the monitoring period. Some associations were found between boreholes but it is thought that these reflect similarities of temporal variation between boreholes which is largely influenced by the two extreme peaks in Na^+ concentration.

Temporal variation of Na^+ concentrations in borehole 1 was associated with borehole 2 ($P<0.0001$, $R^2=0.397$) and borehole 5 ($P<0.0001$, $R^2=0.606$) and a weaker association existed between boreholes 2 and 5 ($P=0.0257$, $R^2=0.138$). An association also existed between borehole 3 and 4 ($P<0.0001$, $R^2=0.308$) and borehole 3 and the canteen supply ($P<0.0001$, $R^2=0.239$). Borehole 4 was also associated statistically with the canteen supply ($P<0.0001$, $R^2= 0.350$). The associations between groundwater Na^+ observations in different boreholes appears to reflect the geology of each borehole. Boreholes 1, 2 and 5 are located in Ballysteen limestone whereas boreholes 3, 4 and the canteen supply are located in the Ringmoylan shale/Ballyderown sandstone series.

7.6.5 Groundwater Potassium:Sodium Ratio Results and Discussion

A summary of the observed K/Na ratios (expressed as K^+ mg l^{-1}/Na mg l^{-1}) observed in boreholes 1 to 5 and the canteen supply can be seen in Table 7.6.

Table 7.6 A summary of K/Na ratios observed at Ballyderown from 1/1/94 to 2/4/96.

Summary	Borehole					
Statistic	1	2	3	4	5	Canteen
mean	0.21	0.18	0.36	0.10	0.12	0.34
median	0.18	0.15	0.35	0.10	0.12	0.37
standard deviation	0.09	0.06	0.06	0.02	0.05	0.12
Standard error	0.01	0.01	0.01	0.00	0.01	0.02
maximum	0.53	0.30	0.56	0.15	0.29	0.54
minimum	0.08	0.08	0.24	0.04	0.03	0.02
range	0.45	0.21	0.32	0.11	0.25	0.53
sample size	65	64	65	65	51	58

Mean observed K/Na ratios observed during the sampling period ranged from 0.10 to 0.36 in boreholes 4 and 3, respectively. Boreholes 1, 2, 4 and 5 had K/Na ratios <0.3 and borehole

3 and the canteen supply had ratios >0.3. Boreholes 1 and 2 had maximum observed values during the sampling period of 0.53 and 0.3, respectively.

The observed temporal variation of groundwater K/Na ratios can be seen in Figure 7.19. In boreholes 1 and 2 there does appear to be a seasonal trend of K/Na ratios with higher ratios during winter and lower ratios during summer periods.

Temporal K/Na ratio variation observed in boreholes 3 and the canteen supply are similar although borehole 3 appears to be more spiky in appearance compared to the canteen supply. In general there is lot of variation of K/Na ratios in each borehole with the exception of borehole 4 which is quite uniform varying around 0.10.

The ratio of K/Na observed in groundwater at Ballyderown is somewhat miss leading. The only boreholes which regularly breached the ratio of 0.3 were boreholes 3 and the canteen supply. Both boreholes had elevated groundwater K^+ concentrations which were greater than 3 mg l^{-1} (Figure 7.16).

It is likely that the high K/Na ratios and K^+ concentrations observed in these boreholes are a result of geology as both partially penetrate sandstone which has been reported as sometimes causing high K^+ concentrations in groundwater (Deakin, 1994). The occasional high K/Na ratios observed in borehole 1 are likely to reflect the thin depth to bedrock in this plot which may not adsorb mobile K^+ as the soil solution percolates through it.

7.6.6 Groundwater Chloride Results and Discussion

A summary of groundwater Cl^- concentration observations from borehole 1 to 5 and the canteen supply can be seen in Table 7.7. Mean groundwater Cl^- concentrations in each borehole varied from 22.2 to 48 mg l^{-1} in borehole 3 and 2, respectively. Deviation from the mean Cl^- observation in each borehole was generally low, ranging from 1.71 to 6.73 mg l^{-1}, with the exception of borehole 2 which had a standard deviation of 18.56 mg l^{-1}.

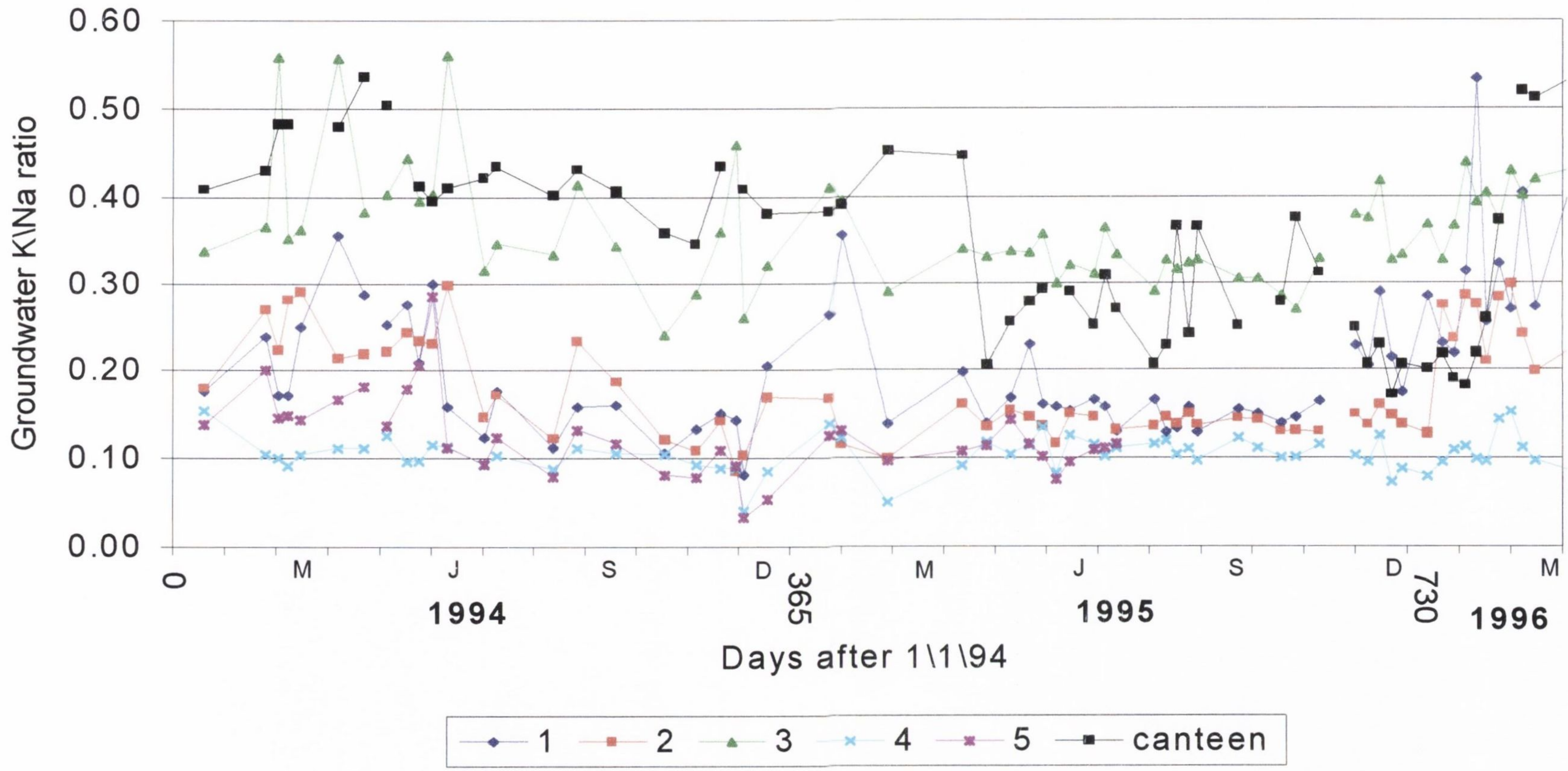


Figure 7.19 Temporal variation of groundwater K/Na ratios observed at Ballyderown (1/1/94 to 1/8/96).

Table 7.7 A summary of Cl^- concentrations (mg l^{-1}) observed at Ballyderown from 1/1/94 to 2/4/96.

Summary Statistic	Borehole 1	2	3	4	5	Canteen
mean	27.7	48.0	22.2	34.1	43.3	27.6
median	27.3	50.2	22.0	33.6	27.9	27.2
standard deviation	2.75	18.56	1.71	6.73	29.9	2.08
Standard error	0.39	2.65	0.24	0.95	4.6	0.31
maximum	35.00	74.60	26.00	53.40	164.5	33.14
minimum	22.70	16.00	16.30	25.20	27.9	24.30
range	12.30	58.60	9.70	28.20	136.6	8.84
Sample size	49	49	50	50	42	43

Temporal variation of groundwater Cl^- concentrations during the monitoring period 1/1/94 until 2/4/96 can be seen in Figure 7.20. The temporal pattern is disrupted between 9/8/94 (day 221) and 20/4/95 (day 475) due to technical difficulties which were mentioned in the methodology section.

Maximum observed Cl^- concentrations ranged from 26 to 164.5 mg l^{-1} in boreholes 3 and 5, respectively. The extremely high Cl^- concentrations observed in borehole 5 during 1996 may have been influenced by the optical brightener tracer test which was carried out in borehole 5 during January 1996. Elevated concentrations of NH_4-N and MRP were also found in borehole 5 in conjunction with the elevated Cl^- concentrations. For this reason results after the Leucophor trace commenced in January 1996 were treated with caution (section 5.5).

During the first six months of 1994, with the exception of borehole 4, groundwater Cl^- concentrations generally varied from ~ 20 to ~30 mg l^{-1}. The Cl^- concentrations at this time in borehole 4 varied between 40 and 50 mg l^{-1}.

After analytical problems were resolved the Cl^- concentration in borehole 4 had decreased from 53 mg l^{-1} on 9/8/94 (day 221) to 32 mg l^{-1} on 20/4/95 (day 475) after which point the Cl^- concentrations remained ~ 35 mg l^{-1} until 21/11/95 (day 690) when Cl^- began to decrease again to <30 mg l^{-1}.

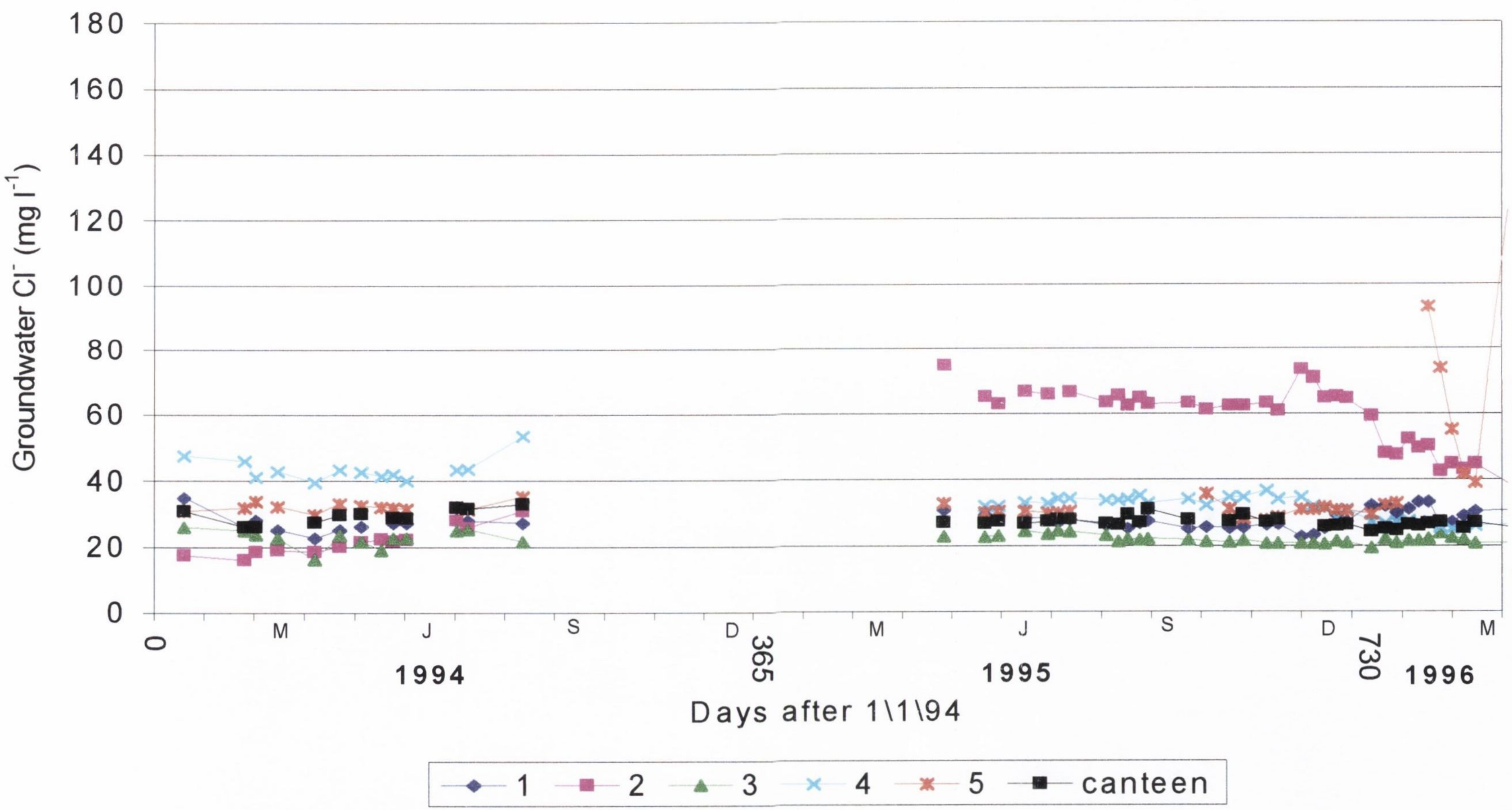


Figure 7.20 Temporal variation of Groundwater Cl^- concentrations observed at Ballyderown (1/1/94 to 1/8/96).

At the same time the Cl^- concentrations in borehole 2 increased from 31 (day 221) to 74 mg l^{-1} (day 475) before decreasing slightly and remaining at ~65 mg l^{-1} from 15/5/95 (day 500) until 7/11/95 (day 676) which was when recharge had begun, as indicated by an increased of water table height on this day. During the 1995/96 recharge period the Cl^- concentrations in borehole 2 initially increased before decreasing to <40 mg l^{-1}. The initial increase in Cl^- concentration on 21/11/95 (day 690) was associated with a slight increase in NO_3-N concentration.

The cause of the increased groundwater Cl^- concentrations in borehole 2 in 1995 was dirty water irrigation on plot 5 (which contained borehole 2) during the summer 1994. The initially high Cl^- concentrations in borehole 4 suggest that dirty water could be the source of the elevated NO_3-N concentrations in this borehole. Other sources, apart from dirty water, of NO_3-N in borehole 4 could be the ploughing and re-seeding of plots 13 and 13a although this process was not associated with elevated Cl^- concentrations. Ploughing and re-seeding of grassland caused a flush of NO_3-N from the soil but there was no source of elevated Cl^- concentrations associated with this activity. The effect of ploughing on groundwater Cl^- concentrations can be observed in borehole 1 in early 1994 and borehole 2 during the 1995/96 recharge period when groundwater Cl^- concentrations decreased from the high levels caused by dirty water irrigation. Another source of both elevated groundwater NO_3-N and Cl^- could be the slurry application before ploughing and re-seeding but this also occurred in plot 12 (borehole 1) in 1993 and when groundwater was analysed for Cl^- on 18/1/94 the concentration was 35 mg l^{-1} whereas at the same time the concentration in borehole 4 was 47.5 mg l^{-1}.

Median concentrations of Cl^- observed in Ballyderown were less than 30 mg l^{-1} except for boreholes 2 and 4 which had Cl^- concentrations >30 mg l^{-1} due to the irrigation of dirty water in the area surrounding each borehole. Lucey *et al.* (1999) found 85% of groundwater samples taken in Ireland between 1995 and 1997 had mean Cl^- concentrations <30 mg l^{-1}. Lucey *et al.* (1999) also concluded that the use of elevated Cl^- concentrations alone is not likely to be a reliable guide to the presence or absence of organic pollution although in the present study elevated Cl^- concentrations were associated with the irrigation of dirty water.

7.6.7 Temporal variation of Nitrate compared to potassium, sodium and chloride

Temporal variation of groundwater NO_3-N was compared to K^+, Na^+ and Cl^- to ascertain if there was a relationship between these observed parameters.

The relationship between temporal variation of all observed groundwater chemical parameters observed in boreholes 1 and 2 are presented in Figures 7.21 (A) and (B), respectively. There is a clear positive relationship between variation of NO_3-N, K^+ and Cl^- in both boreholes.

Regression analysis was carried out between groundwater NO_3-N observations and K, Na, Cl^- and K\Na ratios in each borehole. The R^2 values and significance levels are presented for significant relationships in Table 7.8.

Table 7.8 Regression analysis between NO_3-N (dependent) and the identified parameters (independent), the R^2 value and significance level are presented.

Borehole	K	Na	Cl	K\Na
1	0.443 ***	n.s.	0.450 ***	0.420 ***
2	0.143 *	0.150 *	0.417 ***	n.s.
3	n.s.	n.s.	n.s.	n.s.
4	n.s.	n.s.	0.850 ***	n.s.
5	n.s.	n.s.	n.s.	n.s.
Canteen	0.651 ***	0.438 ***	0.509 ***	0.572 ***

***,**,* correspond to values of $P < 0.0001$, 0.001 and 0.01, respectively, for the specified R^2 value. n.s. signifies non significant relationships.

Temporal variation of NO_3-N was significantly associated with K^+, Cl^- and less frequently with Na^+ and K\Na ratio. Observation of NO_3-N variation in borehole 1 was significantly ($P<0.0001$) associated with K^+ (R^2=0.443), Cl^- (R^2=0.450) and K\Na (R^2=0.420).

