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Nitrate Responses in Groundwater under Grassland Dairy Agriculture

Volume I of II
Text, Figures and Tables

Presented in fulfilment
of the requirements for the degree of
Doctor of Philosophy
December 2003

by

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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 and copied in accordance with College regulations.

Pamela Bartley

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December 2003

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Summary

A considerable body of research already exists on establishing nitrate dynamics in agricultural systems' subsoils. However, the capacity to predict rates of nitrogen arrival at the receiving environment, namely surface or groundwaters, has been elusive in an Irish context. A farm-scale hydrogeological investigation was established on an intensive dairy farm, in north Cork, characterised by a freely draining limestone till which forms the subsoil overlying a karstified-limestone bedrock aquifer. The overburden depth is 2.5m, on average, but undulates in depth from 0-4.5m, consistent with the karst terrain. Part of the farm is located within a source protection zone delineated for a public supply borehole located 1.5km to the northeast, in the direction of groundwater flow. This public supply borehole has demonstrated an upward trend in nitrate-nitrogen concentration over the last twenty years, with periodic breaches of the EU MAC, (EC, 1998) of 11.3 mg/l NO_3-N, in the last decade. Definition of groundwater-nitrate responses was the fundamental aim of the project, with objectives of measurement of the response of the groundwater system to loadings, both meteorological and agronomic, at the farm-scale. Nine specifically designed monitoring boreholes allowed bi-monthly water level- and hydrochemical-monitoring of the groundwater body. Boreholes were instrumented with piezometers to ensure that the groundwater sampled was from a specific depth, 27-30m below ground level (bgl), that was isolated from contamination from the ground surface using bentonite and cement grout seals. The water table is 25m bgl, on average, and has a maximum annual range of 15m. Boreholes were positioned to target either one of four distinct dairy management zones in operation on a typical Irish dairy farm: grazing pasture, grazing and dirty water treatment, one-cut silage and grazing, and two-cut silage and grazing. The stocking density was ~2.4 LU/ha and all plots on the farm received 290 kg N/ha/yr, on average, as inorganic nitrogen fertiliser. There was large spatial variation in the organic nitrogen loading rates in each of the four management zones mentioned. For the 2001-2002 hydrological year nitrate-nitrogen concentrations in groundwater ranged from 3 - 31 mg/l NO_3-N, depending on the location of the borehole within the 50ha farm. The observed range in the succeeding year was 4 – 23 mg/l NO_3-N. In the second hydrological year groundwater concentrations were significantly lower, on average, than those observed in the first year because 50% more effective rainfall fell in the winter of the second year, as compared to the first winter. Simply averaging all piezometer groundwater nitrate concentrations over the entire farm, the mean groundwater nitrate concentrations were 15.2mg/l NO_3-N in the first year and 11.9mg/l NO_3-N in the second year. The observed annual variation in groundwater nitrate concentrations at any particular monitoring location could be as little as 4 mg/l NO_3-N or as great as 19 mg/l NO_3-N. With the onset of the winter recharge season groundwater levels were observed to rise by approximately 8m, on average, by the end of the second month of recharge. The observed groundwater nitrate response at Curtin's farm has a clear temporal dimension. Spring and summer recharge events also affected groundwater level increases. Groundwater nitrate concentrations were observed to rise in response to significant rainfall events in spring and summer but decreased, initially, with autumn and winter recharges. However, despite the initial fall in groundwater nitrate concentrations caused by winter recharges, groundwater nitrate concentrations were observed to later increase again. The response in the groundwater to loadings was observed to be rapid. Moreover, the groundwater nitrate response was discernible in correspondence to differing agricultural practice: groundwater nitrate concentrations were highest in the areas of highest organic nitrogen loading. At the field scale there was found to be a strong relationship between grazing intensity and the following year's average groundwater nitrate concentration. A tracer study indicated dual flow mechanisms in the subsoil: preferentially and through the soil matrix. The tracing investigation also proved connectivity between some piezometers and horizontal groundwater velocity was measured to be ~8m/day. In these conditions, the N response in the groundwater in this karstified hydrogeological environment under grassland does confirm the designation of the area as having a regionally important aquifer of extreme vulnerability and monitoring results highlight the need for careful management measures. The nitrate concentrations found in the groundwater indicate that farming practices as conducted on Curtin's farm in 2001 and 2002 need to be modified in order to ensure future compliance with the Nitrate Directive (EEC, 1991a). With respect to identification of the loadings that most significantly influence groundwater nitrate concentrations – effective rainfall, or hydraulic loading, and the intensity of animal grazing are identified the main drivers on the system. The importance of the contribution of nitrogen loading by grazing animals should not be ignored. The organic nitrogen-loading rate is a crucial factor in managing nitrogen loss to groundwater. This finding validates the requirements of the Nitrate Directive (EC, 1991a) to restrict grazing intensity in vulnerable areas. The risk assessment concept was progressed by successful testing of the RAM model for the karstified hydrogeological system at Curtins farm. The agronomic NCYCLE model was validated as an adequate source term model for definition of peak porewater nitrate concentrations in the root zone.

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Units, Terminology and Abbreviations

Metric units are used throughout this thesis

AOD	Above Ordinance Datum
bgl	Below ground level
BHC.	Bore Hole at Curtins Farm
Br	Bromide
CAN	Calcium Ammonium Nitrate
d	day
DAF	Department of Agriculture & Forestry
DED	District Electoral Division
DOE	Department of the Environment (this department changed names on many occasions, hence multiple references)
DELG	Department of the Environment and Local Government
DEHLG	Department of Health, Environment and Local Government
DPC	Dairy Production Centre
EC	European Community
ECJ	European Court of Justice
EEA	European Environment Agency
EEC	European Economic Community, currently known as the EC
EPA	Environmental Protection Agency
E_t	Evapotranspiration
EU	European Union
DRC	Dairy Research Centre
EQS	Environmental Quality Standard
FIPS	Forestry Inventory Planning Service
g	gram
GFP	Good Farming Practice
GSI	Geological Society of Ireland
ha	area, hectare
IGVs	Interim Guideline Values
K	Potassium
KBr	Potassium bromide
kg	kilogram
l	litre
LU/ha	Livestock units/hectare (i.e. stocking rate)
MAC	Maximum Admissible Concentration
m^2	area, metres squared
mg	milligram
N	Nitrogen
NFGWS	National Federation of Group Water Schemes
NGQMP	EPAs' national groundwater-monitoring programme
NRC	National Research Council
NUIG	National University of Ireland Galway
NVZs	Nitrate Vulnerable Zones
P	Phosphorus
PET	potential evapotranspiration
PSD	Particle Size Distribution
REPS	Rural Environmental Protection Scheme
SMD	Soil Moisture Deficit
SPZ	Source Protection Zone
TD	Total Depth
μg	microgram
UDC	Urban district council
USDA	Unites States Department of Agriculture
WFD	Water Framework Directive
yr	year

CHAPTER ONE INTRODUCTION

1.1. Introduction

It has been estimated that of the total nitrogen used by humans throughout history up to 1992, approximately half was applied from 1982 to 1992 (Vitousek, 1994). Farmers apply nitrogen to enhance plant growth. However, current agricultural nitrogen applications frequently exceed the levels that can be removed in plant and animal products (Whitehead, 1995). When fertiliser or animal waste is spread on farm fields, natural processes in many soils transform it into a nitrogen-hydrogen-oxygen compound called nitrate (Dewar & Horton, 2000). Nitrate (NO_3) leaching is now believed by many (Spalding & Exner, 1993; Heathwaite *et al.*, 1996; Zhang, W. *et al.*, 1996) to be the most widespread contaminant affecting the water quality of groundwater and surface water systems and the levels of contamination are still increasing worldwide (Van Herpe *et al.*, 1999).

Groundwater is an important national resource, supplying Irish local authorities and private rural dwellers with drinking water and providing industry with a vital processing fluid. Groundwater also plays a key role in the hydrological cycle in terms of its baseflow contribution to rivers and in maintaining wetland habitats (EPA, 2003a). It is estimated that there are at least 200,000 wells in Ireland (Wright, 1999) and there are no regulations regarding their construction or situation. Thus, the threat posed to human health from microbial-polluted groundwater is very real and will manifest itself as a serious public health issue in the future (EPA, 2003a).

Groundwater is the usual receiving environment for nitrate leaching from near-surface soils (Meinardi *et al.*, 1995). As a receptor, groundwater is dynamic and may at times be relatively remote from the leaching source, making investigation complex and costly. However, what has been established, mostly through public water supply monitoring by local authorities, is that nitrate concentrations in Irish groundwaters and surface waters are elevated in certain counties (EPA, 2004) and numerous estuarine waterbodies have been classified as eutrophic or potentially eutrophic due to excess inputs of nitrogen (N) and/or phosphorus (P) (EPA, 2001). Increases in waters' nutrient concentrations have been marked since the intensification of agriculture, which has occurred over the past thirty years. However, changes in agricultural practice are not the only contributor to this deterioration in water quality as sewage treatment plants, or lack thereof, can be implicated in population centres.

1.1.1. Groundwater Vulnerability

Groundwater and agriculture are very connected because land that is farmed also acts as a pathway for the transportation of infiltrating rainwater to the underlying groundwater system. Groundwater vulnerability refers to the relative ease with which a contaminant applied to, or near, the land surface can migrate to an aquifer (Zekster *et al.*, 1995) under a given set of agronomic management practices and hydrogeological sensitivity conditions (NRC, 1993). Sub-soils are regarded as the single most important natural feature in influencing groundwater vulnerability to contamination (Daly & Warren, 1998). In Ireland, widespread faulting means that bedrock aquifers often occur as relatively small, discrete units with complex boundaries and many bedrock aquifers are characterised by groundwater flow in fissures (EPA, 2003a), which means that any contaminants present in groundwater undergo minimum attenuation. In some of Ireland's limestone aquifers, extensive karstification has produced conduit systems with rapid groundwater flow rates (e.g. Coxon and Drew, 1999). The Geological Survey of Ireland (GSI) has assessed groundwater vulnerability for approximately half of Ireland's area and comprehensive guidelines are available (Fitzsimons *et al.*, 2003).

1.1.2. European Groundwater Nitrate Status

The European Environment Agency, in their Environmental Signals report (EEA, 2000), highlight that when nitrate is washed out of agricultural soil, it first contaminates shallow groundwater but at a later stage, deeper groundwater in vulnerable positions will be affected, especially fractured limestone with thin soils. They also highlight that most important groundwater drinking supplies in the EU are from deep wells and are therefore not immediately affected by high nitrate concentrations. In Ireland the main flow horizons generally occur in the top 30-40 m, and hence most wells are relatively shallow (Daly, 1995). At EU scale, data from the monitoring period 1990-1996 reveal that the European Union Drinking Water Directive (EC, 1998) guideline value (5.6 mg/l NO_3-N) for drinking water is exceeded at over half groundwater sampling sites and the maximum allowable concentration (MAC) is exceeded at around a quarter of the EU sampling sites (EEA, 2000). It was further elucidated that of those groundwater bodies where the guide value and the MAC are exceeded, more than 50% of sites very frequently exceeded, and more than 25% frequently exceeded the standards.

1.1.3. Point & Diffuse Sources of Nutrients

Scientists commonly categorise water contamination according to the source of the contaminating nutrient, being a specific location (point) or an extended spatial area (diffuse). However, the split is often arbitrary and affected by the scale of the investigation and a separation of sources into point and diffuse is particularly vague in an agricultural context (Kurz, 2002). Point sources can be identified as a specific point of discharge to the environment, *e.g.* from wastewater treatment plants (House & Warrick, 1998). Farmyards, silage pits, septic tanks, underground slurry storage tanks and dairy lagoons are classified as potential point sources on a farm, given that the location of the source can be specified. Diffuse sources of nitrogen from agricultural activities include fertilisers, manure application, and leguminous crops (Almasri and Kaluarachchi, 2003). Other sources include precipitation, irrigation with nitrogen enriched waters and grazing depositions (Cox & Kahle, 1999).

Diffuse source pollution resulting from agricultural activities, and affecting surface- and groundwaters, has received considerable attention during recent years (Dillon & Kelly, 1994; Heathwaite, 1999; Puckett, *et al.*, 1999; USGS, 1999; Novotny, 2003). The widespread upgrading of sewage treatment works (potential point sources) will result in an even greater focus on pollution from farms (McGarrigle *et al.*, 2002). The work described herein primarily concerns leaching of nitrate from diffuse sources. Appropriate consideration was given to likely indications of point source contamination from the farmyard (see chapter five, section 5.5.2.2).

1.1.4. Mechanisms of Nitrate Loss

Whilst average fertiliser application rates may not appear excessive, the cumulative effect of fertiliser, slurries, dirty water irrigation and grazing animal depositions is often not given appropriate consideration as significant further additions of nitrogen (Ryan, 1990). Excess nitrate can easily be washed out of the root zone and displaced into the groundwater with percolating water (Wendland *et al.*, 1998) as the negatively charged clay ion repels the similarly negatively charged nitrate ion, which is soluble in water and highly mobile (Kolenbrander, 1981). If nitrogen loadings to soils repeatedly exceed what can be used in the system, nitrate concentrations in groundwater can build to problem levels (Steinheimer, *et al.*, 1998). It is regularly suggested that if concentrations in soil-drainage water exceed 11.3 mg/l as NO_3-N, groundwater is at risk due to the overlying land use or management activity (McLay *et al.*, 2001). Surface water is often hydraulically connected to groundwater (Winter *et al.*, 1998) therefore groundwater and surface water should be considered an integrated resource. Most of the nitrate found in natural waters is of anthropogenic origin, coming from organic and inorganic sources, the former including waste discharges and the latter comprising chiefly artificial fertilisers (Lucey *et al.*, 1999).

The movement of water, and hence nitrate, from the soil zone to groundwater is influenced both by depth and characteristics of the subsoil and aquifer. Spalding *et al.* (1989) showed that nitrate contamination in groundwater was closely correlated with coarse textured, well-drained soils. Most nitrate-leaching research concentrates on monitoring nitrate concentrations of draining water in the subsoil profile, as this is perceived to be the most technically- and financially-accessible zone for subsurface investigation. Despite the considerable body of research that already exists on establishing nitrate dynamics in agricultural systems' subsoils, the successful application of developed theories, in terms of controlling nitrate leaching, has been elusive, not because of inadequacies in mathematical process description but because of data availability and soil heterogeneity (Thompson & Rojstaczer, 2001). Bohlke (2002) in a review of the impact of agriculturally contaminated recharge on groundwater quality acknowledges that, for some reason, uncertainty and debate persist about the sources and pathways of nitrate in groundwater recharge, even though his review extensively cites worldwide research that demonstrates the connection between agricultural fields and nitrate enrichment of groundwaters.

Two distinct flow paths facilitate nitrate transport to groundwater: flow through inter-granular pore spaces is demonstrated by a smooth trend in nitrate concentration, with little annual variation, whereas fissure flow shows a marked annual variation in concentration. The actual nitrate concentration in groundwater is greatly influenced by rainfall. Areas of higher rainfall tend to have lower nitrate levels due to increased dilution (Archer & Thompson, 1993). The possibility of accelerated climate change presents a major challenge for nitrate leaching studies (Robins, 1998). More frequent and extended warm dry periods in association with higher intensity rainfalls in winter will cause changes in the rates and mechanisms of groundwater recharge and contaminant transport, mobilisation and leaching.

Chapelle (2001) outlines the three key aspects of the nitrogen cycle that affect the behaviour of nitrogen in groundwater as follows:

- The tremendous amount of energy required by the process of fixation naturally limits the rate and amounts of fixation possible;
- Nitrification requires aerobic conditions;
- Denitrification takes place only under anaerobic conditions.

Therefore, for nitrate to accumulate oxygen is required and nitrate depletion requires anoxic conditions – so the nitrogen cycle is truncated depending on the oxygen status of the groundwater body.

1.2. Reasons For Concern About Nitrate

1.2.1. Health Concerns

Traditional reasons (*e.g.* WHO, 1984) for limiting nitrate concentrations in drinking water related to the oxygen deficient condition (methemoglobinemia) in infants. However, more recent health issues concern possible links to increasing risk of non-Hodgkins-lymphona in the general population (Ward, *et al.*, 1996; Ryan, 1998a). Some (*e.g.* Addiscott, 1999; Mulqueen, 2004) debate the issue of whether nitrate is indeed a health hazard but the real focus and drive of measures to curtail nitrate loss to the environment are based on the issue of sustainability of natural resources (McGarrigle *et al.*, 2002), which was endorsed when the UN adopted Agenda 21 (UN, 1992). Sustainable development aims to ensure that the use of resources and the production of waste are minimised and damage to ecosystems is avoided (EPA, 2004).

1.2.2. Environmental Concerns

Groundwater containing high concentrations of nitrate is unfit for human consumption and, if discharging to freshwater or marine habitats, can contribute to algal blooms and eutrophication (Thorburn *et al.*, 2003) with deleterious impacts (Kolpin *et al.*, 1999). Eutrophication, resulting from over-fertilisation of water bodies (Vollenweider, 1971), causes nutrient enrichment states that can render a water body unacceptable for use or consumption, being detrimental visually, recreationally and more importantly to living organisms. Eutrophication also damages the heritage value of resources. Excessive plant growth in water bodies, resulting from eutrophication, can lead to low levels of dissolved oxygen, which can harm fish and other aquatic life (Addiscott, 1996a). The algae also block sunlight from the water, smother larger plants and produce toxins that are harmful or fatal to other aquatic species (Allaby, 1989).

Nutrient concentrations of both nitrogen and phosphorus in the water are factors in determining the risk of eutrophication occurring (Archer & Thompson, 1993). The nature of the water body, whether it is freshwater, estuarine or saline, influences whether nitrogen or phosphorus is the nutrient controlling eutrophic conditions. Phosphorus is most commonly the key nutrient most limiting and responsible for eutrophication in freshwater bodies (Massik & Costello, 1995). In estuaries, coastal ecosystems and marine waters nitrogen was found to be the element more likely than phosphorus to cause eutrophication (Howarth, 1988; Brennan *et al.*, 1998; Service *et al.*, 1998; EEA, 2000; McGarrigle *et al.*, 2002).

Agronomic applications of nitrogen carry an additional environmental hazard. Increased emissions of nitrous oxide and ammonia gasses to the atmosphere are a direct consequence of increased nitrogen fertiliser applications (Kinzig & Socolow, 1994). The nitrogen cycle is particularly complex because nitrogen readily undergoes microbial transformations and can form water-soluble and gaseous compounds, which can be lost to the environment (Watson *et al.*, 1999). Internationally, the increase in the average rate of fertiliser nitrogen applied to agricultural land since the 1950s was responsible, either directly or indirectly, for much of the increase in the amounts of nitrogen leached through the soil and lost in gaseous forms to the atmosphere (Whitehead, 1995).

Whilst the subject of this thesis is water-soluble nitrogen that is available for loss to the environment in the form of nitrate leaching, the extent of the Irish agricultural industry is highlighted due to its significant contribution to greenhouse gas emissions. Agriculture is responsible for 48% of Ireland's total emissions of acid precursors[1], in the form of ammonia emissions, and a significant portion of the burden of meeting Ireland's agreed emissions targets

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[1] When certain chemicals (known as 'acid precursors') are released into the atmosphere, they are converted into acid and fall to earth as dry deposition or acid rain (Convery & Roberts, 2000).

(DELG, 2002), under the Kyoto Protocol (UN, 1997), will fall on the agricultural sector (Convery & Roberts, 2000).

1.3. Agriculture & Ireland

1.3.1. The General Story

Farming is an important national industry that involves 270,000 people, 7 million cattle, 4 million sheep, 1.7 million pigs and 12.7 million poultry (IFA, 2003). Agriculture utilises 64% of Ireland's land area (Fingleton and Cushion, 1999) and grass-based rearing of cattle and sheep dominates the industry (EPA, 2004). Some 91% of the entire agricultural area is devoted to grass, silage and hay, and rough grazing (DAF, 2003). The Irish State is the biggest producer of cattle (Encyclopaedia Britannica, 2003) and milk (Eurostat, 2002) in the European Union, in proportion to human population (Figures 1.1 & 1.2). In 2002, Ireland produced eight times more beef and ten times more milk, than was required to meet national needs (DAF, 2003). These statistics highlight the importance, extent and likely influence, of the Irish agricultural industry. The potential environmental problems arising from this situation has significant implications for Ireland (EPA, 2004).

Overall, the production, management and disposal of agricultural waste require careful management to avoid adverse impacts on the environment. Of all industries in Ireland, agriculture produces the largest quantity of waste. It has been estimated that approximately 65 million tonnes of agricultural waste were generated in 1998 (Crawley, 2001). The majority of this is animal manure (37 million tonnes), along with 20 million tonnes of dirty water from the dairy sector. All animal manures and dairy waters contain significant amounts of nutrients, nitrogen and phosphorus, amongst other constituents (Pain & Smith, 1993). The bulk of this organic waste is landspread on agricultural land. Historically, poor control of animal manure disposal has contributed to continuing unsatisfactory water quality in some counties in Ireland (McGarrigle, *et al.*, 2002). Waste management facilities on dairy farms have been formally identified as an area that require more attention if water quality objectives are to be met and it has been estimated that 25,000 farmers must improve their waste management facilities (Regan, 2001). It is estimated that a further 55 million tonnes, in the form of faeces and urine, is deposited directly on the land by grazing cattle and sheep (EPA, 2003b).