In borehole 2 variation of NO_3-N was significantly associated ($P<0.01$) with K^+ and Na^+ although the R^2 values were only 0.143 and 0.150, respectively, which were lower than observed in borehole 1. The association between NO_3-N and Cl^- was highly significant

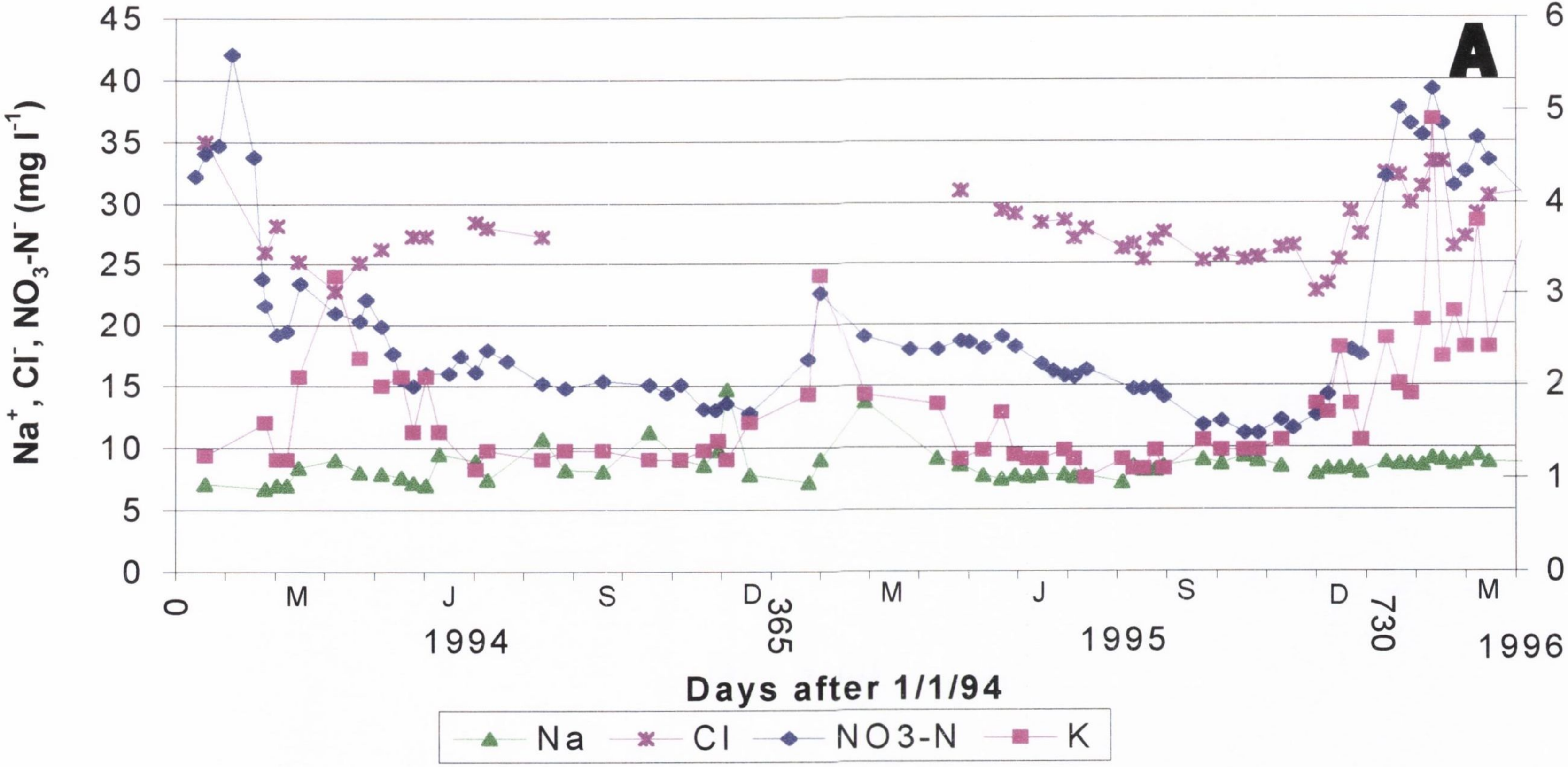


Figure 7.21A Groundwater chemical temporal variation during the monitoring period (A) borehole 1, (B) borehole 2.

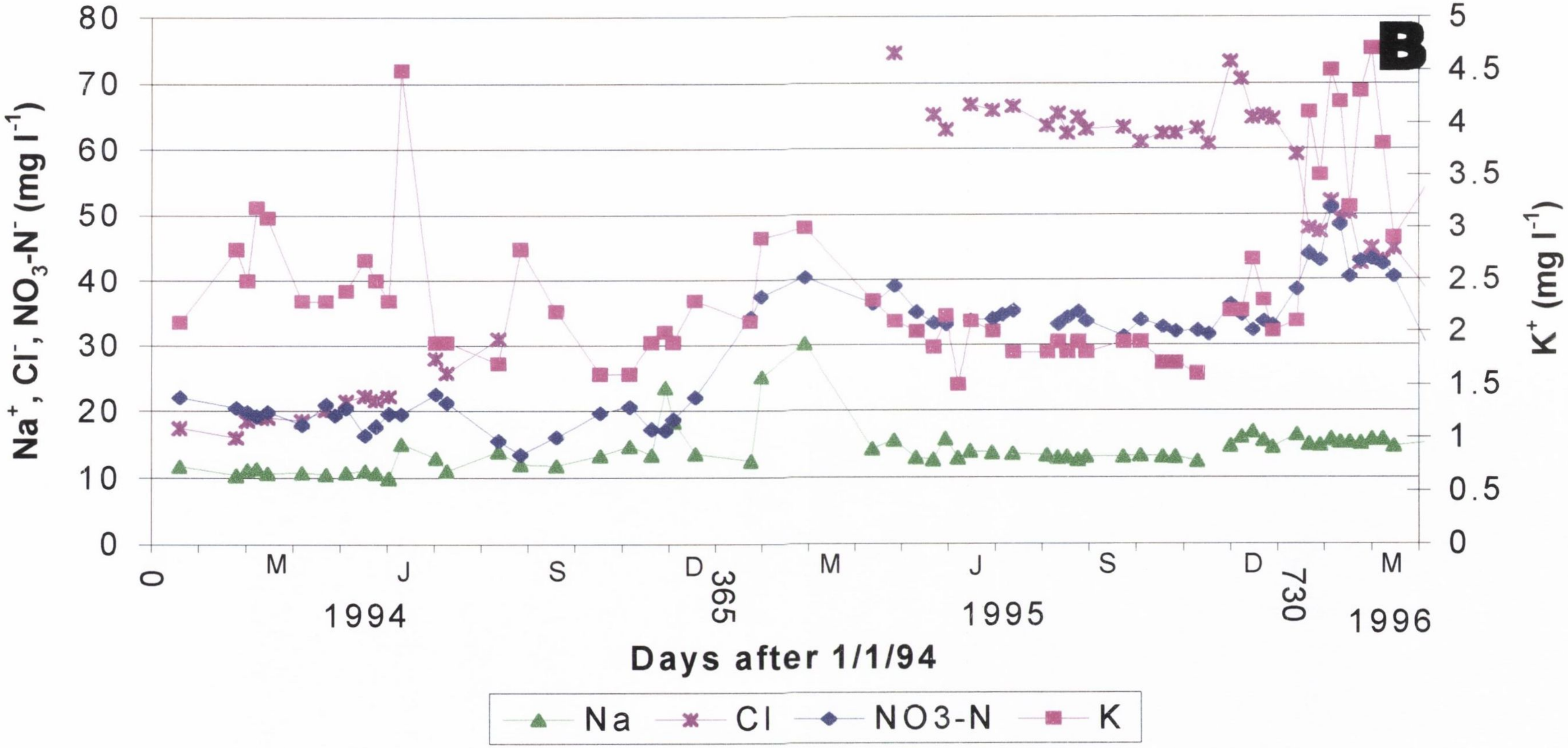


Figure 7.21B Groundwater chemical temporal variation during the monitoring period (A) borehole 1, (B) borehole 2.

($P<0.0001$) with $R^2=0.417$. Variation of groundwater Cl^- concentrations in borehole 2 were also associated with Na^+ ($P<0.0001$, $R^2=0.395$) and K\Na ratio ($P<0.0001$, $R^2=0.336$).

Variation of NO_3-N observed in borehole 4 was significantly associated with Cl^- ($P<0.0001$, $R^2=0.850$). This was the strongest relationship found between temporal variation of NO_3-N and other chemical parameters quantified during the monitoring period, although as already stressed Cl^- determination was not carried out for 8 months which reduced the number of observations from 68 to 47 for comparison. Significant associations were also observed between Cl^- and K^+ ($P=0.0049$, $R^2=0.157$) and Cl^- and Na^+ ($P<0.0001$, $R^2=0.65$).

Temporal variation of NO_3-N concentrations in the canteen supply were significantly ($P<0.0001$) associated with K^+ ($R^2=0.651$), Na^+ ($R^2=0.438$), Cl^- ($R^2=0.509$) and K\Na ($R^2=0.572$). Significant associations were also observed between K^+ and Cl^- ($P=0.0014$, $R^2=0.223$), K^+ and Na^+ ($P<0.0001$, $R^2=0.380$), Cl^- and Na^+ ($P=0.0005$, $R^2=0.258$) and Cl^- and K\Na ($P=0.0049$, $R^2=0.178$).

No significant relationships were observed between NO_3-N and K, Na, Cl^- or K\Na in boreholes 3 and 5.

The strong relationship between NO_3-N and K^+ plus Cl^- indicate that these chemical parameters move by the same pathway to groundwater. When elevated levels of NO_3-N from diffuse pollution are found there is also an associated elevation of both K^+ and Cl.

Thus the use of elevated K^+ and Cl^- concentrations to identify possible point source contaminated groundwater is unwise as elevated K^+ and Cl^- are associated with elevated NO_3-N concentrations as shown from a diffuse agricultural source.

From the comparison of soil solution and groundwater NO_3-N concentrations (section 7.3.4) it was concluded that the soil solution NO_3-N concentrations were very similar to the groundwater concentrations. Thus the groundwater chemistry is indicative of diffuse pollution rather than point source pollution. Farming practices also apply significant quantities of K^+ and Cl^- to soils through inorganic chemical fertilisation and through organic manures in the form of slurry and animal excretion in the field. The soil and quaternary deposits may also be adding to the source of K^+ from the decomposition of K^+containing minerals within the sandstone. These sources in conjunction with summer soil moisture deficits lead to a build up of NO_3-N, K^+ and Cl^- in the soil, the effect of which is to cause considerable temporal variation in groundwater concentrations of each parameter.

The use of indicator chemicals such as K, Cl^- and K/Na ratios to determine the source of pollution as likely to be point source versus diffuse, in the light of these findings, can be grossly misleading and can lead to the false classification of groundwater supplies as being point source influenced. Whereas high concentrations of these indicator parameters has been observed in this study from a diffuse agricultural source which would normally have led to the conclusion that the supplies were point source influenced. Caution must be used in the use of these parameters in delineating whether groundwater sources are indicative of point source or diffuse pollution.

7.7 General discussion of the occurrence of NO_3-N in groundwater

Elevated groundwater NO_3-N concentrations beneath Ballyderown can be attributed to a number of agricultural practices. The majority of groundwater NO_3-N concentration observation on the farm ranged from 20 to 30 mg l^{-1} which was nearly two to three times the EU limit of 11.3 mg l^{-1}. Much higher concentrations in boreholes were observed in some years and these were due to either dirty water application or ploughing and re-seeding.
The effect of dirty water irrigation on elevating groundwater NO_3-N concentrations was observed in borehole 4 during 1994 and in borehole 2 in 1995. The effect of ploughing of permanent grassland can be seen in borehole 1 during the 1993/94 recharge period and in borehole 2 during the 1995/96 recharge period.

Increased nitrate leaching after ploughing and re-seeding of permanent grassland was observed only during the first winter recharge after ploughing. It is interesting to note that there was no apparent increased nitrate leaching during the second year after ploughing (1994). This is in contrast to the findings of Young (1986), who reported increased mineralisation of soil organic N for up to three years after ploughing of grassland. Teagasc do recognise that increased immobilisation of N occurs in the soil biomass in the years following ploughing and re-seeding and this forms the basis for recommending increasing fertiliser application by 25% for grazed swards less than 3 years old (Gately, 1994). The quantity of N mineralised after ploughing of grassland is related to the age of the sward with lowest losses coming from young sward (<2 years old) and the largest losses coming from old permanent pastures (Young, 1979; Cameron and Wild, 1984; Whitehead *et al.*, 1990). The swards in Ballyderown, prior to ploughing were more than 30 years old and so when these were ploughed a large release of N was expected. Both high levels of N fertiliser applied to the grassland and grazing rather than cutting, during the year previous to ploughing, also increased the quantity of N mineralised after ploughing of grassland (Whitehead *et al.*, 1990). Ballyderown had a history of high rates of fertiliser/manure application coupled with intensive grazing which would lead to high rates of N being released from the sward upon ploughing and re-seeding.

Nitrate leaching caused by excessive dirty water/slurry applications was found to significantly increase groundwater NO_3-N concentrations. Groundwater NO_3-N had $\delta^{15}N$ values >+20‰ indicating that an animal source was predominantly responsible for the elevated concentrations. A positive relationship was observed between $\delta^{15}N$ and groundwater NO_3-N concentration which indicates that extremely high groundwater NO_3-N concentrations are caused by excessive slurry or dirty water applications.

The majority of the groundwater NO_3-N was found to originate from soil organic matter or a mixed source of fertiliser/manure as $\delta^{15}N$ values between +4 and +12‰ were observed. A highly significant relationship was observed between soil moisture deficit and mean and maximum groundwater NO_3-N concentrations in the following year. Due to the NO_3-N concentrations having $\delta^{15}N$ within an area often referred to as soil organic matter the effect of soil moisture deficit may be to increase mineralisation as a soil re-wets after a drought rather than being due to a restriction in plant growth during the drought.

When sources of extremely high rates of nitrate leaching are removed from the vicinity of a borehole the groundwater NO_3-N concentrations return to the overall farm average within two winter recharge cycles. This was observed in boreholes 1 and 4 as previously discussed. Thus the question remains as to how to decrease the overall groundwater NO_3-N concentrations on the farm. This will be made more difficult with the implication that mineralisation of soil organic matter may be an important source of nitrate leaching to groundwater on the farm.

CHAPTER 8 NITRATE LEACHING IN THE FERMOY REGION

8.1 Introduction to Irish water nitrate levels

8.1.1 Occurrence of Nitrate in drinking water in Ireland

To review the current situation of NO_3^- pollution of Irish drinking water data was compiled from the EPA drinking water quality reports from 1989 to 1997. Mean exceedance of the NO_3^- MAC of 50 mg l^{-1} (11.3 mg l^{-1} NO_3-N) for drinking water supplies in Ireland from 1989 to 1997 was 0.9% of samples analysed for NO_3, ranging from 0.3 to 1.5% in 1989 and 1996, respectively.

During the period 1989 to 1997 the total number of samples analysed from public drinking water supplies increased from 2883 to 5061 (176%). The largest annual increase in the number of samples being analysed for NO_3^- was in 1993 when it rose from 3456 to 4416 because group and small private supplies were included by some County Councils. The number of public supplies has decreased from 1066 in 1989 to 798 in 1997. The most dramatic increase has been in the number of group water schemes which had water samples analysed for NO_3^- increasing from 562 schemes in 1993 to 1209 schemes in 1997. Small private supplies accounted for 1 to 2 % of total samples analysed for NO_3^- between 1993 and 1996. In 1997 the number of small private supplies increased from 68 to 180 or increased from 1.3 to 3.6% of the total number of samples.

Table 8.1 The total number of samples analysed (the number of supplies) for NO_3^- as reported by the EPA in "The quality of drinking water in Ireland".

Year	Public supplies	Group water schemes	Small private supplies	Total
1989	2883 (1066)	-	-	2883 (1066)
1990	2963 (1083)	-	-	2963 (1083)
1991	3318 (1179)	-	-	3318 (1179)
1992	3456 (1231)	-	-	3456 (1231)
1993	3777 (790)	562 (434)	77 (62)	4416 (1286)
1994	3753 (752)	668 (526)	68 (54)	4489 (1332)
1995	3422 (746)	653 (473)	76 (50)	4151 (1269)
1996	3565 (816)	1090 (656)	68 (31)	4723 (1503)
1997	3672 (798)	1209 (896)	180 (135)	5061 (1829)

In 1997 public supplies, group water schemes and small private supplies accounted for 72.6, 23.9 and 3.6% of total samples analysed for NO_3^-, respectively.

The total number of samples and the number of exceedances of the MAC have increased over the reporting period 1989 to 1997. In Figure 8.1 the number of exceedances of MAC are expressed as the number of exceedances of MAC per 1000 samples analysed.

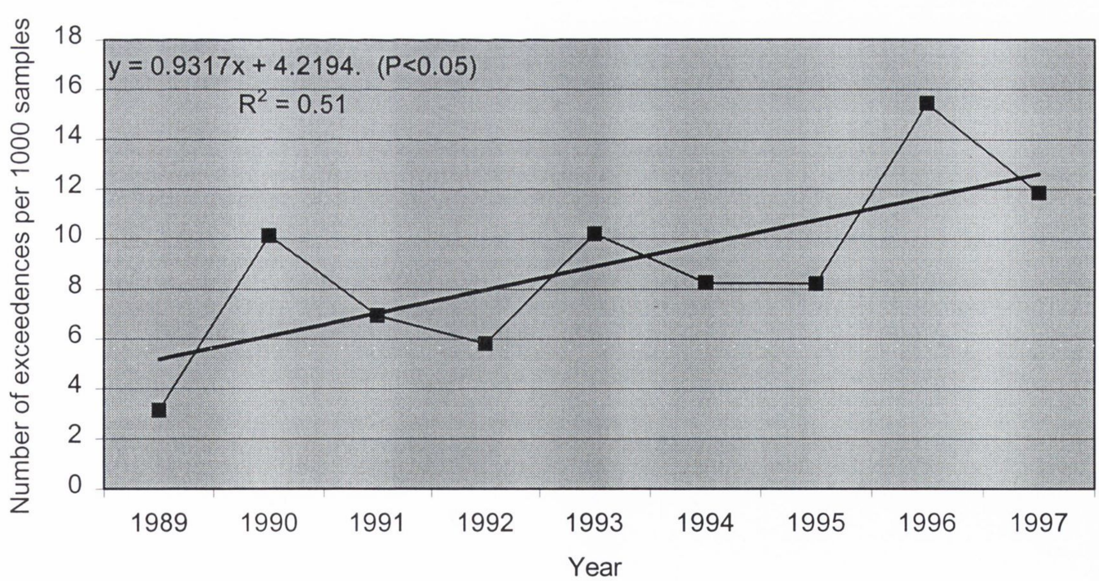


Figure 8.1 The number of exceedances of MAC per 1000 samples taken (compiled from "The quality of drinking water in Ireland" reports).

From 1989 to 1997 the number of exceedances per 1000 samples analysed increased from 3.1 to 11.9. There does appear to be a linear increase in the number of exceedances of MAC over the period 1989 to 1997. A regression of the number of exceedances of MAC per 1000 samples against time yields a significant relationship ($P<0.05$) with an $R^2=0.51$. The years 1990, 1993 and 1996 are under estimated by the regression model due to other factors not included in the regression such as the climate each year. The high number of exceedances of MAC per 1000 samples in 1990 and 1996 occurred in the winter drainage period after the drought conditions experienced during the summers of 1989 and 1995. It is possible that the relationship observed between groundwater NO_3-N concentrations and soil moisture deficit, as described in section 7.3.6 and shown in Figures 7.12 and 7.13, could also be reflected in the national data set on exceedances of MAC. Therefore the high number of MAC exceedances in 1990 and 1996 are possibly reflecting the high soil moisture deficits which occurred during the summer droughts of 1989 and 1995. The elevated number of exceedances in 1993 is not as easily explained as a drought period was experienced in 1993 and thus elevated NO_3^- leaching would be expected in 1994 although perhaps higher amounts of effective rainfall occurred in the autumn of 1993. It is unclear exactly when the exceedances occurred in 1993 and thus it is difficult to explain the high number of exceedances.

A complicating factor in 1993 was the inclusion of group schemes and small private supplies in reporting by the EPA and this may have affected the number of exceedances in 1993 as there appear to be a large number of exceedances in the group water schemes in 1993 compared to 1994 and 1995. The number of MAC exceedances for each supply type from 1993 to 1997 can be seen in Figure 8.2.

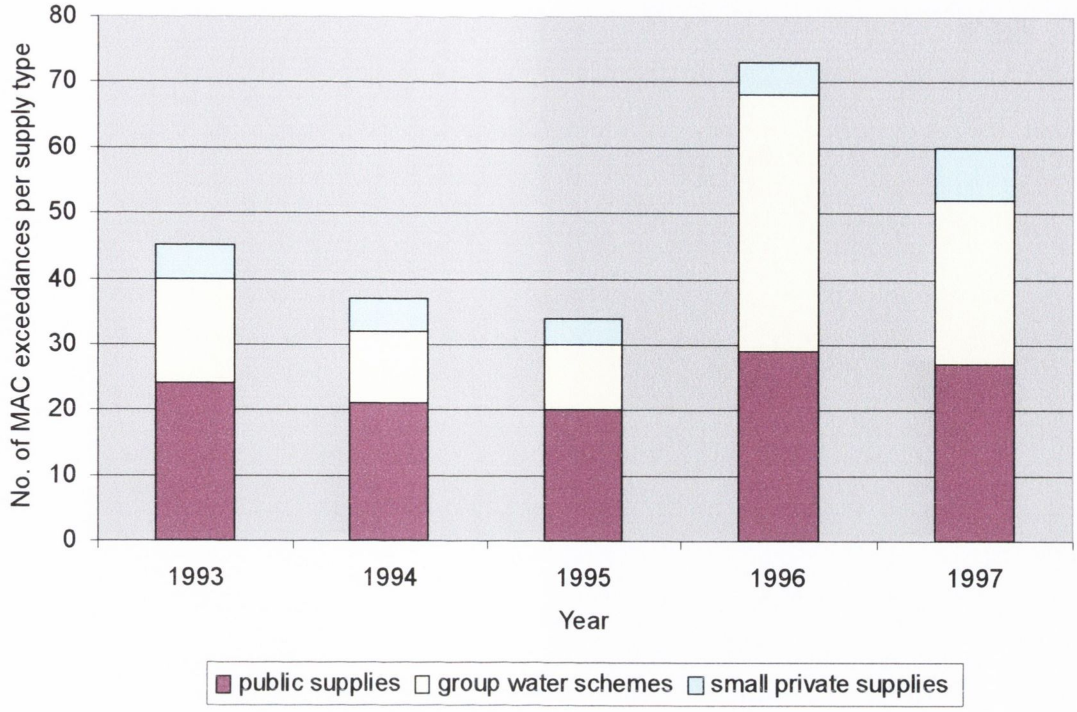


Figure 8.2 The number of MAC exceedances per supply type (Compiled from "The quality of drinking water in Ireland" reports).

Public supplies account for between 20 and 29 exceedances per year with a mean of 24.2 exceedances during this period which is the largest mean number of exceedances for the supply type. Group water schemes account for 10 to 39 exceedances per year with a mean of 20.2 exceedances during the period 1993 to 1997. The smallest number of exceedances observed in each supply type was for small private supplies which ranged from 4 to 8 exceedances per year with a mean of 5.4 exceedances during 1993 to 1997.

The public water supplies generally comprise of the most MAC exceedances for NO_3^- ranging from 40% in 1996 to >50% in 1993. In 1996 there was an increase in the percentage of exceedances in group water schemes primarily due to a large increase in Co. Louth from 13 in 1993 to 23 in 1996. Small private supplies generally account for about 10% of the MAC exceedances for NO_3^-.

Although lowest number of exceedances occurred in the small private supplies these also accounted for the lowest number of samples analysed for NO_3^-. In 1997 the number of samples analysed from public supplies, group water schemes and small private supplies was 3672, 1209 and 180, respectively (Table 8.1). If the exceedances are expressed as the number of exceedances per 100 samples, public supplies, group water schemes and small/ private supplies had mean exceedances from 1993 to 1997 of 0.7, 2.3, and 6.2, respectively.

During the period 1989 to 1997 there have been a total of 331 exceedances of MAC reported by the EPA and these have been observed in 24 different reporting areas. The reporting of drinking water quality is carried out by the sanitory authorities and the reporting areas are based on the sanitary authorities geographic location. Of the 331 exceedances, a total of 259 (or 78%) have been observed in 9 reporting areas. The total number of exceedances from 1989 to 1997 for these 9 reporting areas are shown in Figure 8.3.

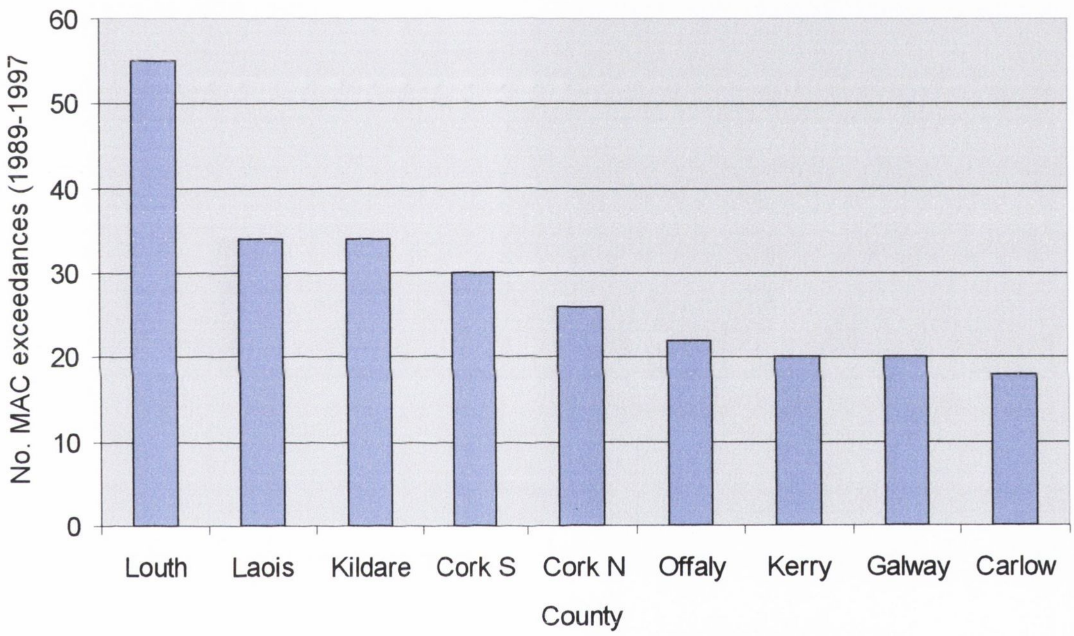


Figure 8.3 The number of MAC exceedances (1989-1997) for counties with >15 exceedances (Compiled from "The quality of drinking water in Ireland" EPA reports).

County Louth has the highest total number of exceedances of the NO_3^- MAC i.e., 55, with 49 exceedances occurring in 1990, 1993 and 1996 of which 1993 had 13 and 1996 had 28 exceedances.

Some of the public drinking water supplies have exhibited consistently high NO_3^- concentrations between 1989 and 1997. In North Cork the Glanworth and Downing bridge supplies have breached MAC on numerous occasions during this period. NO_3^- concentrations obtained from "The quality of Drinking water in Ireland" reports for the Glanworth supply can be seen in Figure 8.4. The Glanworth public drinking water supply which sources from a surface spring serves a population of 3400 people and has a daily usage of 680 m^3 day^{-1}.

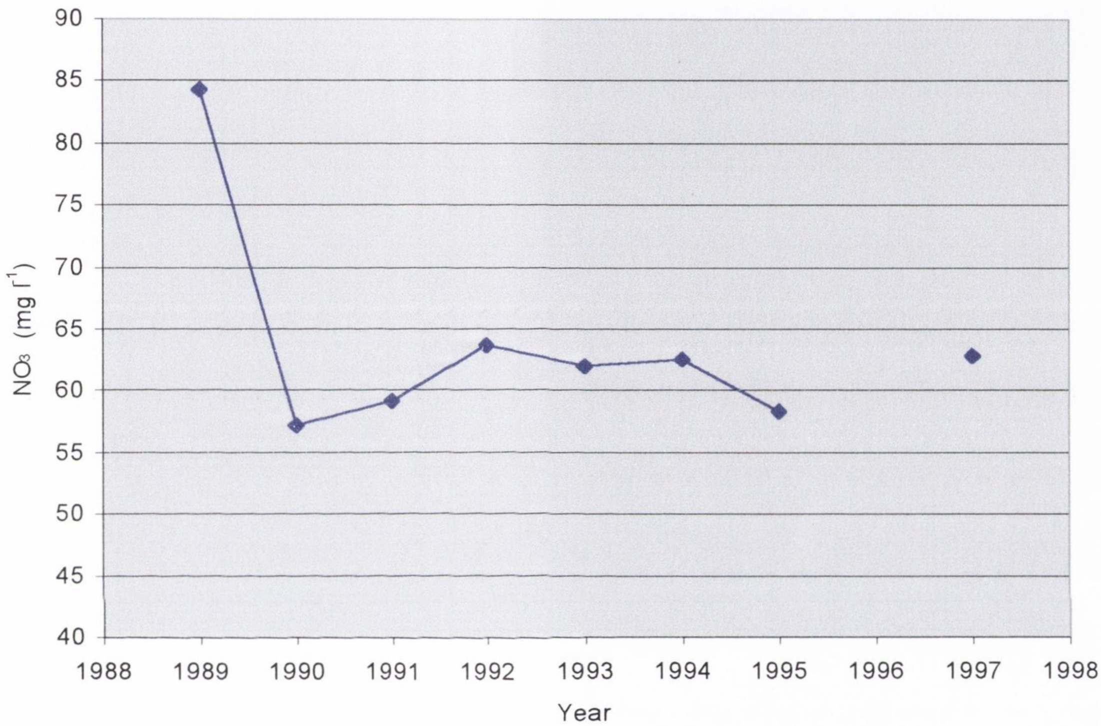


Figure 8.4 Mean annual NO_3 concentrations in the Glanworth public supply (compiled from the EPA "The quality of drinking water in Ireland" reports).

There appears to be no systematic relationship between mean NO_3^- concentrations in the Glanworth supply and time. The Glanworth drinking water supply consistently exceeds MAC during the period from 1989 to 1997.

8.1.2 Occurrence of nitrate in groundwater in Ireland

In 1995 the EPA commenced a National Groundwater Quality Monitoring Programme (NGQMP) with monitoring being carried out twice per year to coincide with groundwater levels being at their lowest and highest. As part of this programme 556 groundwater samples were taken between 1995 and 1997. Mean concentrations of less than guide level (GL) were observed at 155 of the 193 sampling points (or 80% of sampling locations) and exceeded MAC at five locations (2.6% of locations). Maximum concentrations greater than MAC were observed in 26 individual samples, 15 of which were from supplies with mean concentrations greater than MAC. Thus 11 samples greater than MAC were observed in supplies with mean concentrations less than MAC (Lucey *et al.*, 1999). NO_3^- concentrations greater than MAC were observed in counties Carlow, Kildare, Limerick and Louth. NO_3^- concentrations greater than MAC were not related to NO_2^-, NH_4^+ or bacterial contamination which indicates that the source of the NO_3^- was diffuse agricultural contamination (Lucey *et al.*, 1999).

In a review of the 'State of the Environment in Ireland' Stapleton (1996) reports, from investigations of groundwater NO_3^- concentrations in the south and north-east of Ireland, that 97% of samples had NO_3^- concentrations which were less than the MAC. Stapleton (1996) suggests that NO_3^- contamination occurs in individual boreholes and wells, probably due to the proximity of waste sources such as silage and slurry pits, but that the general bodies of groundwater are relatively free of this contamination.

A study of the Nore river basin by Daly and Woods (1994) showed that 24% of groundwater samples had elevated NO_3^-, K or Cl^- concentrations. This was high as the groundwater sampling deliberately tried to avoid contaminated supplies. Lowland areas had 31% of supplies contaminated compared to 15% in upland areas. Contamination was observed more in low yielding wells compared to high yielding wells and springs which tap a significant volume of groundwater.

Numerous small scale groundwater sampling projects have been carried out in different areas of the country. Leane (1998) sampled 29 groundwater supplies in north Tipperary during the summer of 1998 and found 13 greater than MAC and 20 greater than GL with only 9 less than GL.

Of the 13 samples which were greater than MAC four had traces of point source pollution due to elevated PO_4 concentrations with a further four samples less than MAC and greater than GL also having high phosphate concentrations. Thus it is likely that the 9 sites sampled which had

NO_3^- greater than MAC can be attributed to diffuse sources pollution such as agriculture rather than point source pollution.

Daly and Daly (1982, 1984) observed that 36% of 59 boreholes sampled in the Barrow valley in Co. Carlow had NO_3^--N concentrations greater than 6 mg l^{-1} which they concluded was due to point sources due to high NO_3^- concentrations being randomly scattered throughout the valley. They suggest that this is not related to a widespread, relatively homogeneous dispersed source such as inorganic fertilisers.

Rakotsoane (1992) found, in a regional sampling of 50 groundwater supplies in county Waterford, that 8% of samples had NO_3^- concentrations greater than MAC and 28% were greater than GL. Mooney (1990) found in the Ballywater catchment Co. Louth, of 34 wells sampled, that 23 (67%) were less than GL and 1% was greater than MAC, which may have been due to improper siting of the borehole.

A report written by Cork County Council (1998) for the Department of the Environment and Local Government summarises groundwater NO_3^- concentrations from an intensive survey of water supplies with or suspected of having high NO_3^- concentrations in 1997/98. Detailed investigation during the 1997/98 period sampled 33 supplies and found 13 exceeded MAC and 23 supplies had NO_3^- concentrations $\geq$40 mg l^{-1}. Seven supplies had mean NO_3^- concentrations $\geq$MAC, two supplies are having new alternative sources tested, a further three supplies have requested nutrient management plans by the surrounding farmers and one other supply is having its source protection improved.

Peak NO_3^- concentrations in the groundwater supplies were most often observed in March of each year with the majority of peak NO_3^- observations occurring from December to April. Only three supplies had peak NO_3^- concentrations observed outside the December to April period and these were observed in June.

The mean number of samples taken from each supply over the 14 month period was 7 and 8 supplies had $\geq$10 samples (Cork County Council, 1998). Coxon (1992) reported that the NO_3^- MAC was exceeded at 23% of sites during winter and 19% of sites during summer from samples taken in Counties Kildare and Carlow. Page and Keyes (1999) observed peak groundwater NO_3^- concentrations in April each year in Co. Offaly.

There is a growing awareness that groundwater NO_3^- concentrations are increasing in Ireland. Although in the past many of the elevated groundwater NO_3^- concentrations have been attributed to localised pollution sources such as septic tanks and farm yards this now appears to be changing. In a study of groundwater NO_3^- concentrations in Offaly, Page and Keyes (1999), observed widespread elevated NO_3^- concentrations in aquifers in Offaly. Although some localised pollution of boreholes did occur due to intensive agricultural enterprises, the widespread elevated NO_3^- concentrations appear to implicate diffuse agricultural sources as the primary cause.

8.1.3 Nitrate in Surface waters in Ireland

Stapleton (1996) observed increasing NO_3^- concentrations in surface water in Ireland, between 1979 and 1994, with the greatest rate of increase in the south east of the country. The majority of surface water samples had median NO_3^- concentrations <GL although this level was exceeded for short periods during the winter months with the highest concentrations again being observed in the South-east.

Cork County Council (1998) report, for seven surface water drinking sources which were regularly monitored for NO_3^-, that three had maximum observed NO_3^- concentrations $\geq$25 mg l^{-1} with maximum concentrations observed occurring between November and March and minimum values observed between May and August. Neill (1989) also observed maximum NO_3^- concentrations during January and February and lowest concentrations in July and August in rivers in the Southeast of Ireland.

Cork County Council (1998) in a nutrient study of Clonakilty Inner estuary catchment attributed the high N loads primarily due to agriculture. Samples taken from the River Feagle at Ring Bridge, which drains an agricultural catchment, had mean NO_3-N concentrations of 7 mg l^{-1} with a range of 5 to 9 mg l^{-1}. Again the highest observed values occurred during the winter period.

Neill (1989) positively correlated maximum river water NO_3^- levels in the south-east of Ireland with the percentage of land area ploughed (r=0.958) and inorganic N fertiliser application rate (r=0.936). Annual N loss in rivers was positively correlated with the percentage of land ploughed in the river catchment (r=0.993).

8.2 Soil Sampling for Farm Comparison

8.2.1 Introduction to the regional soil sampling

An experiment was designed to examine how the soil mineral N levels at Ballyderown compared to other dairy farms in the Fermoy area. The soils around the Fermoy region are generally similar and are classified as brown earths, which have a sandstone sub-soil. By examining soil inorganic N it was hoped to be able to ascertain how N leaching from Ballyderown compared to other farms in the area. Soil total Kjeldahl N was examined, from soil samples taken in November 1994, to assess the relationship between the total Kjeldahl N status of farms around Fermoy compared to Ballyderown. Soil organic N mineralisation has already been shown to be a very important part of the N cycle on grassland dairy farms (chapter 3.6). The total Kjeldahl status of soils is very important in determining the amount of N available for mineralisation.

8.2.2 Regional soil sampling methodology

For the purposes of comparison soil samples were taken on four dates i.e., March 1994 (period 1), November 1994 (2), February 1995 (3) and November 1995 (4).

In March 1994, six farms were selected in the Fermoy area to carry out a comparative study examining soil N levels. Farms were selected on the basis of inorganic fertiliser usage with two farms > 300 kg N ha^{-1}, two farms 250 to 300 kg N ha^{-1} (a similar level to Ballyderown) and the final two farms < 250 kg N ha^{-1}. In November 1994, a dairy/piggery farm located beside Ballyderown was added to the field sampling programme for soil N comparison. Also in November 1995 three further farms located close to Ballyderown were added to the sampling regime (all sample farms are shown in Figure 8.5).

Five fields from each farm were selected and representative soil samples taken using a 1 cm screw auger to a depth of 30 cm, bulked for each depth at each farm, for soil sampling periods 1, 2 and 3 whereas period 4 had soil sampled to 45 cm described in 6.2.2. Soil samples were extracted immediately on return to the laboratory and analysed for NO_3-N and NH_4-N as described in 3.6.3. All samples were analysed within 24 hours of sampling.

The soil samples remaining after inorganic N determination in November 1994 were air dried for Kjeldahl N determination. The method used was as follows: the soil was finely ground using a mortar and pestle and a 1 g sub sample added to a 100 ml Kjeldahl flask with a drop of distilled water. A Kjeldahl tablet (0.1 g $LiSO_4$ and 0.05 g Se) to act as a catalyst, a glass bead to prevent bumping and 10 ml of concentrated H_2SO_4 was added to the Kjeldahl flask which was heated over a gas flame for 2 hours. The cooled liquid was made up to 100 ml with distilled water. This was then filtered through a Whatman No.2 filter paper and the filtrate was analysed on a Chemlab continuous flow auto analyser. Results are expressed as %N on a dry weight basis.

The results from farms of both soil inorganic N and soil Kjeldahl N were compared using the analysis of variance (ANOVA) procedure. If the ANOVA null hypothesis (that all means are equal) was rejected ($P<0.05$) then the general alternative hypothesis that the means are not all equal was accepted and the Bonferroni multiple comparison procedure was carried out using Datadesk to determine which means were significantly different (Velleman, 1993). The Bonferroni method guarantees that the probability of any false rejection among all comparisons made is no greater that the stated P value (Moore and McCabe, 1998).