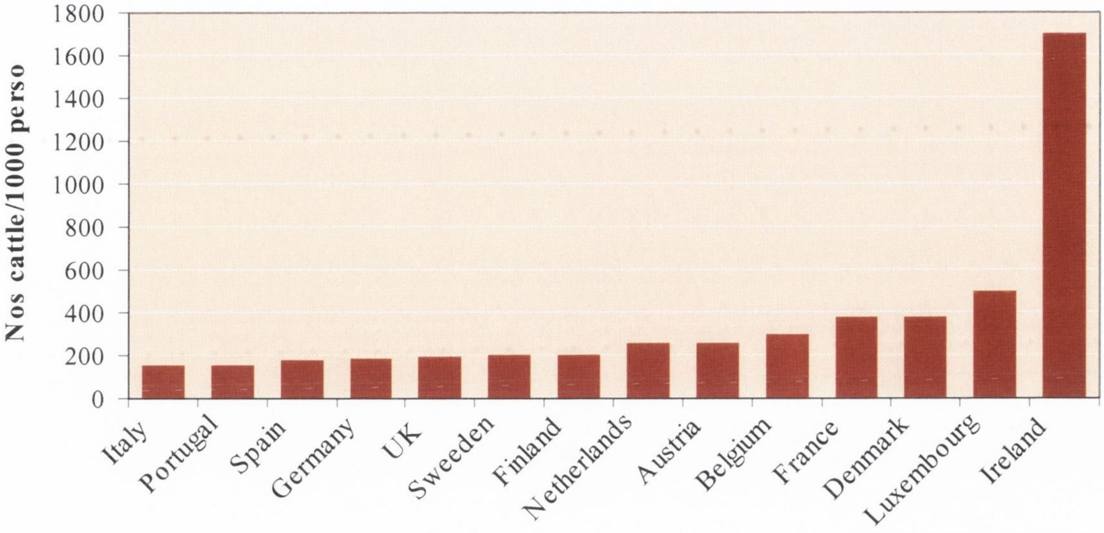

Figure 1.1 Cattle production, 2002, in 14 EU States compared with human population (reproduced from EPA, 2004, source: Encyclopaedia Britannica, 2003).

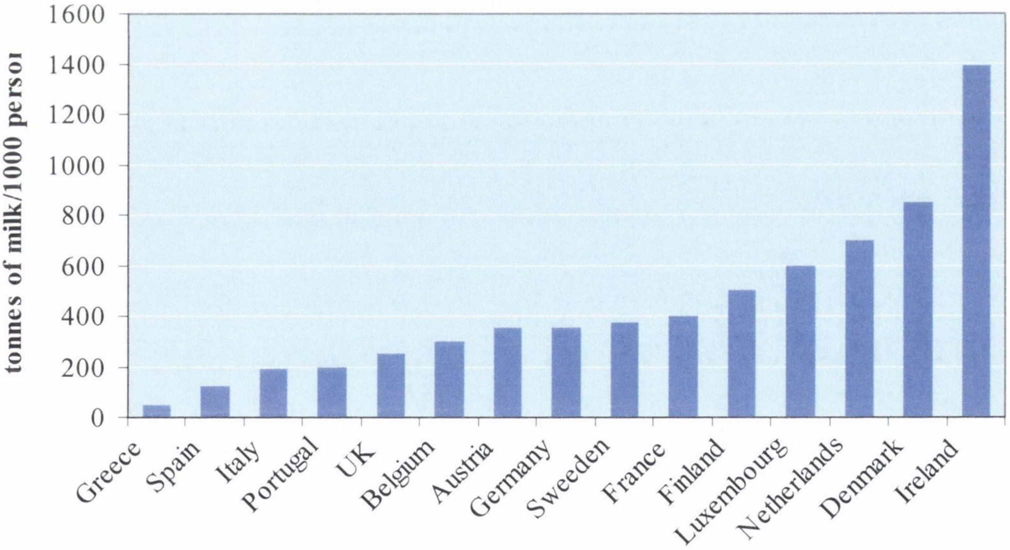

Figure 1.2 Collection of cow's milk in the EU States, 2000, compared with human population (reproduced from EPA, 2004, source: Eurostat, 2002).

1.3.2. Agriculture & Irish Water Quality

In 2002, the Irish EPA believed that there was strong evidence to suggest that agriculture was the single biggest source of pollution problems in Irish rivers and lakes (McGarrigle *et al.*, 2002). One year later, more specific information quantified that agriculture is the largest source of inputs to Irish waters of phosphorus and nitrogen, contributing an estimated 73% and 82% of total inputs, respectively (DEHLG & DAF, 2003). Some 30% of Irish river channel length is affected by pollution to some extent, primarily due to phosphorus-driven eutrophication, long-term serious eutrophication problems are reported in many of the larger lakes, and elevated nitrate levels are reported in approximately 20 percent of well sampling stations (McGarrigle *et al.*, 2002). Eutrophication of inland waters is considered to be Ireland's most serious environmental pollution problem (DEHLG & DAF, 2003).

1.3.3. Irish Groundwater Nitrate Status

> "Nitrate contamination is not considered to be widespread and is generally observed in low yielding wells, in close proximity to waste sources such as silage and slurry pits: However, it is of particular concern in some areas of Carlow, Cork, Kerry, Louth and Waterford". (EPA, 2003a)

This quotation is based on monitoring data that are available for Irish groundwater. Groundwater quality in Ireland is generally good. The quality of groundwater is assessed through different monitoring programmes for drinking water supplies, licensed activities, and the EPA national groundwater-monitoring programme (NGQMP), initiated in 1995 (EPA, 2003a). Groundwater samples are collected twice yearly, in January when groundwater levels are at their highest and in late summer when at their lowest. The NGQMP monitoring network, although carefully chosen to be fully representative of the major aquifers, consists mostly of existing large capacity public supply wells that draw water from a relatively large area and hence ensure significant dilution of any small point source contamination sources. Previous review articles regarding groundwater quality have concluded that nitrate contamination is generally not an issue (Thorn and Coxon, 1991; Lee *et al.*, 1994; Stapleton, 1996; Lucey *et al.*, 1999). However, where groundwater is intensively monitored, nitrate contamination problems have been identified, for example in Kildare and Carlow (Thorn and Coxon, 1991), Cork county (Cork County Council, 1998), north Cork (Richards, 1999) and Offaly (Page and Keyes, 1999).

The most recent EPA report on drinking water quality (McGarrigle *et al.*, 2002) indicates that breaches of the prescribed standard for nitrates in drinking water supplies (public and private) were recorded in 15 counties throughout Ireland (Carlow, Cavan, Cork, Galway, Kerry, Kildare, Kilkenny, Laois, Louth, Meath, Offaly, Tipperary, Waterford, Wexford, Wicklow). In July 2000, 14 groundwaters in counties Carlow, Cork, Kerry and Louth were identified as 'affected waters' (DEHLG & DAF, 2003) under the Nitrate Directive (EEC, 1991a).

1.4. Legislation Protecting Water Quality

1.4.1. Legislative Framework

Health and environmental issues are reflected in a number of EU Directives and associated national legislation (Regulations/Statutory Instruments) aimed at the direct or indirect control of releases to the natural environment. The Irish Government's Department of the Environment, Heritage and Local Government (DEHLG) is responsible for policy and legislation in relation to water quality issues and for the implementation of EU Directives, together with local authorities. However, the primary statutory responsibility for water management and protection in Ireland rests with local authorities (DEHLG, 2003a).

The EU Directive is the most commonly used legal act in the field of the environment and it is generally necessary for Member States to adopt the contents of the Directive in some form of domestic legislation (Kiely, 1997). Essentially a Directive binds Member States to achieve certain standards but allows certain freedom of choice in the methods employed to achieve said standards. Flanagan (1992) relates that the Minister for the Environment may grant departures from a Directive's stated limits, where the parameters concerned are to be influenced by exceptional climatological or geological conditions. However, he stresses that such departures constitute approved waivers for individual parameters, as there are no blanket waivers of Directive provisions.

Appropriate implementation of EU law is controlled at the European Court of Justice (ECJ), where case law is established on rulings delivered concerning each Member State's compliance to Directives. Management of water quality in the EU was placed on a new and more comprehensive footing by the adoption of the Water Framework Directive (EC, 2000): a framework for Community action in the field of water policy (EPA, 2004). The Groundwater Directive (EEC, 1980a) and the Water Framework Directives are the only pieces of EC legislation relating specifically to groundwater (EPA, 2003a).

The European Parliament and the Council adopted the sixth EU Environmental Action Programme in July 2002 (EP & CEU, 2002), which is intended to cover the period up to 2012. In pursuance of its objectives, this programme will promote the precautionary and 'polluter pays' principles as well as encouraging sustainable production and consumption patterns so that there is a decoupling of economic growth and the use of natural resources (EPA, 2004).

New reform of the Common Agricultural Policy, within Agenda 2000 (EC, 1999) is another EU instrument to reduce agronomic pressures on environmental objectives. The European model of agriculture foresees functions beyond the supply of food and the reformulated set of objectives for the CAP, in association with Agenda 2000, will involve integration of environmental concerns into agricultural economic policy, among other things (Walsh, 2004).

1.4.2. Regulating Nitrate Concentrations in Water

Numerous EU Directives impose standards for nitrate concentrations in water, among many other water quality parameters. The Surface Water Directive (EEC, 1975) and the Groundwater Directive (EEC, 1980a) aim to protect raw water quality in the European Union. A new European Drinking Water Directive (EC, 1998), replacing the Drinking Water Quality Directive (EEC, 1980b), protects all water intended for consumption. The requirement of each of the three aforementioned Directives is that for nitrate, in particular, the parametric value must not exceed 50 mg/l nitrate (equivalent to 11.3mg/l as NO_3-N)[2]. A guide level (GL) of 25 mg/l NO_3 (equivalent to

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[2] The Nitrate Directive refers to concentrations in the form of nitrate (NO_3) and the limit is 50mg/l. More commonly, in the Irish scientific community concentrations are reported in the nitrate-nitrogen form (NO_3 -N) and when reported in this format the limit is equivalent to 11.3mg/l NO_3-N. In this work it is the latter format that is referred to when discussing observed groundwater nitrate concentrations. In addition, the parametric limit is more commonly referred to as Maximum Admissible Concentration (MAC) and so MAC terminology is adopted throughout this work.

5.6 mg/l as NO_3-N) is also specified in the EU Drinking Water Directive (EC, 1998), and is recommended as an indication of contamination (McGarrigle *et al.*, 2002). The Drinking Water Directive also sets standards for another 65 parameters. With respect to water quality, Flanagan (1992) provides more comprehensive information on a number of Directives, including those mentioned above and the Directives concerning the Quality of Freshwater Supporting Fish (EEC, 1978) and Dangerous Substances (EEC, 1976).

In order to provide Irish legal force to EU Directives, the Minister for the Environment of this State must enact Regulations (Flanagan, 1992). The Water Pollution Act (DELG, 1977) and Amendment Act (DELG, 1990), and the regulations made there under constitute the main national legislation in this regard. The introduction of IPC licensing, under the Environmental Protection Agency Act (DELG, 1992), intensified controls on the effect of industrial activities on water quality. Statutory Instruments provide Regulations, such as the Phosphorus Regulations (DELG, 1998a) and the Drinking Water Regulations (DELG, 2000), to enact Directives. The only specific standards for groundwater in Irish Legislation are the EQS set for List 1 substances in the Water Pollution Regulations, 1999 (DELG, 1999).

In relation to agriculture specifically, the Water Pollution Acts enable local authorities to (DEHLG, 2003a):

(i) Make bye-laws regulating certain agricultural activities where the local authority considers this to be necessary so as to prevent or eliminate pollution of waters, and

(ii) Issue notices requiring farmers to prepare nutrient management plans with the aim of ensuring that nutrients applied to land from chemical fertilisers and organic farm wastes, *e.g.* slurries, take account of nutrients already available in the soil and are consistent with recommended application rates, crop requirement and the need to avoid water pollution.