8.2.3 Results of the regional soil sampling

Inorganic soil N concentrations

The results of soil inorganic N from all farms on the four separate sampling dates are presented

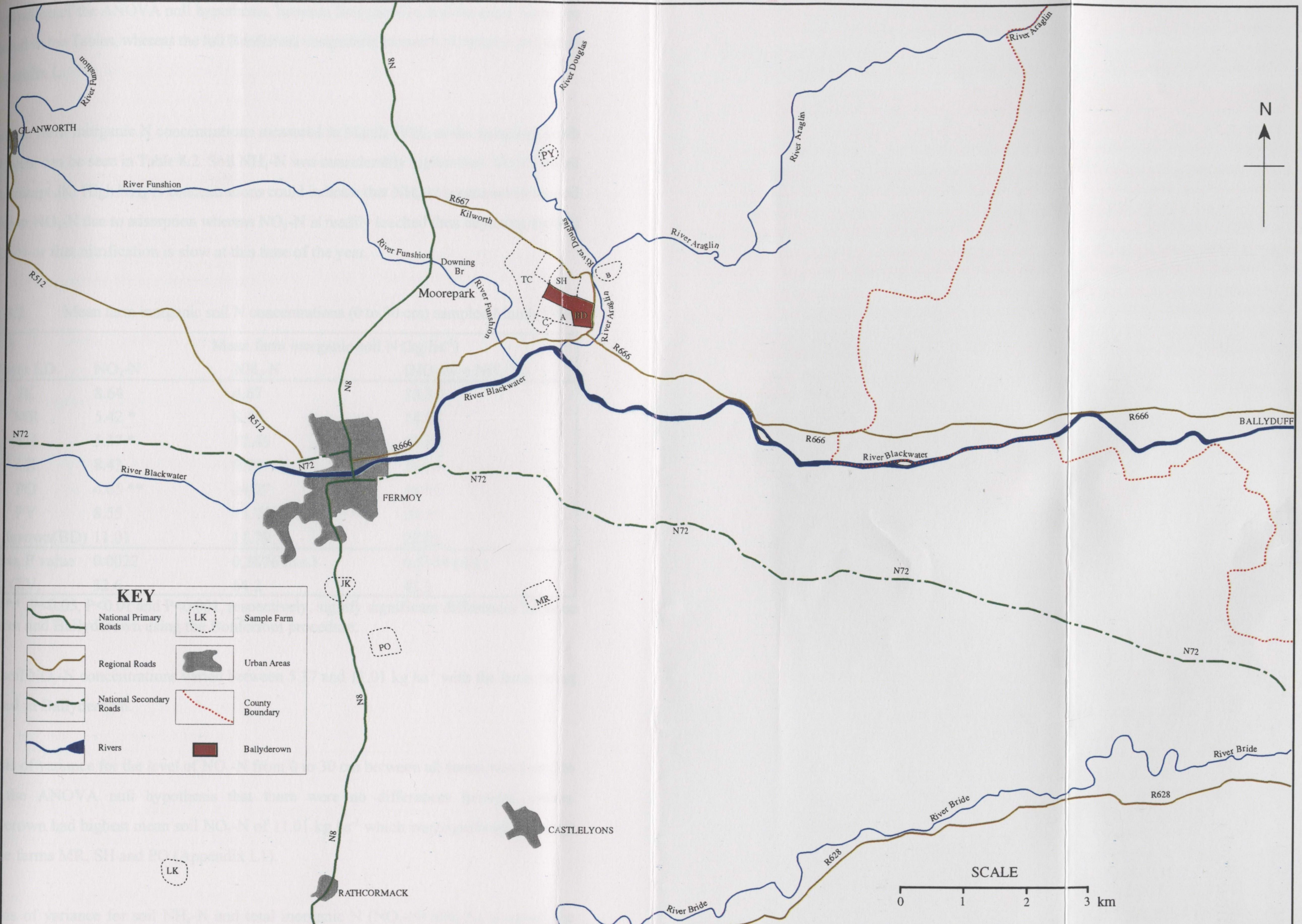


Figure 8.5 Regional soil sampling farm locations and identities.

in Tables 8.2, 8.3, 8.4 and 8.5. Only significant differences, using the Bonferroni procedure, after rejection of the ANOVA null hypothesis, between Ballyderown and the other farms are presented in the Tables, whereas the full Bonferroni comparison between all farms is presented in Appendix L.

The mean farm inorganic N concentrations measured in March 1994, at the sampling depth 0 to 30 cm, can be seen in Table 8.2. Soil NH_4-N was considerably higher than NO_3-N on all farms, except JK. High NH_4-N concentrations could indicate that NH_4-N is retained in the soil more than NO_3-N due to adsorption whereas NO_3-N is readily leached thus depleting the soil of NO_3-N or that nitrification is slow at this time of the year.

Table 8.2 Mean farm inorganic soil N concentrations (0 to 30 cm) sampled March 1994.

	Mean farm inorganic soil N (kg ha^{-1})		
Farm I.D.	NO_3-N	NH_4-N	(NO_3-N + NH_4-N)
JK	8.64	4.67	13.31
MR	5.42 *	9.16	14.57
SH	5.37 *	12.43	17.80
LK	8.43	9.70	18.13
PO	4.65 **	14.27	18.92
PY	8.55	11.75	20.30
Ballyderown(BD)	11.01	11.79	22.81
Anova P value	0.0022	0.3876 (n.s.)	0.5354 (n.s.)
C.V.	32.6	64.2	43.3

*, **,*** $P<0.05$, $P<0.01$ and $P<0.001$, respectively, signify significant differences between that farm and Ballyderown using the Bonferroni procedure.

Mean soil NO_3-N concentrations varied between 5.37 and 11.01 kg ha^{-1} with the latter being observed in Ballyderown.

Analysis of variance for the level of NO_3-N from 0 to 30 cm between all farms was found to reject the ANOVA null hypothesis that there were no differences between means. Ballyderown had highest mean soil NO_3-N of 11.01 kg ha^{-1} which was significantly greater than the farms MR, SH and PO (Appendix L1).

Analysis of variance for soil NH_4-N and total inorganic N (NO_3-N+NH_4-N) accepted the ANOVA null hypothesis that there were no differences between means. Thus there were no significant differences between all farms mean soil NH_4-N and total inorganic N. The Bonferroni procedure was not carried out on the farm means due to the failure to reject the ANOVA null hypothesis. Ballyderown had the highest total inorganic soil N of 22.81 kg ha^{-1} but this was not significantly different to the other farms sampled.

The ANOVA Coefficient of Variation was 64.2 and 43.3% for soil NH_4-N and total inorganic N, respectively, which was higher than 32.6% for the soil NO_3-N. Most of the variation appeared to be in soil NH_4-N and this could be due to the fertilisation or slurry application of some plots within a farm and not other plots which increased the within farm variation. Information was not available on the fertilisation practices carried out on a plot basis which would have improved results interpretation.

Soil sampling results from farms carried out in November 1994, from 0 to 30 cm, can be seen in Table 8.3. Farm soil NO_3-N ranged from 15.8 to 37.6 kg ha^{-1}, NH_4-N ranged from 7.6 to 34.6 kg ha^{-1} and total inorganic N ranged from 24.7 to 56.1 kg ha^{-1}.

Table 8.3 Mean farm inorganic soil N concentrations (0 to 30 cm) sampled November 1994.

	Mean farm inorganic soil N (kg ha^{-1})		
Farm	NO_3-N	NH_4-N	(NO_3-N + NH_4-N)
PO	17.0 ***	7.6	24.7
MR	15.8 ***	10.3	26.0
JK	21.9 ***	9.2	31.0
SH	22.2 ***	10.0	32.2
LK	20.3 ***	13.3	33.6
Ballyderown (BD)	37.6	10.6	48.2
TC	26.2 ***	25.3	51.5
PY	21.4 ***	34.6	56.1
Anova P	<0.0001	0.1662 (n.s.)	0.0526 (n.s.)
C.V. %	12.1	113.3	47.4

*, **,***, P<0.05, P<0.01 and P<0.001, respectively, signify significant differences between that farm and Ballyderown using the Bonferroni procedure.

Analysis of variance of farm soil NO_3-N rejected the null hypothesis that there were no differences between means. The Bonferroni procedure showed that Ballyderown had significantly higher ($P<0.001$) soil NO_3-N levels that all the other farms sampled (Appendix L2).

Analysis of variance for soil NH_4-N and total inorganic N failed to reject the null hypothesis showing no significant differences between the farms. Again it is interesting to note the high variation within the soil NH_4-N which had a C.V. of 113.3% whereas soil NO_3-N had a much lower C.V. of 12.1%. Once more the lack of information for plot fertilisation hinders interpretation of the high variability observed in the soil NH_4-N.

The results of soil sampling from 0 to 30 cm depth, in February 1995, can be seen in Table 8.4. Farm mean NO_3-N varied from 8.48 to 16.28 kg ha^{-1}, soil NH_4-N varied from 7.96 to 13.77 kg ha^{-1} and the total inorganic soil N varied from 16.44 to 30.05 kg ha^{-1}. The ANOVA null hypothesis was rejected for soil NO_3-N, NH_4-N and total inorganic N (NO_3-N + NH_4-N).

Table 8.4 Mean farm inorganic soil N concentrations (0 to 30 cm) sampled February 1995.

	Mean farm inorganic soil N (kg ha^{-1})		
Farm	NO_3-N	NH_4-N	(NO_3-N + NH_4-N)
JK	8.48 **	7.96	16.44
PO	11.35 **	8.57	19.92
LK	11.54	8.75	20.28
PY	11.21	9.63	20.84
MR	11.44 *	10.53	21.97
SH	11.69	10.30	21.99
Ballyderown	15.82	8.63	24.45
TC	16.28	13.77 **	30.05
Anova P	<0.0001	0.0002	0.0002
C.V. %	22.7	18.8	19.8

*, **,***, $P<0.05$, $P<0.01$ and $P<0.001$, respectively, signify significant differences between that farm and Ballyderown using the Bonferroni procedure.

Ballyderown had the second highest NO_3-N level of 15.82 kg ha^{-1} which was significantly higher than JK, PO, and MR at $P<0.01$, $P<0.01$ and $P<0.05$, respectively. The farm TC had significantly higher soil NO_3-N than JK, MR and PO.

Ballyderown had a mean soil NH_4-N level of 8.63 kg ha^{-1} which was the second lowest observed and significantly lower than TC ($P<0.01$). The farm TC had significantly higher soil NH_4-N levels than all farms with the exception of SH (Appendix L3). Ballyderown had the second highest soil total inorganic N but this was not found to be significantly different to the other farms using the Bonferroni procedure. Although the null hypothesis was rejected for the ANOVA of soil total inorganic N, the only significant differences were TC was greater than JK, LK, MR, PO and PY.

Unlike the two previous soil sampling dates the variation of soil NH_4-N and total inorganic N were much lower with C.V. of 18.8 and 19.8%, respectively. The most significant reduction in C.V. was observed for soil NH_4-N which reduced from 64.2 and 113.3 % in the previous samplings to 18.8 %. Sampling in February rather than March appears to have given soil which had not yet had fertiliser applied to it but again the lack of farm management history limits interpretation.

The results of farm soil sampling in November 1995 at the 0 to 45 cm sampling depth can be seen in Table 8.5. An extra three farms were included in the soil sampling for this period. Mean farm soil NO_3-N levels ranged from 3.6 to 66.7 kg ha^{-1}, NH_4-N ranged from 4.4 to 26.4 kg ha^{-1} and total inorganic N ranged from 15.5 to 74.5 kg ha^{-1}.

Table 8.5 Mean farm inorganic soil N concentrations (0 to 45 cm) sampled November 1995.

	Mean farm inorganic soil N (kg ha^{-1})		
Farm	NO_3-N	NH_4-N	(NO_3-N + NH_4-N)
A	3.6	11.9	15.5
SH	13.7	4.4	18.1
C	6.2	13.1	19.3
LK	5.5	14.4	19.9
B	5.5	14.4	19.9
PO	10.6	12.0	22.6
Ballyderown (bd)	34.8	6.6	41.4
MR	17.9	26.4 **	44.3
PY	37.0	8.8	45.8
JK	57.0	13.6	70.6
TC	66.7	7.6	74.2
ANOVA P	<0.0001	0.0036	<0.0001
C.V.	54.9%	60.5%	43.9%

*, **,***, P<0.05, P<0.01 and P<0.001, respectively, signify significant differences between that farm and Ballyderown using the Bonferroni procedure.

The range of mean farm NO_3-N was much greater on this sampling date compared to November 1994 which only had one farm > 30 kg ha^{-1} whereas in November 1995 there were four farms > 30 kg ha^{-1}, two of which were greater than 50 kg ha^{-1}. The higher levels are likely to reflect the deeper sampling depth of 0 to 45 cm in November 1995 than 0 to 30 cm in November 1994. Three farms had higher soil NO_3-N than Ballyderown but there were no significant differences between Ballyderown and any other farm. The main differences between means were observed for the farms TC and JK which both had significantly higher soil NO_3-N levels than A, B, LK, MR, PO and SH.

Mean soil NH_4-N at Ballyderown was the second lowest observed with SH having the lowest mean level. The ANOVA null hypothesis was rejected at a P value of 0.0036 and after carrying out the Bonferroni procedure. Only one farm, MR, was observed to be significantly different to Ballyderown. MR had the highest soil NH_4-N content and this was attributed to slurry application to plots a few weeks before soil sampling was carried out.

The total inorganic N from 0 to 45 cm was high ranging from 15.5 to 74.5 kg ha^{-1}. Five farms had soil total N levels >40 kg ha^{-1} and of those a further two were >70 kg ha^{-1}. The six farms <40 kg ha^{-1} had levels of <25 kg ha^{-1} with five farms being <20 kg ha^{-1}. The ANOVA null hypothesis was rejected and when the Bonferroni procedure was carried out Ballyderown was shown to be not significantly different from any of the other farms sampled (Appendix L4). The significantly different farms were TC and JK which were significantly greater than A, B, LK, PO and SH. This was also observed with the soil NO_3-N for both of these farms.

The variation was quite large again with coefficients of variation of 54.9, 60.5 and 43.9 % for soil NO_3-N, NH_4-N and total inorganic N, respectively.

Total Kjeldahl N analyses of farm comparison soils

Soil total Kjeldahl N results from farms sampled in November 1994 can be see in Table 8.6. The total soil N was highest in the 0 to 15 cm sampling depth with farm means ranging from 0.24 to 0.32 %N whereas at 15 to 30 cm the means ranged from 0.14 to 0.21 %N.

Table 8.6 Soil Kjeldahl N from soils sampled in March 1994.

	Mean farm Kjeldahl N (%N)	
Farm	0-15 cm	15-30 cm
PO	0.24	0.14
MR	0.25	0.18
SH	0.26	0.18
Ballyderown	0.27	0.15
LK	0.30	0.21 *
PY	0.30	0.20
JK	0.30	0.18
TC	0.32	0.17
ANOVA P	0.0021	0.0013
C.V.	10.4	13.8

*, **,***, signify differences at P<0.05, P<0.01 and P<0.001, respectively, using the Bonferroni method, between Ballyderown and the farm followed by the symbol.

Analysis of variance was carried out at each sampling depth to determine if any farms had significantly different mean soil total Kjeldahl N at each sampling depth. Differences between the farm means were shown at each depth with the null hypothesis being rejected at P values of 0.0021 and 0.0013 for the 0 to 15 and 15 to 30 cm sampling depths, respectively.

The Bonferroni mean comparison procedure was then used to examine the differences between all farm mean soil Kjeldahl N. No significant differences were found between Ballyderown and the other farms at the 0 to 15 cm sampling depths (Table 8.5 and Appendix L6). There was only one significant difference ($P<0.05$) at the 0 to 15 cm sampling depth and that was TC > PO.

At the 15 to 30 cm sampling depth Ballyderown was found to have significantly ($P<0.05$) lower soil Kjeldahl N than LK. No other significant differences were found between Ballyderown and the other farms at this sampling depth although PO was significantly ($P<0.01$) lower than LK and PY.

8.2.4 Discussion

Comparison of soil inorganic N observed in this study with other ranges reported in the literature is difficult due to different sampling depths and techniques, laboratory analytical techniques, agronomic activities and units of reporting. Younie and Watson (1992) reported for grass/clover farms soil NO_3-N levels, from 0 to 30 cm depth in October 1990, of 27.1 and 29.2 kg ha^{-1} for an organic farm system (zero N) and conventional system (270 kg N fertiliser). In March 1991 soil NO_3-N levels from 0 to 30 cm were 18.5 and 18.6 kg ha^{-1} for the organic and conventional farm systems. Watson *et al.* (1992) observed for grass/clover pastures grazed by beef steers autumn soil NO_3-N levels <10 kg ha^{-1}, when fertiliser N was between 100 and 300 kg ha^{-1}. Soil NO_3-N increased to >40 kg ha^{-1} with 500 kg fertiliser N ha^{-1}. Titchen and Scholefield (1992) observed mean autumn soil inorganic N (NO_3-N+NH_4-N) levels from 0 to 30 cm of 38.6 and 39.2 for undrained and drained grazed grassland in the U.K. which was similar to the mean farm soil N of 37.9 kg ha^{-1} observed in Fermoy in Autumn 1994, although three farms had soil N >45 kg ha^{-1}.

The trend of higher soil inorganic NO_3-N levels in autumn compared to spring by Younie and Watson (1992) was also observed in Fermoy in 1994. Soil NO_3-N levels which ranged from 16 to 37.6 kg ha^{-1} in autumn compared to the lower range from 4.7 to 11 kg ha^{-1} in spring 1995.

On the first three sampling periods Ballyderown had one of the highest soil NO_3-N levels observed indicating a greater load of NO_3-N available for leaching on the sampling date. In November 1994, after leaching commenced, Ballyderown had significantly ($P<0.001$) more soil NO_3-N available for leaching than was measured at the other farms on this sampling date.

Thus NO_3-N leaching at Ballyderown could be considerably higher than at the other farms sampled.

Caution should be used in the interpretation of these results as there may be slightly different meteorological, hydrological and agronomic practices occurring at each farm. Slight differences in the amount of rainfall or soil permeability could lead to the soil NO_3-N being leached beyond the shallow sampling depth of 30 cm for the first three sampling dates and 45 cm on the last sampling date. Thus if NO_3-N is removed from the sampling depth we get a biased sample which may indicate low NO_3-N whereas higher NO_3-N leaching loads may have already moved beyond the sampling depth.

During 1995 the soil NH_4-N levels at Ballyderown appeared to be lower than at the other farms although there was a large amount of within farm variation. Ballyderown had significantly lower soil NH_4-N levels compared to TC and MR in February and November 1995, respectively. On these dates Ballyderown had the third and second lowest soil NH_4-N levels.

Comparison of the soil total inorganic N between the farms sampled showed no significant differences between Ballyderown and the other farms. The two sampling dates in 1994 failed to show any differences between any farm means as the ANOVA failed to reject the null hypothesis that there were no significant differences between farm means. On the last three sampling periods the farm TC had significantly higher soil total inorganic N within the sampling interval than some farms. Thus TC appeared to have the highest potential N leaching rates of all the farms sampled, although TC was never significantly different to Ballyderown.

Soil total Kjeldahl N levels were generally not significantly different for Ballyderown compared to the other farms sampled. Observed variation was much lower of Kjeldahl N was lower than for inorganic N with, CV of 10.4 and 13.8% for the sampling depth 0 to 15 cm and 15 to 30 cm, respectively. Thus similar rates of organic matter mineralisation may be expected at each of the farms, although there are other factors which do affect mineralisation such as organic carbon contents of the soil.

8.3 Kilworth/Downing Bridge Supply

8.3.1 Introduction to the Kilworth village supply (Downing Bridge)

As part of the weekly groundwater sampling protocol at Ballyderown samples of the local public supply from Kilworth village were taken. This supply is operated by Cork County Council and the production well is located beside Downing bridge. The supply is referred to as the Downing bridge supply by the Environmental Protection Agency (EPA) in their annual water quality reports.

Borehole geology and drilling details

The borehole supply was drilled in 1983 and was reported to be 17 m deep with 12.6 m of gravels/sand and boulder clay overburden. The borehole was drilled 3.8 m into reef limestones with gravel infilled cavities. A strong water flow was met at 12.6 m (limestone/overburden interface) (Devlin, 1983). The borehole has 36 cm casing down to 12.6 m after which drilling continued through the casing at 36 cm diameter to a depth of 17 m b.g.l.. Pumping tests carried out showed a specific capacity of 4.42 m^3ph/m draw down, the calculated well permeability was 98.2 m^3pd/m^2.

Sampling carried out by Devlin (1983) showed the borehole water to be hard with coliforms and NH_3 present. McGuire (1991) comments on the NO_3-N fluctuations observed in the Downing bridge supply and notes there was considerable variation with no clear trend detectable between 1983 and 1990, inclusive.

8.3.2 Methodology

The Downing bridge supply is used as a source of drinking water for the farm and a near by house. An external tap beside the farm yard is the location where samples were taken. The tap was turned on for 5 minutes before a sample was taken and returned to the laboratory for chemical analysis. Chemical analysis was carried out as described in 7.2.1.

8.3.3 Kilworth results and discussion

A summary of the observed groundwater chemistry for the Kilworth supply during the sampling period from 1/1/94 to 2/4/96 can be seen in Table 8.7.

Table 8.7 Summary of the groundwater chemistry for the Kilworth supply, (1/1/94 to 1/8/96).

Summary Statistic	NO_3-N	K	Na	Cl	K\Na
mean	9.2	1.7	10.5	25.9	0.2
median	9.1	1.6	10.4	25.7	0.2
standard deviation	0.7	0.3	0.7	1.4	0.0
standard error	0.09	0.035	0.1	0.21	0.004
maximum	10.8	3.1	14.8	32.2	0.3
minimum	7.5	1.2	9.5	23.4	0.1
range	3.3	1.9	5.3	8.8	0.2
Sample size (n)	79	57	57	42	57

The NO_3-N concentrations during the sampling period ranged from 7.5 to 10.8 mg l^{-1} with a mean concentration of 9.2 mg l^{-1}. Mean K, Na and Cl^- concentrations were 1.7, 10.5, 25.9 mg l^{-1}, respectively. Variation of NO_3-N from the Kilworth supply from 1/1/94 until 2/4/96 can be seen in Figure 8.6.

The results in Figure 8.6 show that there were no observed values greater than MAC. The minimum observed concentration of 8 mg l^{-1} was observed on 9/8/94 (day 221) and 17/10/95 (day 655). (A single low concentration of 7.5 mg l^{-1} was observed on 24/1/96 (day 754) but this is suspected as being anomalous). Groundwater NO_3-N concentrations ≥ 10 mg l^{-1} were observed on 25/4/94 (day 115), 1/11/94 (day 305), 20/4/95 (day 475), between 4 and 31/5/95 (days 489 to 516) and 2/4/96 (day 823). With the exception of May 1995 the highest

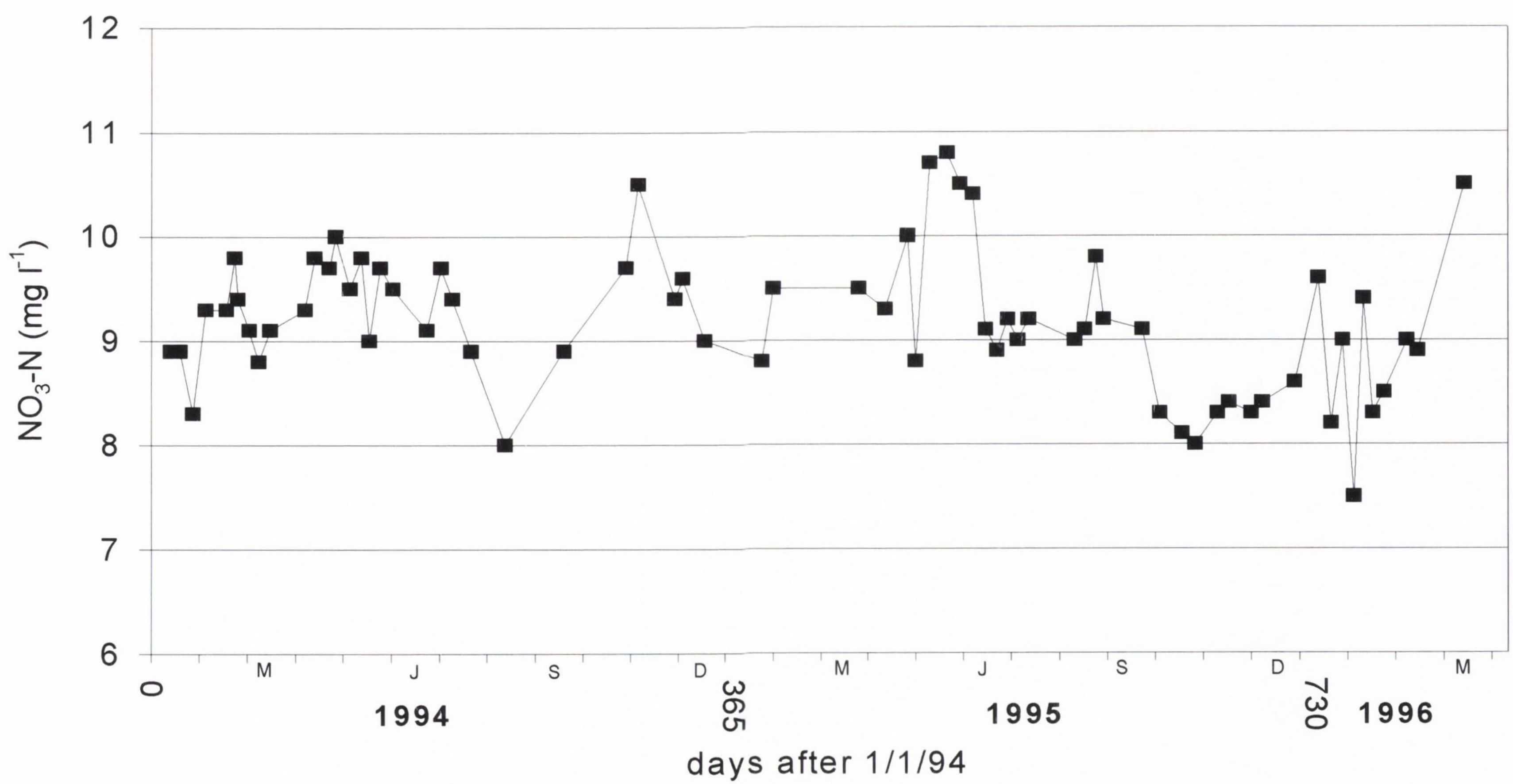


Figure 8.6 Kilworth groundwater NO_3-N concentrations from 1/1/94 to 2/4/96.

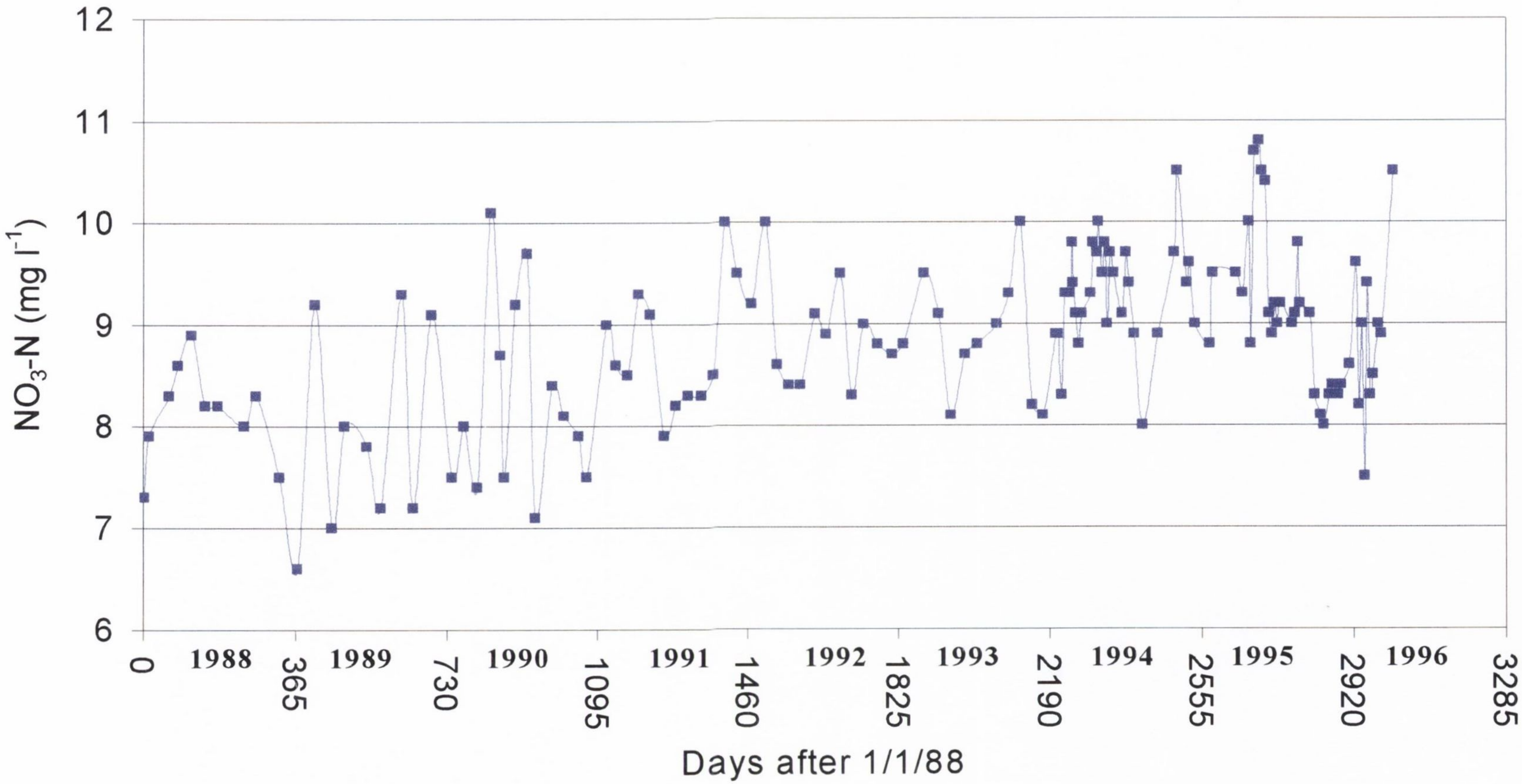


Figure 8.7 Long term variation of NO_3-N concentration in the Kilworth supply from 1/1/88 to 2/4/96.

groundwater NO_3-N concentrations occurred during the winter period peaking in April of each year.

Temporal NO_3-N concentration variation between 1/1/88 and 2/4/96 can be seen in Figure 8.7. A large amount of annual variation is present, for example NO_3-N concentration during the 1991/92 winter recharge period increased from 8.3 to 10 mg l^{-1}. There does appear to be a temporal trend of increasing NO_3-N concentration with time although this is obscured by the large seasonal variation.

The trend of increasing groundwater NO_3-N concentration over the period 1/1/88 to 31/12/95 was investigated using regression analysis with mean annual NO_3-N concentration as the dependent variable and time expressed as years as the independent variable (Figure 8.8).

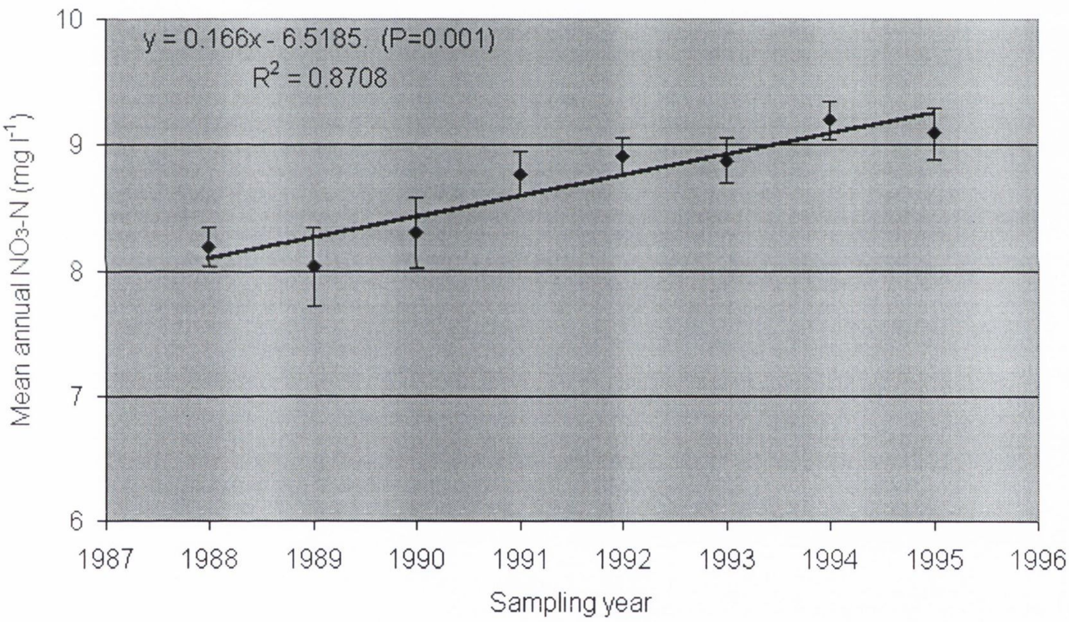


Figure 8.8 Increasing mean annual NO_3-N concentrations in the Kilworth supply (vertical bars are one S.E. of the yearly mean).

A regression of mean annual groundwater NO_3-N concentration and time showed a significant relationship (P=0.001) with an R^2=0.87. Thus it appears that, although there is annual variation present, when this is removed by calculating annual mean NO_3-N concentrations there is a definite linear increase of groundwater NO_3-N concentration with time.

The relationship observed between groundwater NO_3-N concentration and the previous year's soil moisture deficit, described in section 7.3.6, was investigated with observed groundwater NO_3-N concentrations from the Kilworth supply. No significant relationship was observed between groundwater NO_3-N and either maximum s.m.d., mean summer s.m.d. or the number of days with a s.m.d. >30 mm.

Groundwater NO_3-N concentrations observed in the Kilworth supply are increasing over time from 1988 to 1995 which is also related to summer drought conditions, as quantified by maximum s.m.d. and the number of days which had s.m.d. >30 mm. No significant relationship was observed between time (years) and either measure of s.m.d.. Thus the increasing NO_3-N concentrations with time are not directly related to s.m.d. and thus could be indicating changes in agricultural practice such as an increase in the quantity of N applied or in the proportions of different agricultural systems such as an increase in the percentage of arable land in the catchment area.

8.4 Fermoy regional nitrate situation

8.4.1 Introduction

In order to ascertain what the overall groundwater quality in the Fermoy region was, a large number of private drinking water supplies were sampled. In general agricultural practices in the Fermoy region are intensive and a number of public drinking water supplies have had NO_3-N concentrations which breached MAC. Groundwater samples taken were analysed for a wide range of chemical and biological parameters in order to ascertain the source of any pollution. Detailed surveys were also carried out which characterised the protection given to each well and the number of potentially polluting activities which may have been located close to the borehole.

8.4.2 Methodology

Boreholes locations were found by carrying out door to door surveys and asking for permission to sample private supplies. Groundwater samples were taken from the kitchen tap. Firstly the water was run for 5 minutes and then the tap was sterilised using an alcohol flame and the tap was run for a further 5 minutes.

Samples for chemical analysis were taken by filling a 1.5 litre clean disposable bottle; samples for coliform determination were taken using a sterile 250 ml container which was filled by placing it rapidly beneath the running tap. After it filled and was sealed it was placed in a cool box for immediate return to the laboratory. Samples were returned to the laboratory for analysis within 24 hours of sampling. After sampling was completed a well head survey was carried out and a questionnaire completed on the borehole construction.

Total and faecal coliforms were determined as described in Appendix I and chemical determination was carried out as described in Appendix I.

8.4.3 Results and discussion

A map of all supplies sampled together with the supply identity code is shown in Figure 8.8.

Of the supplies sampled 20 (37%) were located in fields, 16 (30%) were located in gardens, 7 (13%) were located in farmyards, 3 (6%) located in woods and 8 (15%) could not be determined. The borehole lining was protruding above ground level in 12 (22%) of supplies, flush with the ground level in 21 (39%) supplies, was below ground level in 8 (15%) supplies and could not be determined in 13 (24%) supplies. The well head was surrounded by a concrete plinth at 35 (65%) of supplies, 10 (19%) supplies had no surrounding plinth and the status of 9 (17%) supplies could not be determined. The well head was covered by a pump house at 20 (37%) supplies, had a water tight cap at 13 (24%) supplies, had a badly fitting loose cap at 6 (11%) supplies; 6 (11%) supplies had no covering and 9 (17%) supplies could not be determined.

The depth of each borehole was ascertained from the records of the supply owner. Borehole depths from the 34 supplies with records ranged from 22 to 120 m with a mean depth of 55 m. Of the 40 supplies for which the yaer of drilling was known, borehole ages ranged from <10 years old to 40 years old with a median age of 10 to 20 years old. All boreholes sampled were drilled and not hand dug. Access to 18 boreholes allowed the measurement of water table depth which ranged from 0 for springs to 22.7 m b.g.l., the mean water table depth was 10.06 m b.g.l..

Sources of localised pollution within the vicinity of each borehole were examined. Septic tanks were located within 100 m at 22 (41%) supplies, 14 (26%) supplies had no septic tanks nearby, 7 (13%) supplies had septic tanks between 100 and 400 m from the borehole and with 12 (22%) supplies the possibility of septic tanks being located nearby was unknown. Of the 22 supplies with septic tanks within 100 m 17 (31%) supplies had one septic tank system and 5 (9%) supplies had two septic tank systems within 100 m of the borehole.
Septic tanks located within 300 m of boreholes served between 2 and 7 people with a mean population served by septic tanks of 4.2 people and a standard deviation of 1.5. The majority of septic tank systems had soak pits (17, 32%) and only four (7%) septic tank systems had percolation areas.