In certain areas, local authorities have implemented bye-laws (e.g. Cork County Council, 1999) to regulate farming practices in designated catchment areas but these by-laws differ from region to region according to the intrinsic vulnerability of the region in question, which is decided by the local authority. Humphreys *et al.* (2003) provide a comprehensive overview of current measures initiated by Irish local authorities in relation to agricultural activities in an attempt to control any potentially deleterious impact on the environment and in respect of obligations under Agenda 2000 (EC, 1999) agreements.

The Directives, Acts and Regulations, discussed above, concern quality standards set for waters. However, the EU created another type of Directive to deal with controlling the sources of contamination based on the quality of a receiving environment. The Nitrate Directive (EEC, 1991a) concerns pollution by nitrates from agricultural sources and the Urban Wastewater Directive (EEC, 1991b) concerns discharges from urban wastewater treatment plants. Both of these Directives concern nutrient impact on groundwaters and surface waters with regard to controlling eutrophication. Updated statutory Regulations were applied to discharges from local authority sewage treatment plants in 1994 and again under the Urban Waste Water Treatment Regulations (DELG, 2001). It is the Nitrate Directive (EEC, 1991a) that relates to the study in hand. The following quotation from the Irish EPA, although referring generally to environmental policy, is relevant to the current situation with the Nitrate Directive:

> "The efficacy of these provisions is wholly dependent on the extent to which they are enforced; as in the many other areas of regulation, this is the aspect that is often in default, whether through lack of resources on the part of the enforcement agencies, or in some cases, through less than wholehearted political support." (EPA, 2004)

1.4.2.1. The Nitrate Directive

It is 13 years since the Nitrate Directive (EEC, 1991a), concerning the protection of waters against pollution caused by nitrates from agriculture, was adopted at European Union level. The objectives of the Directive are to reduce water pollution caused or induced by nitrates from agricultural sources and prevent further incidences. Where water bodies have been identified as having breached the 50mg/l NO_3 limit (equivalent to 11.3 mg/l as NO_3-N), or are likely to do so in the absence of pollution controls, and in situations where there is a risk of nitrogen contributing to eutrophication, the Directive requires that legally binding measures be taken in respect of farming practices so as to reduce nitrate loss to waters (DELG & DAF, 1996).

The Directive defines waters that are polluted or are liable to pollution as follows:

(i) Surface freshwater, that is intended for drinking water, or groundwater which contain or could contain, if preventative action is not taken, nitrate concentrations greater than 50mg/l NO_3;

(ii) Natural fresh water lakes or other water bodies, estuaries, coastal waters and marine waters, which are found to be already eutrophic or may become so if preventative action is not taken.

The main measures of the directive are as follows.

(i) Restrictions on the timing, rate and other conditions for the application or fertilisers;

(ii) Closed periods for slurry spreading and minimum storage capacities for slurry;

(iii) Limiting the amount of livestock manure that can be applied to land on each farm to 170 kg N/ha/yr. This organic nitrogen limit must include that deposited by animals while grazing (DEHLG & DAF, 2003).

Interestingly, the Nitrate Directive (EEC, 1991a) is now seen as a legislative tool for action in relation to eutrophic waters, even where eutrophic conditions are due primarily to phosphorus, rather than nitrates, from agriculture: the judgement of the European Court of Justice (Case C-258/00 Commission v France), in June 2002, was one of the decisions informing the Irish strategy for implementation of the Nitrate Directive (DEHLG & DAF, 2003).

1.4.2.2. Implementation of the Nitrate Directive in Ireland

The Nitrate Directive requires that each Member State must either apply national general binding rules for all farmers or designate specific areas as Nitrate Vulnerable Zones (NVZ's), where nitrogen application restrictions would apply to specifically designated areas only. Ireland was slow to act in either regard. However, Regulations (DEHLG, 2003b) made by the Minister for the Environment, Heritage and Local Government formally identified the whole territory of Ireland as the area to which an action programme under the Nitrate Directive will be applied. However, in

March 2004, the ECJ judged (Case C-396/01-2004) that Ireland is non-compliant with the Directive by virtue of not having yet established an action programme (DEHLG & DAF, 2004).

Ireland's 'Draft Action Programme under the Nitrate Directive' (DEHLG & DAF, 2003), released for consultation in December 2003, details the background to the implementation of the Directive in Ireland, the rationale for the whole country designation and the current National Action Programme. Following submissions from interested parties and ECJ rulings, a revised consultation document concerning Ireland's 'Action Programme under the Nitrate Directive' (DEHLG & DAF, 2004) was issued. This later document provides more detail on how and when the actual Action Programme is to be adopted (on a phased basis commencing on 1st January 2005), the proposed schedule of implementation, and details regarding the planned derogation application. Where a Member State proposes to fix an organic nitrogen limit higher than 170kg/ha, they must seek approval for a higher amount, which is generally known as 'a derogation' (DEHLG & DAF, 2004).

It is estimated that some 90% (120,000) of farms in Ireland operate within the organic nitrogen limit of 170 kg N/ha/yr (DEHLG & DAF, 2003). Regardless of this, Irish farming lobbying groups (e.g. Teagasc, IFA) have succeeded in generating political support for a derogation application. The Irish government gave a commitment in the national partnership agreement *Sustaining Progress* to seek to secure EC approval for organic nitrogen limits of up to 250 kg/ha/yr (DEHLG & DAF, 2004). The Directive, when enacted in 1991, also made provision for a transitional limit up to 210 kg N/ha/yr limit during their first four-year action programme. Some 130,000 Irish farms (over 95%) operate within this limit (DEHLG & DAF, 2003). However, Judgements of the ECJ have clarified that this discretion related only to a four-year period commencing at the latest on 19th December 1995 and this discretion is no longer available to Member States (DEHLG & DAF, 2004).

Measures already taken towards implementation of the Nitrate Directive include the development of the 'Code of Good Agricultural Practice to protect Waters from Pollution by Nitrates' (DELG & DAF, 1996) and the 'Code of Good Farming Practice' (GFP) booklet (DAF, 2001). Both publications have been issued to ensure farmers are aware of and comply with their responsibilities under law. Under the Agenda 2000 agreement (EC, 1999), all farmers receiving payments under various direct payment schemes must practice farming in accordance with certain environmental requirements. Protection of the direct payments (€1.6 billion) Ireland receives from the EU annually is vital to the agricultural community (Walsh, 2004). Statutory support for adherence to GFP standards will be provided (Duggan, 2002) to ensure compliance in all regions of the Irish Republic because the DEHLG must now ensure that the role of agriculture in fresh- and estuarine waters' eutrophication is curtailed. Humphreys *et al.* (2003) refer to the rules of Good Farming Practice (DAF, 2001) in Ireland but acknowledge that the Rural Environmental Protection Scheme (DAF, 1994), which is voluntary, involves more stringent requirements.

New Irish Regulations, expected in October 2004 (DEHLG & DAF, 2004), towards further implementation of the Nitrate Directive (EEC, 1991a) will give further effect to certain requirements arising under other Directives including the Dangerous Substances Directive (EEC, 1976), the Framework Waste Directive (EEC, 1991c) and the Water Framework Directive (EC, 2000).

1.4.2.3. Appropriate Nitrate Reference Concentration

Previous discussion (section 1.4.2) has referred to EU legislation that regulates nitrate concentrations in water by defining a MAC concentration of 50 mg/l NO_3 (11.3 mg/l NO_3-N), in the Drinking Water Directive (EC, 1998), and a similar threshold in the Nitrate Directive (EEC, 1991a). The issue of eutrophication of water bodies has also been discussed (section 1.2.2). Water bodies that fall under the remit of the Nitrate Directive (EEC, 1991a), outlined in section 1.4.2.1 above, include estuaries. A nitrogen criterion for eutrophication in Irish estuaries and coastal waters is defined as 2.6 mg/l N for tidal freshwaters (EPA, 2001). The issue of which limit (11.6 mg/l NO_3-N or 2.6 mg/l N) should be referenced when assessing water quality monitoring results, with respect to EU legislation or those levels known to cause eutrophic conditions, is an issue just emerging in Ireland. One approach under discussion (Duggan, *pers comm. 2003;* Daly, *pers comm. 2004*) is to adopt the EU guide level [GL] of 25 mg/l NO_3 (5.6 mg/l NO_3-N). The rationale for adopting the GL value is that there is then potential for dilution of groundwater by Irish rivers, prior to discharge to estuaries. This issue should be borne in mind when considering the groundwater nitrate concentrations reported in this thesis.

1.4.3. The Water Framework Directive

The Water Framework Directive (EC, 2000) aims to establish management of resources on a hydrological catchment basis with ecology as the key criterion. Thus the quality and quantity of surface and groundwaters are defined in terms of impact on established ecologies. The Water Framework Directive (WFD) is an integrated catchment approach that recognises all water bodies to be habitats/ecological systems that are supported by the continuous integration of groundwater and surface water resources. It establishes a strategic framework for managing the water environment and sets out a common approach to protecting and setting environmental objectives for all groundwaters and surface waters within the European Community. It is a far more comprehensive piece of legislation that will have far greater implications than the Nitrate Directive. Indeed, the quality goals of the Directive are likely to prove extremely difficult if not impossible in many situations (EPA, 2004). This Directive was adopted in Ireland under Regulations made in December 2003 (DEHLG, 2003c).

In Ireland, the EPA has responded to initial requirements of the WFD, with respect to characterisation of water bodies, by publishing the preliminary 'Towards Setting Guideline Values for the Protection of Groundwater in Ireland' (EPA, 2003a) and that document outlines the most pertinent issues regarding groundwater and the WFD:

(i) Specifically for groundwater, the Directive aims to protect, enhance and restore all bodies of groundwater, as well as maintaining and/or attainment of 'good chemical status'.

(ii) In the absence of criteria adopted at Community level, Member States are required to establish appropriate criteria at the latest five years after the date of entry into force of the Directive (McGarrigle, *et al.* 2002).

(iii) Article 17 of the WFD requires that the Parliament and Council adopt measures to prevent and control groundwater pollution. These measures will be in the form of a new groundwater directive. To assist in this the EC established an Expert Advisory Forum on Groundwater.

The DEHLG is promoting and funding the establishment and operation, by local authorities, of river basin monitoring and management systems to support implementation of the Water

Framework Directive. All significant impacts from all sources on all inland surface waters, groundwaters, estuaries and coastal waters will be identified. Quality objectives will be set and management measures will be put in place to achieve those objectives (DEHLG & DAF, 2004). A total of seven river basin districts (RBD's) have been identified (four within the State and three shared with Northern Ireland) and work has commenced on the implementation of the Directive in two, the South Eastern and the Shannon Eastern, and it is expected that the remaining RBD's will be implemented in 2004 (EPA, 2004).

1.5. Study Overview

1.5.1. Evolution of this work

The work presented in this thesis commenced in 1998 at the Teagasc Environmental Research Centre, Johnstown Castle, under the 'Walsh Fellow' scholarship scheme. The Johnstown Castle farm work had dual aims: to design and test groundwater piezometer instrumentation for investigation of nitrate leaching to groundwater from dairy farming and development of an appropriate model for nitrate leaching to groundwater. Grassland based dairy farming was the farming practice under investigation. Originally it was conceived that the study would be entirely based at Johnstown Castle but results dictated otherwise. After two-years of monitoring, the piezometers worked well but groundwater nitrate concentrations were observed to be consistently low with little seasonal trends. With background leaching rates observed at Johnstown castle it was not possible to build a model to describe nitrate leaching. Therefore, a different study site was required.

Early in 2000 the Irish Environmental Protection Agency, funded under the National Development Plan, called for research applications under many environmental headings, including 'Eutrophication from Agricultural Sources'. A large consortium of scientists and a number of international experts, co-ordinated by Teagasc, were awarded the contract. Overall, the 'Eutrophication from Agricultural Sources' project has been funded to the amount of €3.4 million and is one of the largest environmental research programmes ever funded in the history of the State (McGarrigle *et al.*, 2002).

Within the 'Eutrophication from Agricultural Sources' project, separate research groups investigated nitrogen and phosphorus loss. With regard to nitrogen, an integrated research programme carried out three concurrent field investigations on the same dairy farm in an intrinsically vulnerable area. This project was envisaged as part of a first-step towards systems-scale research appropriate to the Nitrate Directive [Project reference: M1-LS-2.3]. The three field investigations focussed on different subsurface zones on the same 50ha farm: the farm is a fully productive dairy farm, which is called Curtin's farm.

Work commenced in November 2000 for three years. Firstly, a farm-scale soil-drainage-water study, led by Dr. Michael Ryan of Teagasc, Johnstown Castle, investigated nitrate leaching concentrations at 1m-depth in the subsoil, at ninety-six locations on Curtin's farm using ceramic cups under suction. Those ceramic cups were installed in operational farm plots to collect soil water in such a way as to not interfere with normal grazing practices. This subsoil instrumentation, in one plot, was used for the subsoil-monitoring component of the tracer experiment conducted by myself and described herein (see sections 5.4 & 6.5).

A team from National University of Ireland, Galway (NUIG), led by Dr. Michael Rodgers, carried out the second facet of the integrated project. The NUIG team investigated nitrate leaching again by installation of ceramic cups and extracting soil-water samples under suction, through successive depths in the entire soil profile, in response to different sources (*e.g.* fertiliser, slurry and dirty water) and rates of nitrogen applications. The NUIG component of the study instrumented experimental plots, the plot-scale, rather than investigate the entire farm-scale: isolation of nitrogen source applications would not be possible at a working farm level. Animals did not graze the NUIG plots.

Paul Johnston, University of Dublin, Trinity College (TCD), led the third facet of the research programme: to establish a farm-scale hydrogeological investigation concerning groundwater nitrate concentrations and responses to loadings. I worked on Curtin's farm for three years under his supervision. My responsibilities encompassed the field implementation of the hydrogeological investigation, which involved organising and supervising the installation of groundwater piezometers by private well drilling contractors, groundwater monitoring, sample collection, some laboratory analysis, analysis of monitoring results, data preparation and reporting.

The integrated project was co-ordinated by Dr. Owen Carton (Teagasc, Johnstown Castle), overseen by a representative of the EPA and reviewed by an international panel with expertise in agronomic research and nitrogen efficiency. In 2004 the integrated results from the three simultaneous projects will be reported and published by the EPA. My work on the groundwater of Curtin's farm represents the major field and analysis effort of this doctorate study.

1.5.2. Introduction to the Principal Study Area: Curtin's Farm

Teagasc's Moorepark Dairy Research Centre manages Curtin's farm. This 50 ha intensive dairy farm in north Cork carries a stocking density of ~2.4 LU/ha on land characterised by freely draining sandstone till which forms the subsoil overlying a karstified-limestone bedrock aquifer.

Carbonate karst terrains cover nearly 20% of the Earth's land surface (White, 1988), and the waters associated with karst aquifers supply nearly a quarter of the world's population with water (Ford & Williams, 1989). Karst aquifers consist of a carbonate rock matrix that is usually fractured with a network of connected conduits, which have openings ranging from a few centimetres up to tens of metres (Gale, 1984). Low storage and rapid flow are features of conduit flow and in karst systems the rock matrix, a relatively impermeable matrix of limestone or dolomite plays little role in groundwater flow (Loop & White, 2001). Karst aquifers are notoriously effective at transmitting rather than treating pollutants: This arises from the unfortunate fact that the relatively large capacity for self treatment found in many groundwater systems is comparatively poorly developed in karst (Ford & Williams, 1989).

The farm chosen is situated in a potential area for nitrate loss to the environment because of the practice of intensive agriculture in an intrinsically vulnerable area. More specific details for this study area are presented in chapter four. A substantial area of Curtin's farm is located within a source protection zone delineated for a public supply borehole located 1.5km to the northeast, in the direction of groundwater flow (see chapter four for further details). This public supply borehole has demonstrated an upward trend in nitrate-nitrogen concentration over the last twenty years, with periodic breaches in the last decade (Cork county council, 1998, 2003), of the 11.3 mg/l NO_3-N MAC specified in the Drinking Water Directive (EC, 1998).

It is important that the flow system is defined in order to determine the path of the solutes (Follet *et al.*, 1991). Evaluation of the groundwater flow system includes identification of recharge areas and mechanisms of solute flow, aquifer delineation, identification of confining beds and possible discharge areas. The location of the recharge area is the primary point of entry for contaminants from the land's surface to the aquifer. The complexities in the distribution of nitrate even in relatively simple hydrogeologic settings can confound interpretations of how groundwater relates to agricultural practices at the land surface (Follet & Hatfield, 2001). In this regard, the farm chosen for in-depth study, Curtin's farm, is ideal because it sits on a plateau topographically elevated with respect to the surrounding farmland in the area.

1.5.3. Aims, Objectives & Originality of this work

In the context of determining relationships between surface nitrogen loadings and nitrate receipt at a groundwater receptor, scale is a very important factor. Traditionally, Irish nitrate leaching investigations have isolated processes for study usually in one-dimension, in the vertical direction, at lysimeter or plot-scale (e.g. Ryan & Fanning, 1996; Mulqueen *et al.*, 1999). However, recent international research focus has attempted to more comprehensively describe combined catchment responses at scales more appropriate to environmental policy than production research (e.g. Birkenshaw & Ewan, 2000a & b; Lord & Anthony, 2000; van Herpe *et al.*, 2002). The work described herein concerns nitrogen loadings to groundwater at the farm scale, which is the scale of most relevance to the implementation of the Nitrate's Directive (EEC, 1991a) in Ireland.

Other work (Richards, 1999) has investigated the amount of nitrate leaching, as a result of dairy farming activity, through the unsaturated zone and observed the nitrate concentrations in the receiving groundwater body in a similarly vulnerable area in the same geographical region as the study described herein. However, my work is novel in that the primary aim of this study was as follows:

- To define groundwater nitrate responses to surface loadings on the farm.

The primary and secondary project objectives are discussed in more detail below.

Objective 1: Define groundwater nitrate responses to surface loadings on the farm.

Internationally, little monitoring data exists to interpret temporal trends of nitrate in groundwater (Follet & Hatfield, 2001). Assessment of the response of groundwater to nitrogen applications should allow identification of specific dairy farming practices that require control, particularly under the remit of meeting this country's obligations under the Nitrate Directive (EEC, 1991a). The investigative approach involved quantification of all loadings, both meteorological and agronomic, and monitoring of the response of the groundwater system at numerous locations on the farm. Achievement of this objective was realised by the following objectives:

(i) Determine effective hydraulic loadings: meteorological modelling was applied to recorded daily weather data for determination of effective hydraulic loadings.

(ii) Quantify nitrogen loadings: all farm activities involving applications of nitrogen were recorded, at farm plot detail, and analysed. Nitrogen applications were fertiliser, slurry and dirty water and also the load contributed by grazing animal depositions.

(iii) Characterise the response of the groundwater body to surface loadings: Curtin's farm was instrumented with groundwater piezometers, which were monitored for hydrological and hydrochemical response. In addition to nitrate, other nitrogen forms (nitrite and ammonium), phosphorus concentrations and other hydrochemical parameters were investigated, with respect to determining, what is sometimes referred to as the 'agricultural signal' (Sapek, 2000; Bohlke, 2002) in the groundwater.

(iv) Investigate the mechanism of nitrate movement from the ground surface to groundwater: understanding the cause-effect link between source and receptor is fundamental to the evaluation of the ultimate impact of agricultural practice on groundwater quality, nitrate concentrations in particular. A surface applied tracer was applied at one location and was monitored as it leached through the soil to groundwater, and as it moved laterally in the groundwater to other piezometers.

The secondary aims of this work were essentially singular tasks; they were as follows:

Objective 2: Apply GSI groundwater vulnerability assessment methodology.

The Geological Survey of Ireland (GSI), under the wider remit of groundwater protection, has developed comprehensive guidelines for assessment of groundwater vulnerability (Fitzsimons *et al.*, 2003). This methodology forms a basis for the preparation of Groundwater Protection Schemes and adopts a risk-based matrix approach to vulnerability mapping dependent on subsoil depth and permeability (DELG *et al.*, 1999). The GSI vulnerability assessment methodology was applied and tested in light of measurement of nitrate response on two Teagasc dairy farms: Curtin's farm and Johnstown Castle.

Objective 3: Review methods for modelling nitrate leaching from dairy farming to groundwater, with a view to selection of a modelling strategy appropriate for Irish application.

There is much available information regarding modelling nitrate leaching from agriculture. Much has been written on this subject but it has been presented by dispersed sources that tended to focus on specific models, topics or scales of model application. No single resource was found to provide a cohesive view on modelling nitrate leaching from agriculture and so achievement of this objective adds to the novelty of this work. The modelling review provides information regarding modelling nitrate leaching to groundwater, through different subsurface zones, in addition to specific descriptions of existing models. For each model discussed the input parameters, model structure, governing equations and expected model outputs have been tabulated. The information presented collates published views and experiences of modelling nitrate leaching from agriculture. This review served to inform an appropriate modelling strategy for modelling nitrate leaching to groundwater at Curtin's farm. The strategy was chosen with due consideration that the data demands were commensurate with nationally available data and resources.

1.5.4. The Structure of this Thesis

This thesis comprises seven chapters. Chapter one introduces this work, details the significance of agricultural impact on water quality, explains the environmental, health and legislative reasons for concern about nitrate and provides an overview of my research and the structure of this thesis.

The second chapter discusses nitrate leaching from grassland, the various processes operating within the nitrogen cycle, discusses available literature and outlines the key concepts informing the focus of the investigation.

The third chapter contains a review of modelling nitrate leaching from agriculture to groundwater. The chapter considers concepts of importance to effective modelling of nitrate leaching through each subsurface zone, discusses the results of field-applications of many models and modelling approaches. The extent of the literature review is reflected by both the extensive nature of the subject in association with a temporary ban on all fieldwork at the beginning of the research contract. The project to investigate Curtin's farm commenced in November 2000 and shortly afterwards the national foot and mouth scare resulted in Teagasc restricting field work activity, as a precautionary measure, on all its farms for a number of months. It was during this period that the third objective received concentrated attention and most of the review of modelling strategies was completed. The literature review and learned concepts revealed that there are so many existing, tested models that development of a new model was not necessary and a combination of 'off the shelf' models was adopted for application at Curtin's farm. At the end of chapter three an appropriate modelling strategy for Irish conditions is proposed.