Sources of localised farm pollution within 300 m of each supply were also investigated. Farmyards were located within 300 m of 25 (46%) supplies and were not within 300 m of 24 (44%) supplies. Sources of pollution within farmyards were investigated. Of the 25 supplies which had farmyards within 300 m, 20 had milking sheds, 24 had animal housing, 18 stored dung in dungsteds, 18 collected slurry in tanks and 19 had silage clamps.

From the site investigation survey it was possible to see that 41% of supplies sampled had septic tank systems within 100 m of the borehole although the majority only had one septic tank system to serve a mean of 4.2 people. Farmyards were located within 300 m of 46% of supplies sampled and the majority of farmyards had numerous sources which could potentially pollute groundwater.

A general summary of the chemical and biological parameters analysed in samples taken during the regional sampling programme can be seen in Table 8.8.

Table 8.8 Descriptive summary of the regional sampling for all observations (n=54).

Parameter conc. (mg l^{-1})	mean	median	S. deviation	minimum	maximum	%>GL	%>MAC
NO_3-N	7.85	6.90	4.70	0.50	20.50	59	28
NH_4-N	0.02	0.00	0.10	0	0.65		4
MRP	0.015	0.000	0.040	0	0.199		
*T. Coliform	26	1	56	0	200		50
*F. Coliform	11	0	34	0	200		28
K	4.52	2.50	5.21	0.20	25.70	9	9
Cl	23.23	21.80	7.75	11.50	60.30	22	0
K\Na ratio	0.34	0.21	0.78	0.03	0.47		33
Ca	48.08	26.90	41.60	2.90	137.90		0
Mg	5.74	5.25	2.48	0.70	14.60		0
Na	13.19	11.71	6.67	7.39	55.00		0
Mn	0.02	0	0.11	0	0.72		4
Cu	0.01	0	0.02	0	0.07		0
Fe	0.03	0	0.18	0	1.20		4
Zn	0.09	0.01	0.27	0	1.90		2

* Coliforms are expressed as counts per 100 ml of sample.

The MAC for NO_3-N, NH_4-N, total and faecal coliforms, Mn, Fe and Zn were all exceeded by some supplies in the regional sampling. The MAC for NO_3-N and NH_4-N of 11.3 and 0.38 mg l^{-1} were exceeded by 28% and 4% of samples, respectively. Total and faecal coliforms were present in 50% and 28%, respectively, of supplies sampled, although coliform counts greater than 10 per 100 ml were observed in 26% and 15% of supplies for total and faecal coliforms, respectively. Concentrations of K^+ greater than the MAC of 12 mg l^{-1} and a GL of 10 mg l^{-1} was observed in 9% of supplies sampled. The MAC for Cl^- of 200 mg l^{-1} was not exceeded by any supplies sampled although the GL of 25 mg l^{-1} was exceeded in 22% of supplies sampled. A total of 4% of supplies sampled had Mn and Fe concentrations exceeding the MAC of 0.05 and 0.2 mg l^{-1}, respectively. Concentrations of Zn above the MAC of 1 mg l^{-1} was observed in one (2%) supply.

The main aim of the regional sampling was to determine the spatial variation of groundwater NO_3-N concentrations in the Fermoy region. A histogram distribution of groundwater NO_3-N concentrations from the regional sampling can be seen in Figure 8.9.

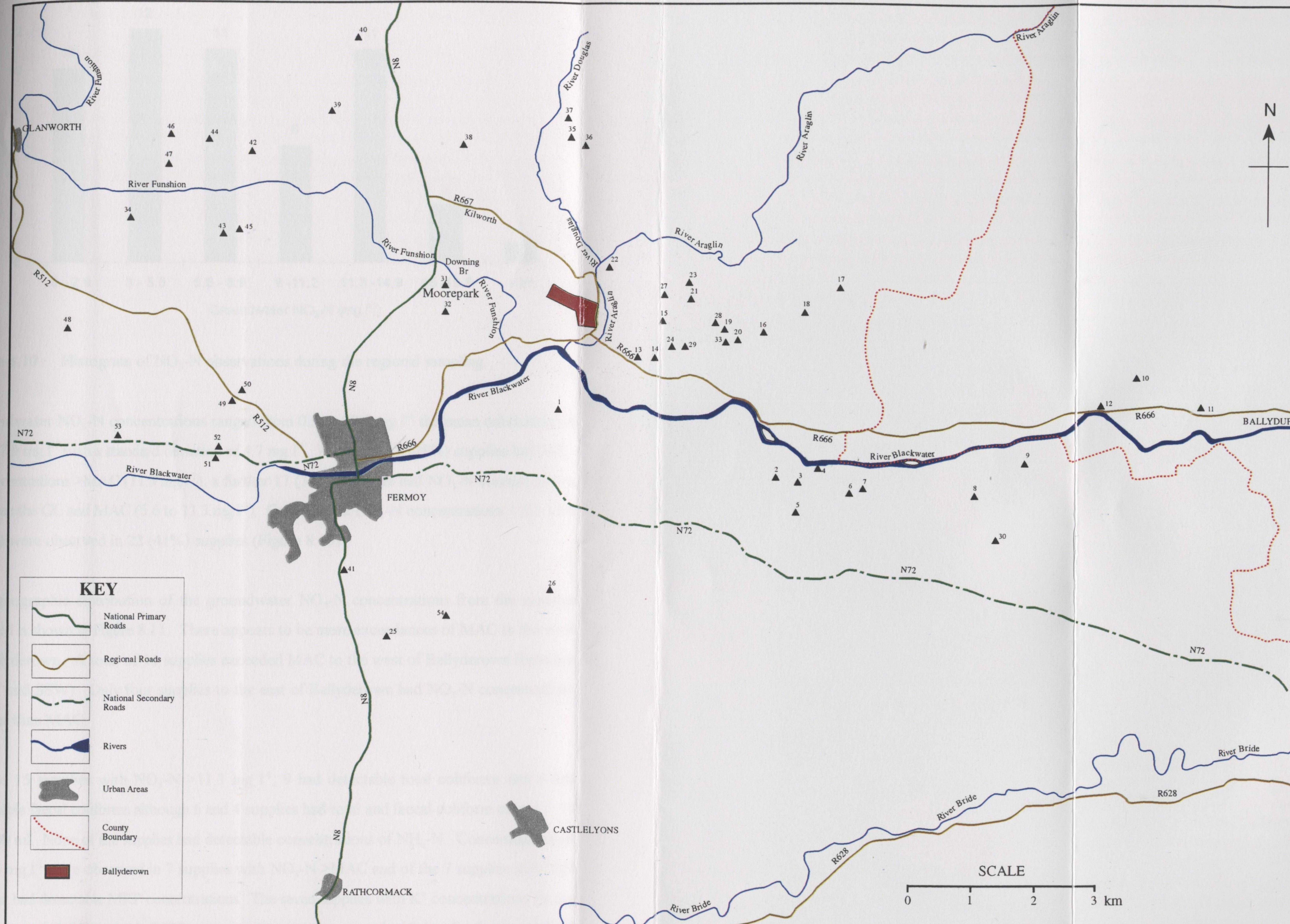


Figure 8.9 Fermoy region groundwater survey supply locations and identities.

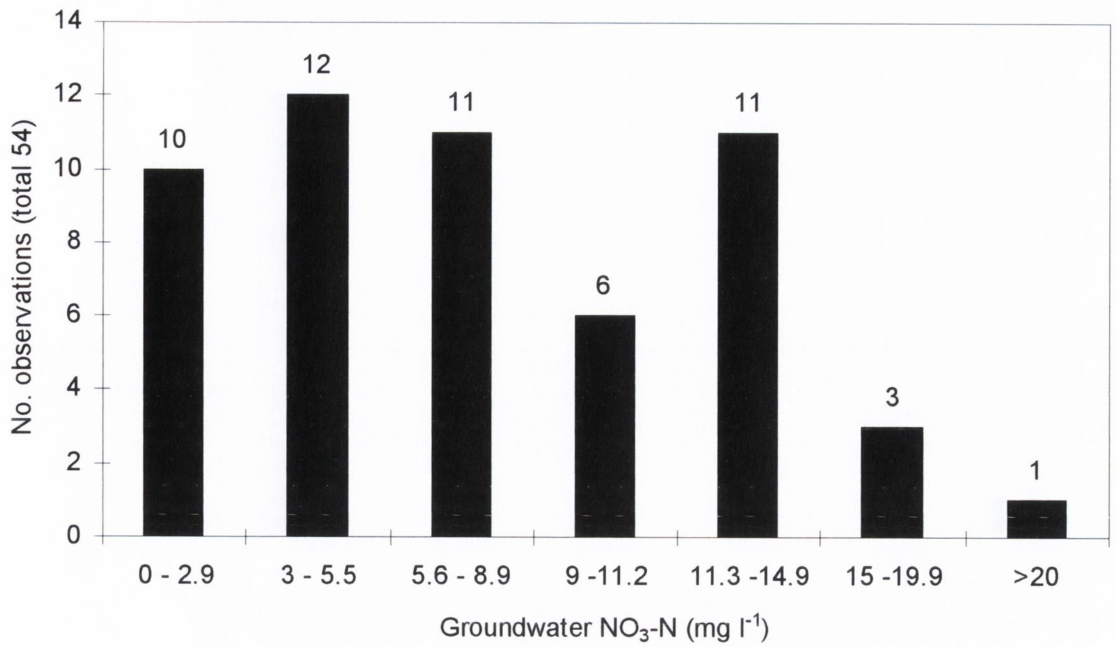


Figure 8.10 Histogram of NO_3-N observations during the regional sampling.

Groundwater NO_3-N concentrations ranged from 0.5 to 20.5 mg l^{-1} the mean concentration being 7.9 mg l^{-1} with a standard deviation of 4.7 mg l^{-1}. A total of 15 (28%) supplies had NO_3-N concentrations >MAC (11.3 mg l^{-1}), a further 17 (31%) supplies had NO_3-N concentrations between the GL and MAC (5.6 to 11.3 mg l^{-1}). Groundwater NO_3-N concentrations < GL (5.6 mg l^{-1}) were observed in 22 (41%) supplies (Figure 8.10).

The geographic distribution of the groundwater NO_3-N concentrations from the supplies sampled is shown in Figure 8.11. There appears to be more exceedances of MAC to the west of Ballyderown. A total of 11 supplies exceeded MAC to the west of Ballyderown (between NNW and SSW). Only four supplies to the east of Ballyderown had NO_3-N concentrations greater than MAC.

Of the 15 supplies with NO_3-N >11.3 mg l^{-1}, 9 had detectable total coliforms and 6 had detectable faecal coliforms although 6 and 4 supplies had total and faecal coliform counts > 10 per 100 ml. None of the supplies had detectable concentrations of NH_4-N. Concentrations of K^+ >4 mg l^{-1} were observed in 7 supplies with NO_3-N >MAC and of the 7 supplies with high K^+ four had detectable MRP concentrations. The seven supplies with K^+ concentrations >4 mg l^{-1} and associated detectable MRP concentrations are associated with localised point sources

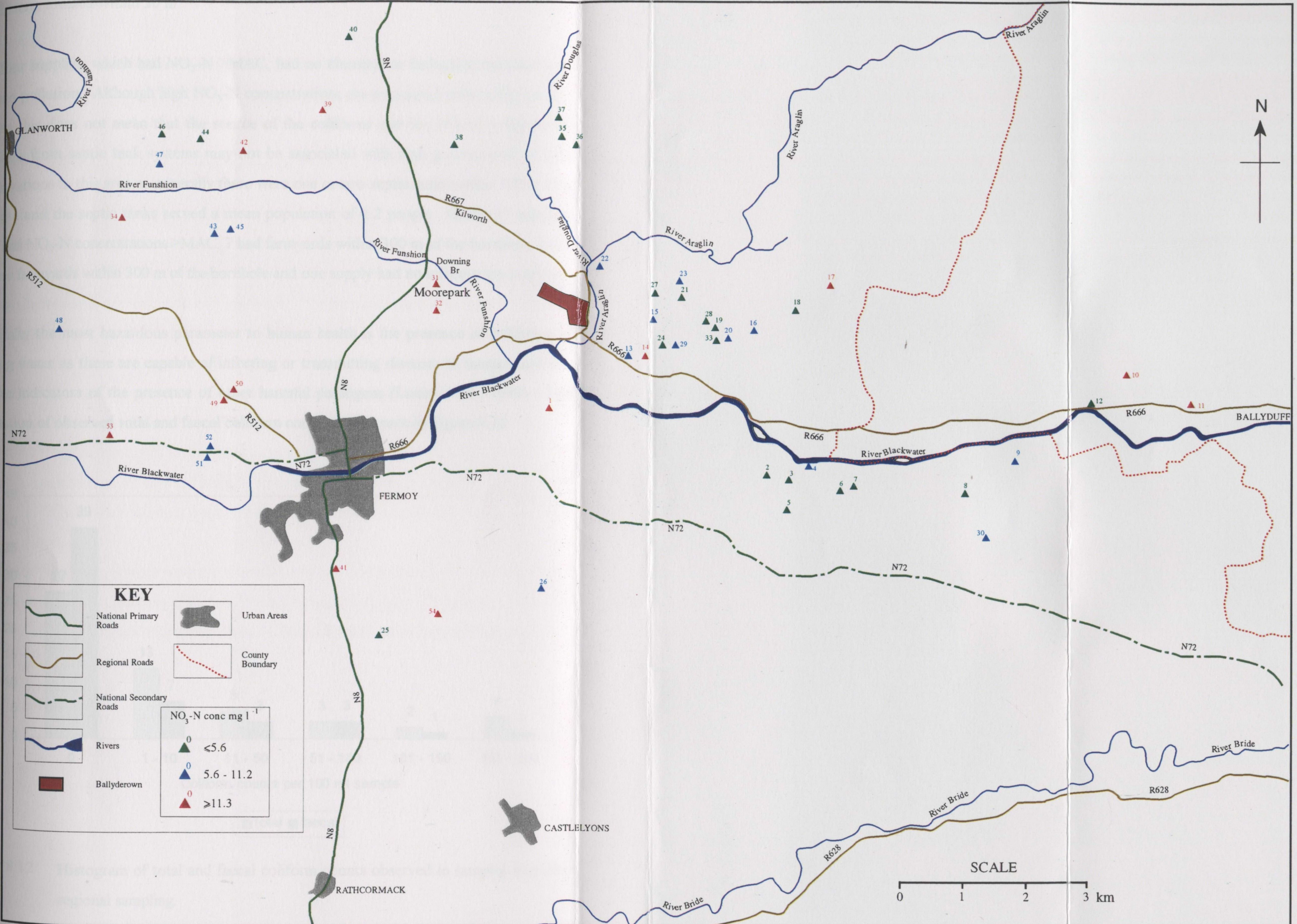


Figure 8.10 Geographic distribution of groundwater NO_3 -N results from Fermoy regional sampling.

of pollution as five supplies had farmyards within 300 m of the borehole and a further one had a septic tank located within 50 m.

Only four supplies, which had NO_3-N >MAC, had no chemical or biological indications of localised pollution. Although high NO_3-N concentrations are associated with coliforms in 9 supplies this does not mean that the source of the coliforms and the NO_3-N is the same. Coliforms from septic tank systems may not be associated with high groundwater NO_3-N concentrations in this area as generally there were one or two septic tanks within 100 m of a borehole and the septic tanks served a mean population of 4.2 people. Of the 15 supplies which had NO_3-N concentrations >MAC, 7 had farmyards within 300 m of the borehole, 7 did not have farmyards within 300 m of the borehole and one supply had no information available.

Potentially the most hazardous parameter to human health is the presence of coliforms in drinking water as these are capable of infecting or transmitting diseases to humans and are possible indicators of the presence of other harmful pathogens (Lucey *et al.*, 1999). The distribution of observed total and faecal coliform counts can be seen in Figure 8.12.

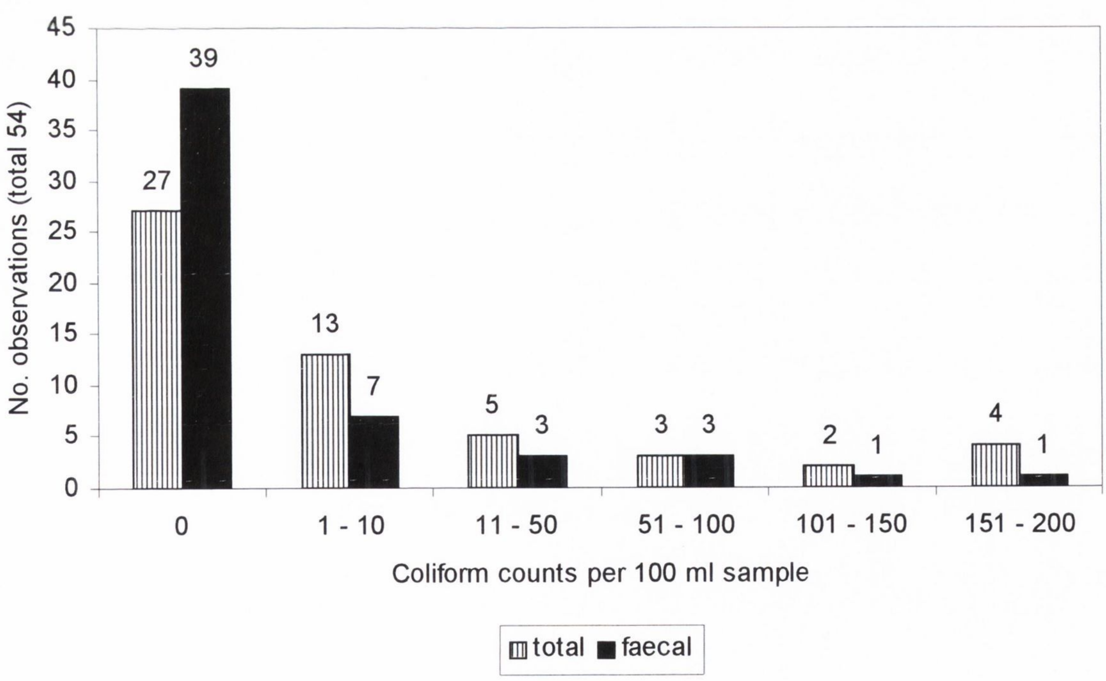


Figure 8.12 Histogram of total and faecal coliform counts observed in samples from the regional sampling.

Total coliforms were present in 50% of samples (Figure 8.12) although 26% had total coliform counts >10 per 100 ml, counts ≤10 per 100 ml are thought to be of little sanitary significance (WHO, 1984). A total of 28% of samples had faecal coliforms present and 15% had >10 counts per 100 ml at the time of sampling (Figure 8.12). Total and faecal coliform counts >100 per 100 ml were observed in 11% and 4% of supplies sampled.

Only three samples had NH_4-N concentrations >0.1 mg l^{-1}. The presence of NH_4-N in samples is indicative of localised pollution due to low mobility in soil and conversion via nitrification to NO_3-N. Presence of NH_4-N concentrations >0.1 mg l^{-1} is indicative of sewage, industrial effluent or animal waste (Lucey *et al.*, 1999) and thus it is often found in association with coliform contamination. Of the three samples with detectable NH_4-N, two also had detectable MRP and high counts of total and faecal coliforms. The mean concentration without the two grossly contaminated supplies was 0.01 mg l^{-1}. Of the 14 supplies with detectable MRP, 9 had total coliforms present although only 6 of these had total coliform counts > 10 per 100 ml. Faecal coliforms were present in 7 supplies although only 4 had coliform counts > 10 per 100 ml. Potassium concentrations > 3 mg l^{-1} were associated with detectable P in 5 supplies. Only four (29% of supplies with detectable P concentrations) had coliform counts <10 per 100 ml and K^+ concentrations <3 mg l^{-1}. Thus the majority of groundwater MRP detections in this study are associated with localised pollution from manures/septic tanks and silage effluent.