Chapter four provides details on the study area locations: Curtin's farm and the Johnstown Castle farms, and hydrogeological conditions in each area. My work on Curtin's farm represents the major field and analysis effort of the thesis, whereas the work at the Johnstown Castle site could have been considered a pilot study for instrumentation methods employed at Curtin's farm. However, the relevance of the Johnstown Castle work, with respect to vulnerability concepts, and to the results of the investigation at Curtin's Farm was later realised and it is for this reason that study area details for the Johnstown Castle site are provided in chapter four.

Chapter five provides all relevant theory and detail of the research strategies employed during research at Curtin's farm: including site instrumentation and monitoring; subsurface characterisation; investigation of the mechanisms of nitrate leaching. This chapter also outlines the methods used to calculate all hydraulic and agronomic nitrogen loadings from all nitrogen sources, and quantifies all loadings for Curtin's farm.

Chapter six provides results of all field investigations and monitoring at Curtin's farm. Groundwater quality is discussed, groundwater response to hydrological and agronomic loadings is analysed and the results of the tracer experiment are presented and discussed in the context of other field monitoring results. This chapter also presents application of the GSI vulnerability assessment methodologies to the two contrasting hydrogeological environments (Johnstown Castle and Curtin's farm) and results of testing the selected modelling strategy, with respect to observed groundwater nitrate concentrations at Curtin's farm.

The final chapter, seven, draws conclusions based on the research findings and provides recommendations of relevance to dairy farming practice in vulnerable areas in the context of providing protection to groundwater resources.

The appendices to this work are lengthy as it is important to provide all results. Firstly, the modelling review resulted in lengthy model descriptions that were placed in Appendix A. During the course of reviewing modelling literature, much overlap was found with catchment scale and surface water modelling approaches. This information was also placed in Appendix A because, although not strictly relevant to the subject at hand, it will be relevant to integrated catchment management in the future. Most work discussed in the text of chapters five and six is based on calculations or monitoring results that have been placed in Appendices. Determination of hydrological loadings, by meteorological modelling, and aggregation of all nitrogen loadings generated much data. Characterisation of the subsurface yielded substantial amounts of data and analyses results, and this level of detail is potentially useful for future attempts to extrapolate the findings of this work to other Irish regions and future modelling strategies, perhaps in the field of simulating temporal trends in groundwater nitrate concentrations, or efforts towards field implementation of the Water Framework Directive. Field monitoring of groundwater responses, the tracing experiment and characterisation of general groundwater quality also generated lengthy records. All data that was placed in Appendices are referenced appropriately within the text of this thesis.

CHAPTER TWO NITRATE LEACHING FROM GRASSLAND

2.1. Introduction

Originally, nitrate leaching was considered to be a problem associated with arable land only and losses from grassland were considered low (Hood, 1976; Royal Society, 1983). However, the original grassland experiments (e.g. Morrison *et al.*, 1980) were carried out in ungrazed swards. Ryden *et al.* (1984) found that an intensively fertilised grazed sward may have nitrate leachate losses up to six times higher than losses from comparable cut swards (those used for silage production) and also found that nitrate leachate losses from grazed grassland can exceed those from arable land with similar fertiliser rates. Further research (Garwood & Ryden, 1986; Haigh & White, 1986; Scholefield *et al.*, 1988) confirmed Ryden *et al.*'s (1984) work.

At first it was believed that leached nitrate was fertiliser residue (Commoner *et al.*, 1971). However, experiments using labelled fertiliser found that a very small percentage of nitrogen applied as fertiliser is leached (Addiscott & Powlson, 1989). Fifty to seventy percent of nitrogen applied as inorganic fertiliser is recovered in the grass (Whitehead, 1995). Ungrazed grassland, even with high fertiliser inputs, is unlikely to result in substantial nitrate leaching if fertiliser applications are made to match closely the needs of the growing grass crop (Jarvis & Dampney, 1993). Addiscott (1996a) stresses that grass is a safe, non-leaky crop provided you keep cows off it. However, the poor utilisation of dietary nitrogen by ruminants results in a large proportion (approximately two-thirds) of the nitrogen taken up by the animal being returned to the soil as dung and urine (Scholefield *et al.*, 1988), which increases the pool of potentially leachable nitrogen.

2.2. Literature

When grassland is mown or lightly grazed leachate losses are normally less than 20kg N/ha/year, even if fertiliser is applied, but intensive grazing, on regularly fertilised land, can result in more than 100 kg N/ha/year leached as nitrate, much of it derived from the nitrogen in urine (Whitehead, 1995). Animal populations in catchments have a dominant influence on nitrate leaching (Hack-ten Broeke, 2000). Simply, the current understanding of nitrate leaching is that the more fertiliser nitrogen applied results in increases in the amount of organic matter in the system (where fertiliser applications support livestock). Then, the proportion of the organic matter that is not taken up by the plant, and harvested, remains as organic nitrogen in the soil. This organic nitrogen is then available to soil microbes to be mineralised to form leachable inorganic nitrogen. Most nitrogen containing compounds can be oxidised to nitrate in the soil. Ammonia, for instance, does not readily leach due to its positive charge, however, it easily leaches once it is converted to nitrate within days or weeks of being added to the soil (MAFF, 1993).

Nutrient loss to ground or surface waters can occur via the following pathways (Smith & Chambers, 1998):

-rapid loss to surface waters via surface runoff (more likely with phosphorus than nitrogen) or under-drainage systems;

-soil nutrient enrichment (especially after grazing) and subsequent loss via erosion or more gradual loss via leaching.

Additionally, it is well documented internationally (Kladivko *et al.*, 1991; Edwards *et al.*, 1993; Shipitalo *et al.*, 1994; Golabi *et al.*, 1995; Delin and Landon, 2002) that preferential flow can result in rapid transport of agricultural chemicals to groundwater with minimal degradation. The issue of preferential flow will be discussed more fully in the results section, chapter six.

Leaching tends to be a phenomenon associated with freer draining soils whereas clay soils, in an agricultural context, will be artificially drained and hence nutrient loss will occur through drainage flow to surface water bodies. Addiscott (1996a) reports a threefold increase in nitrate loss from the soil subsequent to the installation of an efficient drainage system.

Jordan & Smith (1985) carried out intensive monitoring of nitrate losses from intensive grassland through drains and explored the effects of different climatic trends on antecedent nitrate losses. They conclude that the greatest losses of nitrate occurred after heavy rainfall following prolonged dry periods and that leaching losses increase with autumn/winter rainfall, but optimum crop-water supplies in the summer can reduce overall leaching losses during the year. Nitrate accumulates in the topsoil during dry periods as a result of the input of dung and urine, and mineralisation of soil organic matter and plant material (Rodda, 1993). In the wetter winter months nitrate is flushed from the soil by excess rainfall. The literature suggests that peak nitrate concentration, in leachate, is normally associated with the first 100mm of drainage, whether drainage is via tile drains, by runoff or by percolation through coarse textured soils (Scholefield *et al.*, 1991; Lord & Sheppard, 1993). Warrick *et al.* (1971) are reported by Singh & Sekhon (1978/1979) to have found that the maximum nitrate concentration occurs at a depth above which the total water in the profile is just equal to cumulative infiltration.

Nitrogen uptake in plants depends on crop and weather conditions. Generally, uptake by a given crop will be lower in dryer years due to restricted growth – leaving more nitrogen available to leaching during the autumn. However, the final concentration of nitrate leaving the root zone also depends on the amount of water percolating. Although 'by-pass' flow may influence the short-term leaching of nitrate, the amount leached during a winter season as a whole is usually determined by two factors: (i) the total quantity of water passing through the soil profile, and (ii) the concentration of nitrate in the soil at the onset of leaching (Whitehead, 1995).

A careful and conservative nitrogen management strategy on a farm will be reflected in a consistently low nitrogen balance deficiency, which will have an overriding impact on potential nitrate leached (Follet *et al.*, 1991). The balance between inputs (fertilisers and feedstuffs) and outputs (grass and products) dictates what is available for loss to the environment. This means that the nitrate concentration at a point of groundwater abstraction depends on the overall balance of agriculture in the catchment (Archer & Thompson, 1993) or the efficiency of agricultural systems in a catchment. The main cause of the increased nitrogen losses from agriculture and increased nitrate concentrations in groundwater is the fact that the inputs of fertilisers and animal manures to agricultural land have increased much more than the output of nitrogen in harvested products (Oenema *et al.*, 1998).

Reporting of average concentrations over a winter period obscures the possibly large variation in nitrate leached over time. The complex pattern of nitrate leaching throughout the leaching season reflects the many factors that interact within the processes of the nitrogen cycle: the 'factory' that creates the nitrate that is available for leaching. Variation in the amount of available nitrate that leaches with time is caused by factors such as pore-size distribution, the partitioning of nitrate between micropores and macropores, and the intensity and duration of rainfall (Whitehead, 1995).

Nitrogen is a production governing resource that ranks at or among the top of the agricultural crop production inputs, in economic and thermodynamic terms, but its propensity to leak beyond the rooting zone, under certain conditions, requires careful consideration (Follet *et al.*, 1991). Nitrate-nitrogen is an intermediate product in the complete nitrogen cycle but it is the primary form of nitrogen taken up by plants (Bauder *et al.*, 1993). The nitrogen cycle is particularly complex because nitrogen readily undergoes microbial transformations and can form water-soluble and gaseous compounds that can be lost to the environment (Watson *et al.*, 1999). A brief overview of the components of the nitrogen cycle is presented in the following section.

2.3. The Nitrogen Cycle

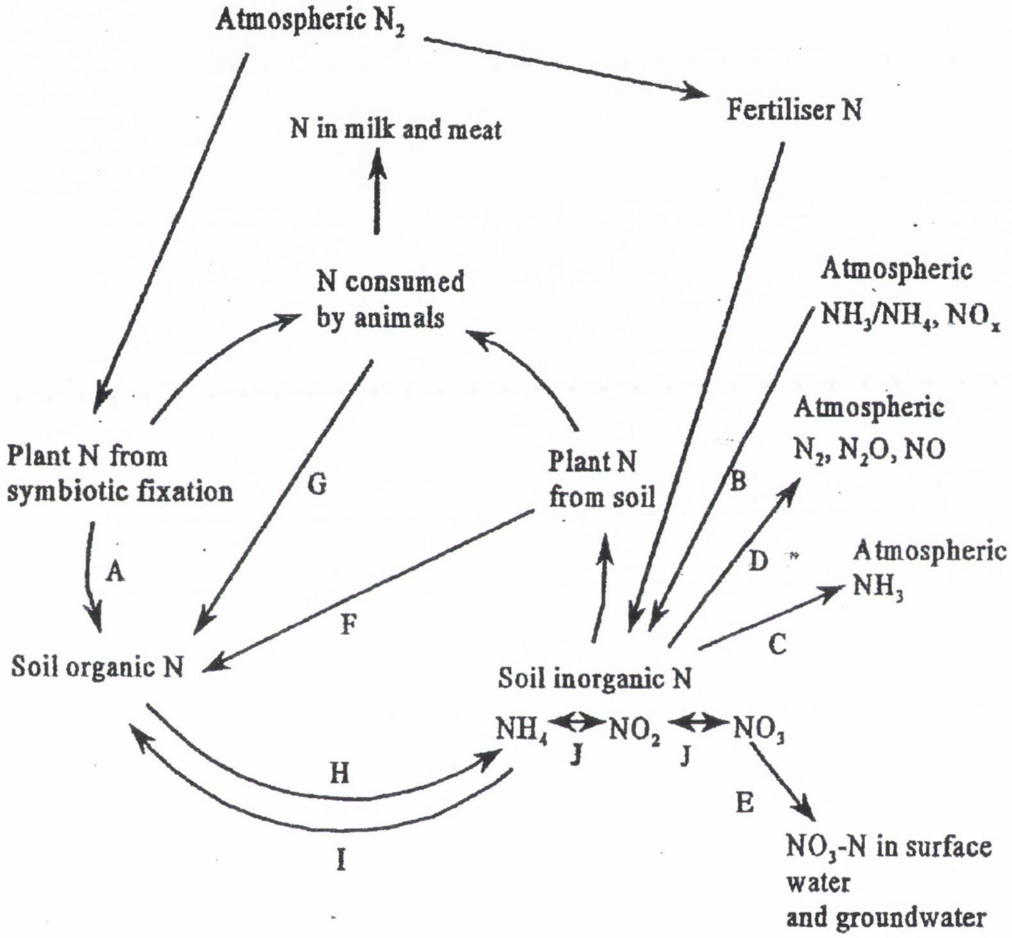
> "The natural biogeochemical cycle of nitrogen in terrestrial systems is conservative. Disruption of the natural biological controls over nitrogen cycling opens up the cycle and causes significant leaching losses. Natural ecosystems are characterised by a tight internal cycling of nitrogen and losses, both leaching and gaseous, are generally less than a few kg N/ha/year." (Gundersen & Bashkin , 1994)

There are eight principal processes in operation within the nitrogen cycle: fixation; mineralisation; immobilisation; nitrification; assimilation; volatilisation; denitrification and leaching. All biological processes of the nitrogen cycle depend on soil temperature and moisture conditions. Surface additions of nitrogen enhance the nitrogen mineralisation capacity of the soil to release nitrate from soil organic matter. Interference in the nitrogen cycle by humans opens up the nutrient cycle to transform the landscape into an 'agrogeochemical ecosystem' characterised by the following (Gundersen & Bashkin, 1994):

(i) High nitrogen export in crops;
(ii) Appearance of nitrate in groundwater;
(iii) Increased denitrification.

No modern intensive agricultural system can be 100% efficient in its use of nitrogen, nitrate leaching is a natural part of the process and some loss each year is inevitable (Archer & Thompson, 1993).

The biogeochemical nitrogen cycle in its simplest terms is the reduction of atmospheric dinitrogen (N_2) to ammonia (NH_3) with the subsequent reoxidation of this ammonia back to N_2. The dynamics of the nitrogen cycle is influenced by microbial activity and governed by soil, climate and substrate conditions (Ryan and Fanning, 1995). Soil mineral pools receive nitrogen from: fertilisers and manures, atmospheric deposition, depositions by grazing animals, fixation by soil microbes, mineralisation of litter and humus and nitrification, but lose nitrogen by: plant uptake and removal in product, immobilisation to litter, leaching, denitrification and volatilisation. Nitrogen cycle processes in operation in grassland are shown in Figure 2.1 and discussed in more detail below.



A: Fixation by legumes

B: Wet and dry deposition

C: Ammonia volatilisation

D: Denitrification

E: Nitrate Leaching

F: Decay of plant tissues

G: Dung and urine deposition, manure Application

H: Mineralisation

I: Immobilisation

J: Nitrification

Figure 2.1 Major transformations of nitrogen in grassland (from Whitehead, 1995).

2.3.1. Fixation

This is the conversion of N_2 gas from the atmosphere to NH_3. Of all living organisms, only a few bacteria are able to fix atmospheric N_2, some live freely in the soil but those that fix N_2 most effectively are the rhizobia which live symbiotically in the roots of leguminous plants (Whitehead, 1995). Man's commercial production of artificial fertiliser mimics this natural phenomenon. Applied inorganic fertiliser and urinary nitrogen deposited by grazing animals adversely affect fixation rates.

2.3.2. Mineralisation

Mineralisation is a key contributor to nitrate leaching loss from grazed grassland (Jarvis, 1999a). Mineralisation of nitrogen occurs when the organic forms in soil organic matter and in plant and animal residues are converted into inorganic or 'mineral forms (Whitehead, 1995). This is a transformation process whereby ammonia (gaseous) or ammonium (dissolved) is released by soil microorganisms that utilise nitrogenous organic substances as an energy source. Usually 95%, or more, of the nitrogen in surface soils is present in organic forms, the remainder being mineral and fixed ammonium (Ryan & Fanning, 1995). The ammonia released under the mineralisation transformation process is then fixed in the soil, volatilised, nitrified or taken up directly by plants. Although nitrate leaching is a generally perceived as a problem resulting from the application of chemical fertilisers, most nitrate found in the soil is a product of microbial activity. The role of fertiliser in the problem is that fertiliser increases herbage yield that in turn facilitates both increased grazing and consequent excreta loads if the grass is grazed, and therefore promotes mineralisation (Whitehead, 1995). It is estimated that mineralisation directly contributes between 17-86 kg N/ha/yr to the soil (Royal Society, 1983). Most of the heterotrophic microrganisms, which are responsible for mineralisation, prefer aerobic conditions and therefore well-aerated soils promote mineralisation. Good drainage promotes mineralisation and this increases nitrate leaching risk (Scholefield *et al.*, 1991). Mineralised nitrogen is not necessarily taken up by grass to the same extent as inorganic nitrogen supplied by fertilisers (Whitehead, 1995).

2.3.3. Immobilisation

Immobilisation is the transformation of inorganic nitrogen into the organic state; basically it is the reverse of mineralisation. Assimilation of inorganic nitrogen by soil microrganisms, uptake by plants of inorganic nitrogen and the subsequent death and decay of plant tissue, all result in the conversion of inorganic to organic nitrogen and a tendency for organic nitrogen to accumulate in the soil (Whitehead, 1995). Plant enzymes reduce nitrate to ammonia prior to the incorporation of its nitrogen into amino compounds.

2.3.4. Nitrification

The oxidation of ammonium ions to nitrite and nitrate is a microbial process. The bacteria *Nitrosomonas europea* convert ammonia to nitrite, which is then oxidised to nitrate by *Nitrobacter winogradskyi* (Ryan & Fanning, 1995). Nitrogen cycle activity can be examined by observation of the current concentrations of ammonia to nitrite and then to nitrate. Nitrite is a transitory form in the nitrogen cycle. Although both ammonium and nitrate ions are available for plant uptake, nitrification is important because it influences the extent to which nitrogen is lost from the soil (Whitehead, 1995). Nitrification, and hence denitrification, is moisture and residence time dependent (Hopstaken, & Ruijgh, 1994). Appreciable nitrite concentrations in drainage and river waters in Northern Ireland were attributed to the nitrification process, though some reduction of nitrate was also suggested (Burns *et al.*, 1995). In some situations, the nitrification of ammonium from fertilisers or slurries may result in substantial amounts of nitrogen being lost through nitrate leaching or denitrification (Whitehead, 1995).

2.3.5. Volatilisation

Volatilisation is the process by which nitrogen is lost to the atmosphere in the gaseous form of ammonia. Much of the ammonia in the atmosphere is derived from the hydrolysis of livestock urine, and, to a lesser extent, from the interaction of soils with fertilisers containing ammonium- or urea-nitrogen (Whitehead, 1995). Approximately half of the estimated 130,000 tonnes of nitrogen produced through volatilisation of ammonia to the atmosphere from farms in Ireland each year is deposited by prevailing winds in the North Sea, where nitrogen from European agricultural activities is considered to be the main factor contributing to increasing problems of marine eutrophication (Culleton & Tunney, 1994). Volatilisation will only occur if ammonium (NH_4) is present at the soil surface.

2.3.6. Denitrification

Denitrification is the process by which nitrate is converted through nitrite to gaseous nitrogen compounds; firstly to nitrous oxide (N_2O) and then dinitrogen (N_2), which then diffuse into the atmosphere. The bacteria actually grow in anaerobic conditions if nitrate/nitrite is present and these bacteria are numerous in most soils (Whitehead, 1995). Denitrification is favoured by low soil oxygen, high soil nitrate, high soil temperature and readily available carbon substrates; these conditions may arise in the general matrix of the soil or in anaerobic microsites within an otherwise well-aerated soil (Watson *et al.*, 1999). The main product of denitrification is N_2 and so the process can be considered a reverse of the fixation process. Nitrous oxide is a by-product of the nitrification/denitrification process and if dissolved in soil water, may be subject to leaching (Whitehead, 1995). Although NO_2 is an intermediary product that has a relatively short half-life in soils (Jarvis, 1999a) NO_2 concentrations above the allowable maximum were found in surface waters in Northern Ireland (Burns *et al.*, 1995; Smith *et al.*, 1995). The NO_2 concentrations observed in grassland drainage and river waters in the southeast of England were found to be significant with respect to allowable concentrations (Jarvis, 1999a).

2.3.7. Leaching

Nitrate can accumulate in the soil and is potentially available for leaching. The negative charge of soil colloids repels the negatively charged nitrate ion and this is why nitrate leaches; it is a very mobile soluble ion that is very susceptible to loss by either leaching or denitrification. In contrast, the ammonium ion is positively charged and tends to be retained on soil colloids, rendering it relatively immobile, though some ammonium may be leached when concentrations are particularly high, such as beneath urine patches (Whitehead, 1995). It is only possible for nitrate to be leached from the soil when rainfall, excess to evapotranspiration rates, moves downward through the soil profile and carries dissolved material from the soil with it. Leaching occurs mostly in winter and spring and it is the surplus nitrogen in the soil at the end of the growing season that is most liable to leaching. The nitrate in soils may be derived either from direct application as fertiliser or from the nitrification of ammonium; and ammonium can originate from fertiliser application, from the hydrolysis of urea, or from the mineralisation of soil organic matter (Whitehead, 1995). Nitrogen losses can be attributed primarily to the autumn mineralisation of the soil organic matter and secondarily to the direct leaching of the nitrogen fertiliser following heavy rainfall events in spring (Foster *et al.*, 1986). The EC Drinking Water Directive (EC, 1998) MAC concentration of 11.3 mg/l NO_3-N may be exceeded during several leaching episodes despite the average concentration leached throughout the year being much less (Whitehead, 1995).

2.4. Effect Of Grazing Animals On Nitrate Leaching

This section provides information, from literature, regarding the significance of nitrogen loading contributed by grazing animals. In Chapter five (section 5.5.2), all forms of nitrogen generated and applied on a typical Irish dairy farm are quantified as loadings, analysed and discussed. In chapter six (section 6.4.7), the observed effect of grazing animals on groundwater nitrate concentrations is presented.

The high rates of nitrogen cycling on grazed grassland, from excreta of grazing animals, applied manures and slurries and soil organic matter, increase the opportunity for nutrient loss (Jarvis, 1999b). Global research on the fate of urinary deposited nitrogen suggests that much of the nitrogen lost from grassland-based livestock production systems is derived from animal excreta and reflects an inefficient use of dietary nitrogen.