MRP concentrations in groundwater are normally very low due to the strong retention within the soil zone, although leaching may occur under certain conditions. Phosphorus above the detection limit of 0.005 mg l^{-1} was observed in 14 samples and the distribution of supplies with MRP ≥0.005 is presented in Figure 8.13.

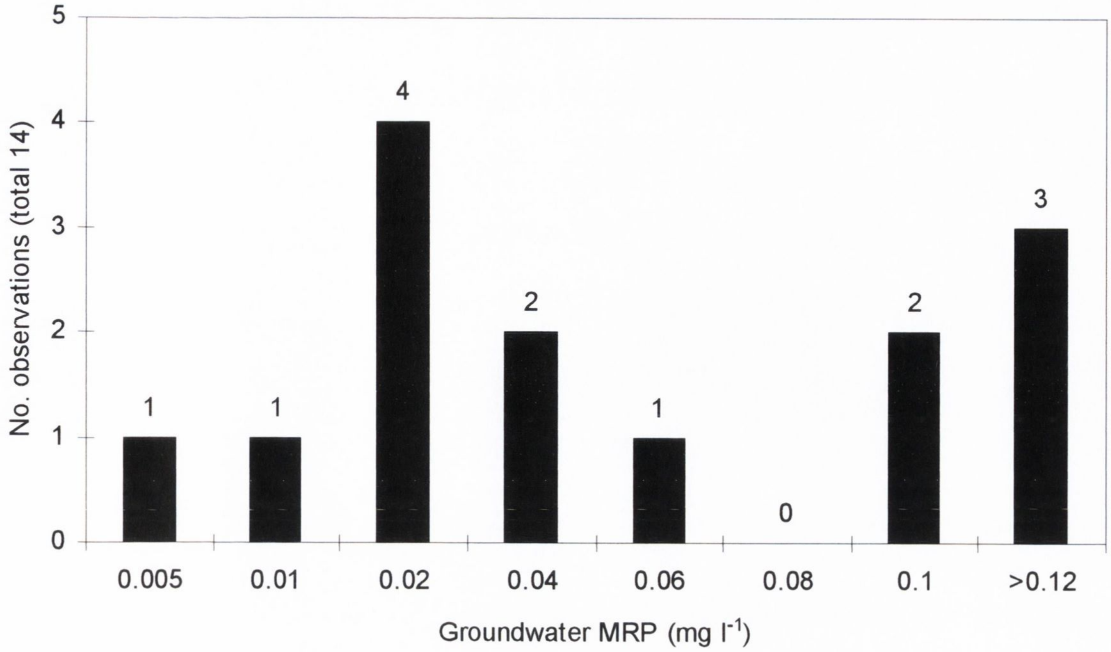


Figure 8.13 Histogram of groundwater MRP concentrations for supplies with detectable P concentrations. Note that the labels on the x-axis are the highest concentrations in each category. The category marked 0.02 mg l^{-1} encompasses the concentration interval 0.011 to 0.02 mg l^{-1}.

Of the fourteen samples with detectable MRP two samples appear to be grossly contaminated by a point source with MRP of 0.13 and 0.153 mg l^{-1} although they were not associated with coliform pollution but had K^+ concentrations of 25.7 and 9.7 mg l^{-1} and K\Na ratios >0.6 indicative of a vegetable source of pollution, possibly silage effluent.

The MRP concentrations in the four supplies with no indication of localised pollution were 0.015, 0.019, 0.034 and 0.199 mg l^{-1} the latter concentration is thought to be due to localised pollution as it is extremely high although there were no further indications of localised pollution.

A histogram of observed groundwater K^+ concentrations can be seen in Figure 8.14.

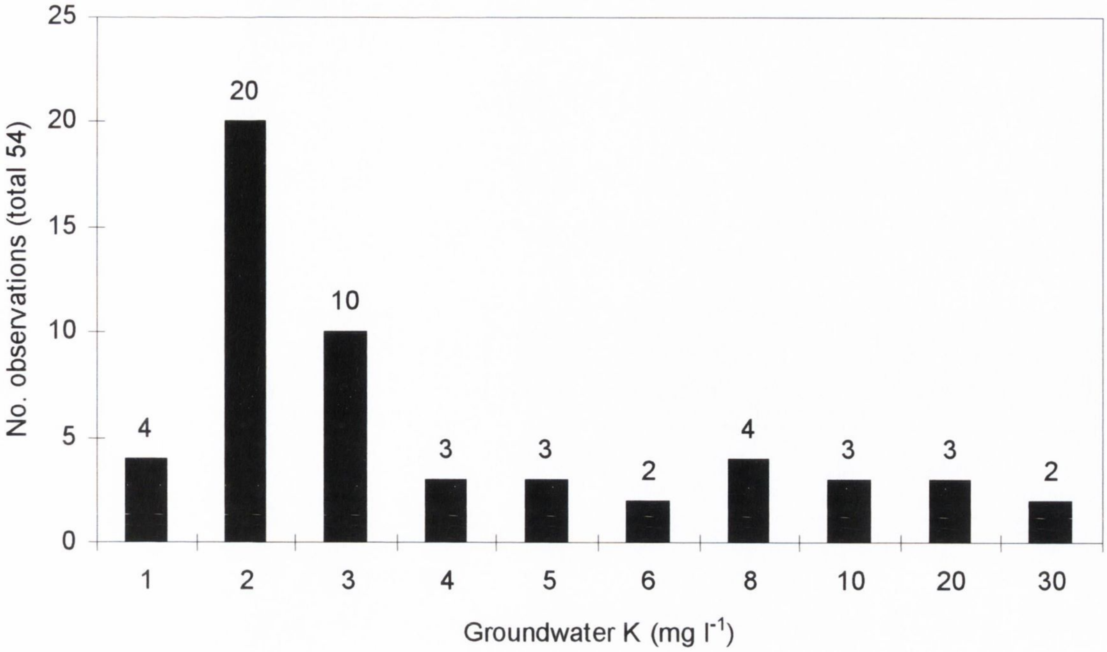


Figure 8.14 Histogram of K^+ concentrations during the regional sampling. Note that labels on the x-axis are the highest concentrations in each category. The category marked 2 mg l^{-1}, for example encompasses the concentration interval from 1.1 to 2 mg l^{-1}.

Observed K^+ concentrations varied from 0.2 to 25.7 mg l^{-1} and the mean was 4.52 mg l^{-1}. The distribution of the K^+ observations is skewed and thus the median gives a better idea of the true location of the centre of the population. The median K^+ concentration was 2.5 mg l^{-1} which is significantly lower than the mean as the mean is high due to a few extreme observations which are influenced by point sources. A total of 17 supplies had K^+ concentrations >4 mg l^{-1}, 8 supplies had septic tanks within 300 m and 7 had septic tanks within 100 m.

Of the 17 supplies with high K^+ concentrations, 11 had farmyards within 300 m and only 3 supplies had no obvious local source of pollution. Thus localised pollution sources such as septic tanks and farmyards were located within close vicinity of 82% of the supplies with high K^+ concentrations.

Elevated K^+ concentrations are a good indicator of localised pollution sources and have been used by workers to identify point source polluted supplies. Deakin (1994) used a K^+ concentration of three times the background level which gave a threshold concentration of 3.9

mg l^{-1}. This threshold was sometimes increased to 4.5 mg l^{-1} due to the possibility of naturally elevated K^+ concentrations in sandstones and volcanic geological situations. A survey of the principal springs in Ireland showed that Kerry springs had a mean K^+ concentration of 2.9 mg l^{-1} and five of the fifteen springs (33%) had K^+ concentrations >4 mg l^{-1} (Daly *et al.*, 1989).

Studies in Ireland have used a K\Na ratio as an indicator of organic contamination which has been used to differentiate between farm waste and septic tank effluent. The decay of organic vegetable matter releases more K^+ than Na^+ and a ratio of ≥0.3 is used to indicate significant contamination by farm waste.

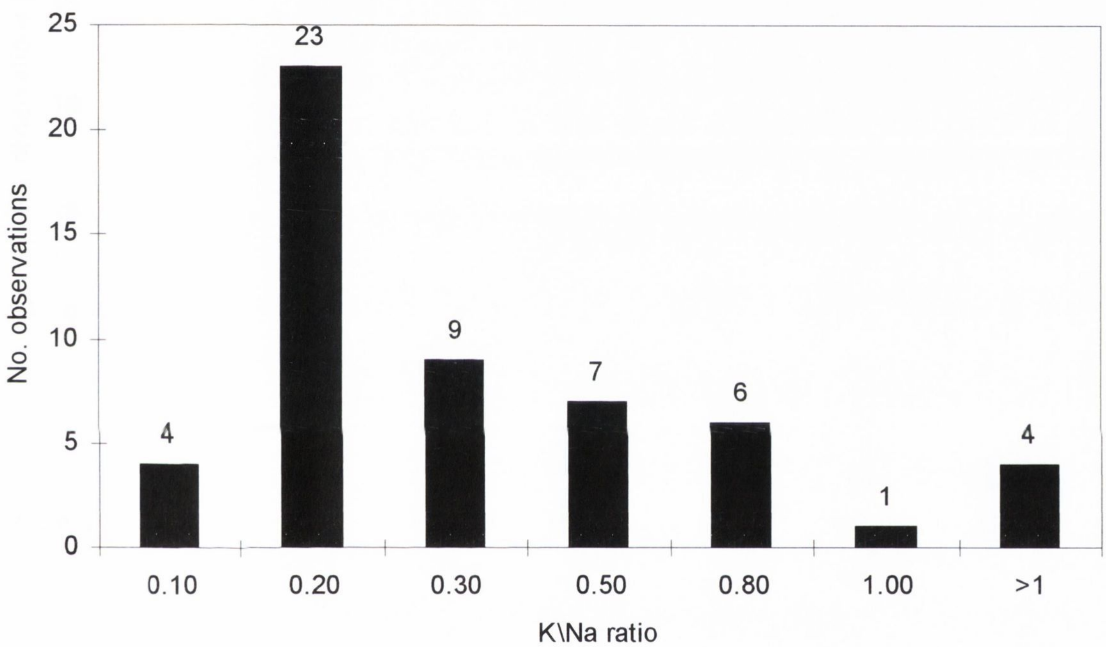


Figure 8.15 Histogram of K\Na ratios during the regional sampling. Note that labels on the x-axis are the highest ratio in each category. The category marked 0.50, for example encompasses the ratio interval from 0.31 to 0.50.

A total of 18 supplies had K\Na ratios >0.3 and also K^+ concentrations >4 mg l^{-1} for 16 of the 18 supplies. Other indicators of localised point source pollution were that 8 supplies had detectable MRP concentrations, one had high NH_4-N, 10 supplies had total coliforms and 8 had faecal coliforms. Five supplies had no evidence of localised pollution other than elevated K^+ concentrations and K\Na ratios. Comparison of K\Na ratios >0.3 to well survey details showed that 10 of the supplies had farmyards within 300 m of the borehole. Septic tanks were located within 300 m of 9 supplies with high K\Na ratios and 8 supplies had no septic tanks within 300 m. Four supplies had no farmyards or septic tanks within 300 m of the supply borehole.

Chloride concentrations varied from 11.5 to 60.3 mg l^{-1} with a mean of 23.23 mg l^{-1} (Table 8.8). The distribution of observed groundwater Cl^- concentrations can be seen in Figure 8.16.

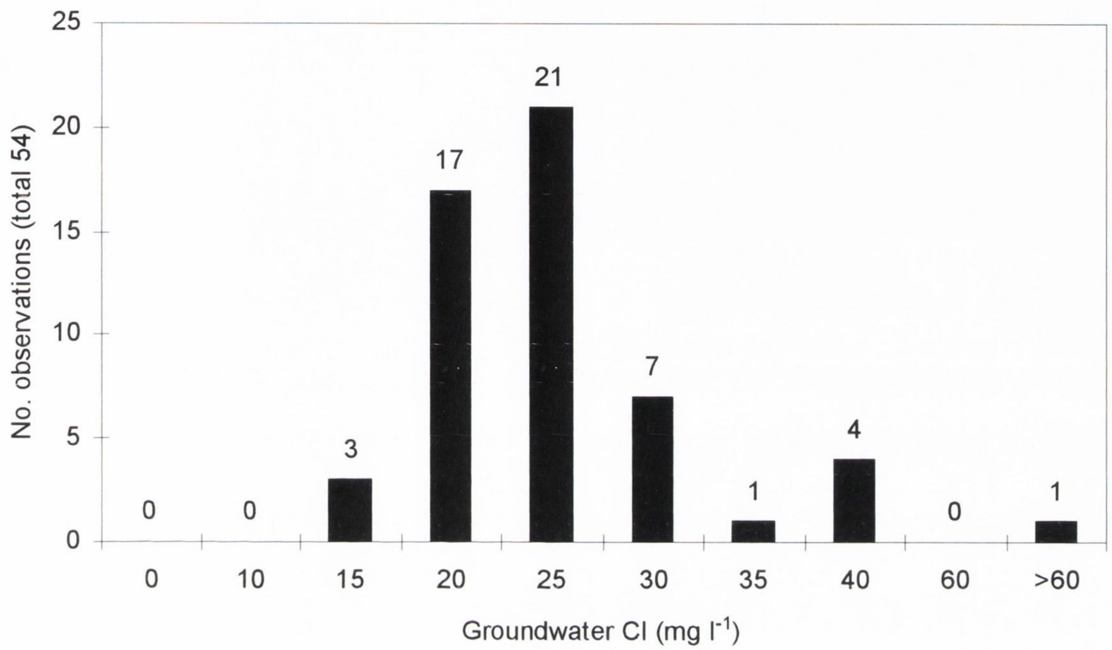


Figure 8.16 Histogram of Cl^- concentrations during the regional sampling. Note that labels on the x-axis are the highest concentrations in each category. The category marked 20 mg l^{-1}, for example encompasses the concentration interval from 15.1 to 20 mg l^{-1}.

The majority (70%) of groundwater Cl^- concentrations observed were located in the range 15.1 to 25 mg l^{-1}. Deakin (1994) observed mean Cl^- concentrations for contaminated and uncontaminated boreholes of 23.4 and 25.1 mg l^{-1}, respectively, which are close to the values observed in the Fermoy region. Irish groundwater Cl^- concentrations reported by Lucey *et al.* (1999) had a mean value <30 mg l^{-1} which accounted for 85% of 886 samples. In Fermoy, 89% of samples had Cl^- concentrations <30 mg l^{-1}, a concentration above which Lucey *et al.* (1999) and Deakin (1994) suggest may be indicative of localised pollution. In the present study only seven supplies had a Cl^- concentration $\geq$30 mg l^{-1} and of these seven supplies five had K^+ concentrations >4 mg l^{-1}, four had K\Na ratios >0.3, three had detectable MRP concentrations, three had total coliforms and one had faecal coliforms. One supply which had a Cl^- concentration of 38.5 mg l^{-1} had no other indicators of localised pollution present. Of supplies with $Cl^- \geq 30$ mg l^{-1}, four had farmyards within 300 m and two had septic tanks within 100 m. The seven supplies with Cl^- concentrations ≥ 30 mg l^{-1} had a mean NO_3-N^- concentration of 12 mg l^{-1} which indicates that elevated NO_3-N concentrations maybe associated with elevated Cl^- concentrations.

The association between groundwater NO_3-N^- and Cl^- concentrations is examined in Figure 8.17.

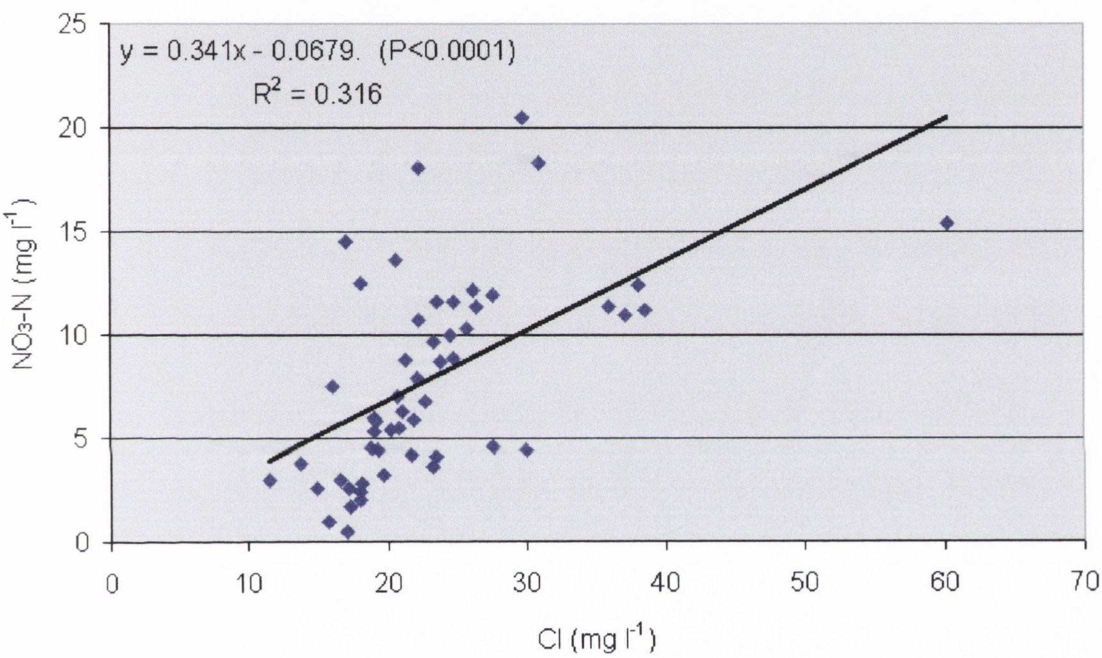


Figure 8.17 Regression analysis between groundwater NO_3-N^- and Cl^- concentrations.

A highly significant ($P<0.0001$) positive association can be observed between groundwater NO_3-N^- and Cl^- concentrations from the 54 samples taken in the Fermoy region. The extreme Cl^- value of 60.3 mg l^{-1} is influencing the least squares regression line but when removed there is only a slight increase in the R^2 value from 0.316 to 0.322 and for this reason it is included in the relationship.

Other significant relationships were observed between NO_3-N^- and other parameters which are displayed in Table 8.9.

Table 8.9 All significant regression associations between observed chemical parameters from the regional sampling (n=54).

	NO_3-N^-	Cl^-	Ca^{++}	Mg^{++}	Na^+	K^+
NO_3-N^-		P<0.0001 R^2=0.316	P=0.006 R^2=0.23	P=0.0014 R^2=0.18	P=0.0146 R^2=0.109	n.s.
Cl^-	P<0.0001 R^2=0.316		P=0.0027 R^2=0.163	n.s.	P=0.0057 R^2=0.141	P=0.0459 R^2=0.076
Ca^{++}	P=0.006 R^2=0.23	P=0.0027 R^2=0.163		P=0.0078 R^2=0.128	n.s.	n.s.

n.s denotes non significant relationships (P<0.05).

Observed NO_3-N^- concentrations were also significantly associated with Ca^{++}, Mg^{++} and Na^+ concentrations in the groundwater. Significant associations were also observed between Cl^- and Ca^{++}, Mg^{++}, Na^+ and K^+ concentrations and also between Ca^{++} and Mg^{++} concentrations.

Coxon (1993) observed highly significant relationships (P<0.001) between Irish groundwater NO_3-N concentration and Ca^{++}, Na^+, Cl^- and K^+ concentration. The strongest relationship was observed between NO_3-N and Ca^{++} concentrations which Coxon (1993) suggests may be due to application of Calcium Ammonium Nitrate fertiliser but also could be indicative of cation exchange with Ca^{++} ions being released when other cations are adsorbed in the soil.

Berg *et al.* (1997) also observed significant relationships between NO_3^- leaching and the cations Ca^{++}, Mg^{++} in a number of forest soils in six European countries which included Ireland. Observed NO_3^- leaching from a forest soil in County Kilkenny was associated significantly (P<0.001) with Ca^{++}, Mg^{++} and Al^- (r=0.601, 0.63 and 0.283, respectively). Cations Ca^{++} and Mg^{++} accompany anions (in nitrifying soils NO_3 was the most dominant) in the soil solution to maintain ionic equilibrium. Berg *et al.* (1997) also observed that Ca^{++}, and to a lesser extent Mg+, dominates the soil solution when Ca^{++} occupies more than 20% of the soil exchange complex.

Hamilton *et al.* (1993) observed that groundwater NO_3-N concentrations in the Delmara peninsula, U.S.A. were significantly ($P<0.01$) related to Ca^{++} ($R^2=0.559$), Mg^{++} ($R^2=0.588$), $Ca^{++}+Mg^{++}$ ($R^2=0.589$), K^+ ($R^2=0.563$), Cl^- ($R^2=0.475$) and to a lesser extent Na^+ ($P<0.05$, $R^2=0.127$). The significant relationship between NO_3-N^- and the other groundwater ions is attributed to agricultural application of lime, potash fertilisers and poultry manures.

Thus significant associations between NO_3-N^- and Ca^{++}, Mg^{++} and possibly Na^+ reflect maintenance of the ionic balance in soil solution leachate which must be associated with diffuse pollution. The observed associations in the present study may confirm diffuse agricultural leaching of NO_3-N^- as the source of elevated groundwater NO_3-N^- concentrations rather than point source pollution.

8.5 Conclusions

Examination of soil inorganic N levels during 1994 and 1995 showed that Ballyderown had similar levels to some farms on all sampling dates with the exception of 1994 when Ballyderown had significantly higher soil inorganic NO_3-N concentrations than all other farms surveyed. Large amounts of variation were observed between soil N levels within each farm, coefficients of variation ranged from 12.1 to 113%. Thus although farm N usage on average is a certain amount this does not mean that N leaching rates will be uniform but varies greatly within a farm and between farms.

Similar levels of soil Kjeldahl N were observed between all farms surveyed at depths of 0 to 15 cm and 15 to 30 cm. Thus similar rates of organic N mineralisation may be expected on all farms surveyed. Variation of farm soil Kjeldahl N was much lower than observed for inorganic soil N.

Regular sampling of the Kilworth water supply showed an increasing trend of groundwater NO_3-N concentrations with time. Groundwater nitrate concentrations were also related in a multiple regression to the previous year's maximum observed s.m.d. and the number of days which had a s.m.d. >30 mm.

A regional sampling of 54 borehole supplies in the Fermoy area showed that 28% of supplies had NO_3-N concentrations >MAC and 59% of supplies were >GL. Total and faecal coliforms were observed in 50 and 28% of supplies, respectively. Although borehole supplies had numerous local sources of pollution within 300 m, NO_3-N was not correlated with any indicators of localised pollution although many boreholes sampled had indications of localised pollution these sources may not be causing elevated NO_3-N levels. Groundwater NO_3-N concentrations were related to Ca^{++}, Mg^{++}, Cl^- and Na^+ which may indicate that the NO_3-N source is diffuse and that these ions contribute to the ionic balance of the diffuse leachate.

Exceedances of NO_3-N MAC appear to be randomly distributed within the sampling area. Other workers have used the lack of geographic distribution to attribute high NO_3-N concentrations to localised sources of pollution such as farmyards and septic tanks. The soil sampling experiment showed that NO_3-N^- leaching was not uniform across areas even at the farm scale. Thus randomly distributed high groundwater NO_3-N concentrations could be reflecting variation of diffuse N leaching at a regional scale rather than localised pollution.

CHAPTER 9 CONCLUSIONS

9.1 REVIEW OF THESIS AIMS

This thesis has aimed to quantify the amount of nitrate leached to groundwater in order to elucidate the source of the elevated groundwater nitrate concentrations observed beneath the study farm. In order to do this a detailed nitrogen budget was needed to determine what possible farm activities might be affecting the concentrations of nitrate in the groundwater. An important aim of the study was to determine the groundwater flow direction in order to help examine the effect which different nitrogen sources have on groundwater nitrate concentrations. A further aim was the extrapolation of the findings on the study farm to a wider geographic area.

9.2 CONCLUSIONS

In order to examine the source of groundwater nitrates a detailed nitrogen budget was calculated for the farm. A farm gate nitrogen budget found that nitrogen inputs to the farm minus nitrogen outputs to the farm had an overall surplus of N on the farm of between 271 and 340 kg N ha^{-1} yr^{-1}. This balance only accounted for gross inputs and outputs and did not allow for the differences in nitrogen inputs due to recycling within the farming system. From examination of nitrogen inputs from fertiliser, slurry, dirty water, soil organic nitrogen mineralisation and atmospheric deposition, total nitrogen loadings to plots containing boreholes ranged from 343 to 1081 kg N ha^{-1}. The mean total (kjeldahl) nitrogen load applied to the five plots which contained boreholes was 528, 809, 405, 720, and 564 kg N ha^{-1} yr^{-1}.

Detailed examination of different parts of the nitrogen budget on the farm yielded some very interesting findings. An estimate of soil organic nitrogen mineralisation on the farm was carried out. Maximum daily mineralisation rates of between 4 and 11 kg N ha^{-1} day^{-1} were observed during 1995. Mean soil organic matter mineralisation rate of 243 kg N ha^{-1} yr^{-1} was observed on the farm. This is a substantial amount of nitrogen recycled within the grassland soil and compares with a mean inorganic nitrogen fertilisation rate of 277 kg N ha^{-1} yr^{-1}.

The temporal variation in the rate of soil organic nitrogen mineralisation was interesting as peak rates occurred during September/October which coincided with the onset of soil re-wetting after the summer drought. This flush of mineralisation resulted in a dramatic increase in the quantity of inorganic N in the soil which was rapidly leached to groundwater.

The mineralisation of soil organic matter appears to be important in controlling the concentration of nitrate in groundwater. An extremely important finding of the research was a highly significant relationship over an eight year period were observed between groundwater nitrate concentrations in one year and the previous years maximum soil moisture deficit. Thus the drier the summer the higher the groundwater nitrate concentrations were in the subsequent year. This relationship would suggest that the peak rate of mineralisation observed during the re-wetting of the soil in autumn is proportional to the extent of the drought experienced during the summer period. High summer soil moisture deficits effect N losses in a number of ways, restriction in N uptake, death of plant roots and soil microbial biomass releasing N and a burst of soil organic matter mineralisation upon soil re-wetting.

The importance of soil organic matter as a source of nitrates in groundwater was also observed in an examination of the natural abundance of the nitrogen-15 isotope in groundwater nitrate ions. Observed natural abundance of nitrogen-15 to nitrogen-14 in nitrate ions from groundwater samples on the farm ranged from +5 to +10 ‰. This range has been proposed by other workers as being indicative of soil organic matter mineralisation, or could be due to a mixed source of fertiliser and animal manure N being the source of groundwater nitrate concentrations. This finding is credible in the light of the previous observations, of the relationship of groundwater nitrate to soil moisture deficit and also the high rates of soil organic matter mineralisation in autumn, i.e. that the natural abundance of nitrogen-15 in the range +5 to +10‰ is indicative of soil organic matter mineralisation on this farm.

During data collection and analysis for the nitrogen budget of the farm dirty water from the farm yard was discovered to be a significant source of nitrogen to plots. Loads of N applied to plots, which received dirty water, varied from 98 to 504 kg total kjeldahl N ha^{-1} yr^{-1}. The concentrations of nitrogen in dirty water varied seasonally with peak concentrations of 600 mg total kjeldahl N l^{-1} being recorded during summer periods and significantly lower concentrations of less than 100 mg total kjeldahl N l^{-1} being observed during winter periods.

The effect of dirty water irrigation to plots could be observed in both the quantities of nitrate leaching through the unsaturated zone and on groundwater nitrate concentrations. Elevated soil inorganic N concentrations were observed in plots which received dirty water. Autumn inorganic soil N concentrations of 168 to 320 kg N ha^{-1}, from 0 to 90 cm below ground level, were available for leaching in plots which had received dirty water in 1995. Peak mean soil solution nitrate-nitrogen concentrations of between 90 and 124 mg l^{-1}, observed in autumn, in dirty water affected plots. This concentration is between 8 and 11 times the EU maximum admissible concentration for nitrate in drinking water. This dirty water irrigation as observed on the study farm is extremely important in exacerbating the high groundwater nitrate concentrations due to the high N loads applied in the dirty water. Dirty water annual loads of Kjeldhal N of 1349 kg and ammonia N of 623 kg were observed on the farm in 1995.

The effect of dirty water irrigations on groundwater nitrate concentrations observed during the study period can also be seen. Dirty water application in plot 5, which contains borehole 2, during the summer of 1994, doubled the groundwater nitrate-nitrogen concentrations from less than 20 mg l^{-1} to a peak greater than 40 mg l^{-1}. Borehole 4 in January 1994 also appeared to be affected by elevated groundwater nitrate-nitrogen concentrations greater than 50 mg l^{-1}, the source of which is believed to be dirty water applied in plots beside where this borehole was located.

A rapid travel time from soil surface to groundwater (23 to 26 m below ground level) of 77 days was observed in a Br^- tracing experiment conducted on the farm. This rapid travel time for solutes from the soil surface to the groundwater indicates that there is only a short time for attenuation of contaminants. This has been suspected in Ireland but no data supported the hypothesis. Changes in groundwater chemistry reflect recent changes in the quality of aquifer recharge passing through the unsaturated zone i.e. the reasonably rapid recovery of groundwater nitrate concentrations observed in boreholes 1 and 4 where nitrate concentrations decreased rapidly from a period of high nitrate concentrations during one winter period to low concentrations which were similar to those observed in other boreholes after aquifer recharge during subsequent winters. The observed decrease in the concentration of nitrate in the groundwater was due to the removal of the source of the elevated nitrate concentrations, such as in the case of ploughing and re-seeding in borehole 1 or dirty water irrigation being moved away from borehole 4. The high temporal variability of groundwater chemistry on site is important in an Irish context as it indicates that groundwater contaminants may be reduced to acceptable levels over a relatively short time period when the contaminant source is removed.

The quantification of nitrate leaching through the unsaturated soil/Quaternary deposits showed that the concentration of nitrate in the soil solution at the 150 cm depth was similar to the groundwater nitrate concentration observed, such as in borehole 2. Soil solution nitrate concentrations were greater than groundwater concentrations in boreholes 1 and 5, whereas the soil solution had lower nitrate concentrations than the groundwater in boreholes 3 and 4. Thus it is possible to observe that the soil solution appears to explain the elevated groundwater nitrate concentrations in borehole 2. Soil solution nitrate concentrations were greater than concentrations observed in the groundwater sampled in borehole 5 which may indicate that a reduction of nitrate concentrations is occurring between 150 cm and the water table or that the groundwater has a low nitrate concentration before reaching this plot and that the high nitrate concentrations observed in the soil solution are being diluted in the groundwater. The concentrations of nitrate in soil solution in plots 16 and 3a are less than in the groundwater which indicates that the groundwater nitrate concentrations are being caused by nitrate leaching from the surrounding area. This has already been suggested as the cause for the high concentrations observed in borehole 4 which it is believed are being caused by dirty water applications to the north of this plot. Soil solution nitrate variability is not necessarily a guide to groundwater nitrate variation or magnitude.

Groundwater flow direction on the farm is from NNE to SSW with a slight groundwater mound in the vicinity of borehole 3 and 4 which is causing the groundwater to flow to the west. The groundwater mound in the vicinity of borehole 4 appears to reflect the geology as this area coincides with a plunging Ringmoylan shale anticline. The Ringmoylan shale has a low transmissivity value as indicated by pumping tests in borehole 3. Thus groundwater flow from the NNE to the SSW is likely to be deflected to the west around the Ringmoylan shale anticline. From the ground water flow directions determined it is possible to attribute N applications on the farm to groundwater nitrate concentration variation.

Comparison of the soil inorganic nitrogen results from Ballyderown with other farms in the Fermoy area showed that, although Ballyderown had high concentrations, many of the farms sampled were not significantly different to Ballyderown. Thus similar rates of nitrate leaching might be expected from these farms as was observed from Ballyderown. Soil total kjeldahl nitrogen levels in soil samples from Ballyderown were similar to other farms in the Fermoy region and this could indicate that the levels of soil organic nitrogen mineralisation observed in Ballyderown may be expected to be similar on the other farms surveyed.

A groundwater supply sampling survey around the Fermoy region also indicated that high rates of nitrate leaching are occurring from other farms in the region. Of 54 supplies sampled 28% of them had nitrate-nitrogen concentrations greater than the maximum admissible concentration (MAC) and 59% were above the Guide Limit. Comparison of nitrate concentrations to other determined chemical parameters found significant relationships between nitrate and chloride, calcium, magnesium and sodium which are not specifically indicators of point source contamination. The lack of statistically significant relationships between nitrate and indicators of point source pollution, such as coliforms, MRP and NH_4-N, tends to suggest that the dominant source of the high nitrate is diffuse pollution.

A review of nitrate exceedances of the EU MAC for nitrate indicated that between 1989 and 1997 a definite increase in the number of exceedances of MAC expressed per 1000 samples analysed was occurring over time. The effect of summer droughts on the concentration of nitrate in drinking water could also be seen as both 1990 and 1996 had significant increases in the number of exceedances of MAC and the previous summer (1989 and 1995) had high soil moisture deficits. Of the total of 331 exceedances of the MAC for nitrate in drinking water 78% of these were observed in nine reporting areas.

A number of public drinking water supplies in the country have reoccurring nitrate concentrations greater than MAC such as the Glanworth supply in North Cork. In order to reduce these concentrations to below the EU MAC limit the nitrate directive must be implemented in the supplies recharge/catchment area. From the drinking water quality reports produced by the EPA it is possible to observed that certain public drinking water supplies are providing water which breaches the EU regulations limiting the intake of nitrate in drinking water.

The findings of this thesis indicate that the nitrate concentrations beneath the study farm are due to the dairy farming practices which occur on the farm. Evidence indicates that the relationship between the dairy farming practices and groundwater nitrate concentrations is complex and that the role of soil organic matter mineralisation is extremely important in determining groundwater nitrate concentrations. In areas where the nitrate concentration in drinking water exceeds 11.3 mg N l^{-1} or 50 mg nitrate l^{-1} from an agricultural source the nitrate directive must be implemented and nitrate vulnerable zones delineated.

From the research carried out in this thesis high groundwater nitrate concentrations would be expected in areas of the country which have similar characteristics as the study farm/area. The farming practice should have a high nitrogen usage which is not only inorganic fertiliser nitrogen but other transfers of nitrogen on the farm are important such as ploughing of old grassland pasture, dirty water irrigation and soil organic matter mineralisation. The soils on which the agricultural practice is occurring is also critical in determining the risk of groundwater contamination by nitrate. Thin free draining soils are the most vulnerable and these soils typically are favoured by dairy farming due to the soils ability to withstand intensive grazing for long periods of the year. Dairy farming has also be shown to be the highest user of inorganic fertilisers and concentrated feeds.

The area around Fermoy has been shown to be vulnerable to nitrate leaching. Public water supplies in this and similar areas should be protected from nitrate contamination from agriculture through the implementation of the nitrate directive and the designation of nitrate vulnerable zones.

9.3 RECOMMENDATIONS

The importance of soil organic matter mineralisation has been highlighted in this thesis. This must be included in farm scale nutrient budget calculations. The observed peak mineralisation rate in autumn also indicates that nitrogen applications to plots during the same time period adds a further risk of groundwater nitrate contamination. Thus extended grazing would be a practice which has a high risk of nitrate contamination by the application of inorganic nitrogen fertilisers and excretal returns from grazing animals.

The delineation of nitrate vulnerable zones in Ireland is crucial to reduce the quantities of nitrate ingested by the public to safe levels, of lees than 11.3 mg NO_3-N l^{-1}, which are defined under the EU nitrate directive. Public supplies investigated in this report are likely to be good candidates for nitrate vulnerable zone delineation.

Dirty water as a source of groundwater nitrate contamination has been highlighted in this thesis. On farms which produce dirty water, management of the land application of this nutrient source should be managed to reduce the risk of groundwater contamination. Dirty water should be applied to a large land area and the rate of application should be as low as possible. One methodology developed and implemented on Ballyderown was that the automatic dirty water irrigator was moved around the grazing plots on the farm after the cows had grazed. Thus the machine was in plots for a limited period of time before being moved on to the next plot.

Nutrient management might play a role in the reduction of groundwater nitrate concentrations but only in agricultural situations where the source of the nitrate is over application of nitrogen to soils. In areas vulnerable to nitrate leaching this may not be enough and this is why the main agricultural control to reduce nitrate leaching is a reduction of the organic nitrogen loads on plots to 170 kg N^{-1} ha yr^{-1}, which it has been proposed equates to 2 livestock units. On many farms vulnerable to nitrate leaching the stocking rates are likely to be significantly higher than this.

9.4 SCOPE FOR FURTHER RESEARCH

Nitrogen budgets calculated for farms could be improved by incorporating the areas investigated during this study and with the addition of field data to quantify the amount of N stored in silage on the farm and an estimate of the amount of nitrogen excreted by animals while grazing.

In order to produce recommendations from this research on the quantity of nitrogen which could be safely applied, while not breaching groundwater nitrate limits, a controlled field based experiment would be advisable.

Ballyderown is a good candidate for further research as the groundwater flow directions are known and this would help in the design of further experiments examining nitrate occurrence in groundwater.

The importance of soil organic matter mineralisation has been highlighted in the conclusions. Only a single year was monitored on one soil type during this study. The effect of different soil organic matter mineralisation rates on groundwater nitrate concentrations would be a topic worthy of further research. Temporal variation of peak mineralisation rates and the relationship to soil moisture deficit would be another area for further work.

Further use of the natural abundance of nitrogen-15 to nitrogen-14 in nitrate ions for source identification would be warranted. Samples with high natural abundance levels had historical records indicating that animal manure is a likely source. The observed natural abundances in the present study indicate that soil organic nitrogen might be the source of the elevated nitrate concentrations is worthy of further investigation. Application of this methodology to public supplies in the country, which are known to have high nitrate concentrations, would be interesting for attributing nitrate sources.

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