Studies from New Zealand (Burden, 1982; Steele *et al.*, 1984; Walker, 1962), the Netherlands (Macduff *et al.*, 1990; Benke *et al.*, 1992), Germany (Steenvoorden *et al.*, 1986), the United Kingdom (Ryden *et al.*, 1984; Garwood and Ryden, 1986), Northern Ireland (Watson *et al.*, 1992) and Ireland (Sherwood, 1986) have shown that grazing animals significantly increase the load of nitrate lost from the grass growth horizon to the environment; losses can be up to three to five times greater in grazed rather than cut swards. Grazing animals excrete more than 80% of all nitrogen consumed and this is the reason that grazed grassland systems are so inefficient and leak most nitrate (Addiscott *et al.*, 1991). Urine patches contain extremely high, but localised concentrations, of plant-available nitrogen that greatly exceed the uptake capacity of the grass (Whitehead, 1995). Uneven deposition of excretal nitrogen by grazing livestock can lead to spot application rates equivalent to 400 to 2000 kg N/ha (Jarvis *et al.*, 1997). Nitrogen deposited by animals in the last part of the growing season cannot be fully utilised by the grass crop and might substantially leach to the groundwater (Hack-ten Broeke *et al.*, 1996).

Given that there must be recharge to drive nitrate to the groundwater body, if there is no effective rainfall nitrate can remain in the soil until it is lost during the autumn and winter. Nitrate is lost through a combination of leaching and denitrification during the autumn and winter re-wetting period. Investigations have found that substantial amounts of nitrate can be observed, under previously marked urine patches, to have travelled to below 1m depth in the subsoil in November despite a soil water deficit of about 15mm (Garwood & Ryden, 1986). Percolation through macropores in the dry soil, followed by the hydrolysis of urea and nitrification of the resultant ammonium are possible reasons for the migration of nitrate to greater than 1m in soil moisture deficit conditions (Whitehead, 1995). This theory is supported by the presence of ammonium with a peak concentration at slightly shallower depths in the soil profile (about 1m) than that of nitrate (Ryden *et al.*, 1984).

In Ireland, nearly twenty years ago, research was conducted to show that the later the urine is deposited in the grazing season, the higher the proportion of urinary nitrate remains and is available to leaching: Sherwood (1986) showed that soil samples at 90cm from grassland plots, which were dosed with cattle urine on seven occasions in the May-November grazing season, retained only 3% of the nitrogen in the urine applied between May and August but that 30-50% of that applied between September and November remained and was therefore susceptible to leaching. Sherwood's work is supported by another experiment (Cuttle and Bourne, 1993), which showed that only urine applications during or after September increased the amount of inorganic nitrogen present in the soil in late November. More recent Irish research has shown that at depths of 80cm in July, the subsoil beneath urine patches contained approximately twenty-five times more available mineral nitrogen than subsoil unaffected by urination: the equivalent of 440kg N/ha was measured beneath urine patches compared to the equivalent of 17kg N/ha in unaffected areas in pastures that had already received 220 Kg N/ha bagged fertiliser (O'Connell, 2002). In the same study, there was found to be no retardation in the observed movements of nitrate beneath the urine patches down through the subsoil profile on heavier or freer draining soils.

It is widely reported that grazing is likely to reduce the value for the rate of fertiliser nitrogen at which leaching becomes appreciable (Barraclough *et al.*, 1992; Kolenbrander, 1981; Walther, 1989). In Kolenbrander's (1981) work about 75% of the total loss was considered to be associated with the nitrogen returned in excreta.

Dung patches hardly affect nitrate leaching, because 65 to 80% of the nitrogen excreted is contained in urine, the area covered by dung patches is relatively small and furthermore the organic nitrogen in dung patches only slowly degrades and so it is usual for dung not to be considered in leaching studies (Hack-ten Broeke *et al.*, 1996).

2.5. Learned Concepts Informing this Investigation

The primary focus of this work is not the definition of individual loss rates attributable to each of the nitrogen cycle components. The NCYCLE model and the associated documentation (Scholefield *et al.*, 1991) already provide good indications of the relative loss rates attributable to each part of the nitrogen cycle in grassland (refer to Chapter three for model details). So much is now known about the complex dynamics of the nitrogen cycle in the soil that many recent publications are review articles on the extensive available knowledge on nitrate loss from the subsoil (Addiscott, 1996a; MAFF, 1999; Wilson *et al.*, 1999; Jarvis, 2000; Follet & Hatfield, 2001). What this work concerns is the loss of nitrate by leaching but more importantly the dominant hydrological mechanisms that govern the leaching to groundwater. The following, acquired from literature, substantiated the focus of the investigation:

1. Given constant fertilisation the variance in the yearly nitrate concentration in the groundwater recharge (percolating water) is mainly a function of the weather (CEC, 1991). For any given soil type, the amount of annual fertilisation and precipitation are the main readily quantifiable factors influencing groundwater recharge nitrate concentrations (Mull & Pfingsten, 1991b).

2. Detailed characterisation of topsoil properties that may govern nitrate production, such as carbon and nitrogen content, mineralisable nitrogen and denitrifying enzyme assay, was found to have limited use on its own for predicting groundwater nitrate status (McLay *et al.*, 2001). The same study found a better relationship between the proportion of dairy farming in a district and regional groundwater nitrate concentrations, than subsoil characterisation with respect to nitrate production.

3. The timing of percolating water, governed by the hydraulic parameters, is more important for the release of nitrate loads from the subsoil than the annual amounts of percolation (Thorsen *et al.*, 2001). Other studies, quoted by Thorsen *et al.* (2001), show that the amount of readily available organic nitrogen present in the soil at the end of the growing season, when recharge is initiated, is the major factor influencing nitrogen loss from the root-zone in northern temperate climates.

4. Water entering the soil top layer as rainfall is added to the current water content. When saturation is reached, further additions of water do not pass through the soil matrix: They

are usually assumed to go by 'by-pass' (preferential) flow to the base of the soil profile. In some areas this potential 'by-pass' component is manifested in loss as surface runoff because of refusal by the soil matrix of further recharge additions. When by-pass flow happens it constitutes a new category of water in the soil, and it can cause rapid loss of solute applied to the surface of the soil (Addiscott & Whitmore, 1991).

5. Application rates not considered to be excessive under current agricultural practices can lead to groundwater nitrate nitrogen levels that exceed the EC standard of 11.3mg/l (Breeuwsma, 1991). Application rate guidelines need to be tailored to soil types or some other parameter (CEC, 1991).

6. As regards potential loss of nitrate from grassland, MAFF (1999) conclude that the underlying assumption is that the number of livestock determines the quantity of nitrogen returned in excretions, as well as indirectly dictating the nitrogen fertiliser input: their national-scale investigations found that the quantity of nitrate lost was greatest in areas of intensive livestock and least in upland areas.

7. The concentration in groundwater reflects both the total amount of nitrate leached per year and the excess winter rainfall. With increasing excess rainfall, there is an increase in the load of nitrogen that can be leached before the concentration will cause breaching of the Maximum Admissible Concentration defined in the EU Drinking Water Directive [EC, 1998] (Whitehead, 1995). Excessive application of nitrogen increases the risk of nitrate leaching but weather controls leaching loss.

CHAPTER THREE MODELLING NITRATE LEACHING FROM AGRICULTURE

3.1. Structure of this Chapter

This chapter reviews available information on the many methods and models employed for nitrate leaching simulations from agricultural land. A general introduction is presented in section 3.2. The spatial scales at which models can be applied and opinions, gathered from available literature, on the applicability of 'scaling up' of process based models are briefly discussed in section 3.3. The ways in which a model's output can be classified are discussed in section 3.4. Data requirements, related issues and future challenges for modelling nitrate leaching are presented in section 3.5.

The techniques employed for modelling nitrate-leaching fall into four groups, as follows:

1) Process-based models;
2) Mass balance approaches;
3) Statistical techniques;
4) Overlay and index methods.

These groupings are far from academic because of the substantial differences in model complexity between each approach: when choosing a model, the level of complexity will dictate both the nature of field investigations and the significance of the results. These different modelling techniques and other important modelling considerations are discussed in section 3.6.

Sources of uncertainty and appropriate methods of analysing uncertainty are explored in section 3.7. The required modelling considerations for each subsurface zone and the consequent selection of an appropriate model for Irish application are presented in section 3.8. This is essentially the heart of this chapter; most of the discussion prior to 3.8 is setting foundations towards understanding the terminology, techniques and implications of certain modelling approaches.

Much detail regarding specific model applications is available in the literature and numerous models were considered in the course of this review. For the purposes of clarity much of the detail has been place in the Appendices of this thesis. The details for each reviewed model and documented successes of specific applications are presented in Appendix A: a table outlining the required model inputs and expected outputs accompanies the discussion of each model. The final two sections, 3.9 & 3.10, draw pertinent modelling information together, outline the modelling strategy selected and conclude this modelling review.

Catchment scale agronomic modelling was also reviewed due to its relevance in regard to the broader issues of modelling nutrient mobilisation within an integrated hydrological resource, e.g. the Water Framework Directive (EC, 2000). Six catchment modelling approaches from the literature, listed in section 3.8.4.5, are presented in Appendix A: model applications are discussed, data requirements are tabulated and conclusions are drawn regarding both surface and groundwater simulations. Catchment and national scale modelling will require the use of geographical information systems (GIS) and so information regarding using GIS to link nitrate leaching models is presented in Appendix A. Many of the modelling applications reviewed referenced other models. In particular, the hydrological model TOPMODEL (Beven & Kirby, 1979; Quinn & Beven, 1993) and river basin model SWAT (Arnold *et al.*, 1993; 1994; 1997) were mentioned widely in the literature concerning modelling at the catchment- or larger-scale. It is for this reason that a subsection of Appendix A also presents these and other relevant hydrological and river basin models.

3.2. Introduction to Modelling Nitrate Leaching to Groundwater

All investigations are controlled by the purpose of the investigation. Models have been designed for farmers requiring information on nitrogen efficiency and farm production, water authorities requiring information on abstraction quality and policy makers evaluating the impact of simulated changes in farm management practices at catchment, regional or national scales (Stockdale, 1999).

Groundwater modelling can be defined as a computer based methodology for mathematical (conceptual) analysis of the mechanisms and controls of groundwater systems, and for the evaluation of policies, actions, and designs that may affect such systems (van der Heijde & Elnaway, 1993). Generally, a model is either developed as a research or management tool and the model equations and components reflect its purpose. Occasionally a model is constructed as an instructional tool and these models are based on simplified representations of fewer processes. The root-zone agronomic model NCYCLE (Scholefield *et al.*, 1991) was originally developed as an instructional tool but was developed further after showing promise in its simplicity. A usable model for a variety of hydrogeologic situations must be accurate, functional, and transferable but aquifers have complex heterogeneous properties and complex boundary conditions, therefore the solution of the mathematical equations that describe the transport processes generally requires the use of deterministic, distributed-parameter, digital simulation models (Konikow, 1976).

For scientists interested in the processes of nitrate loss, rather than simply the outcome, a model with a physical basis is required (Stockdale, 1999). Hence, these models are more complex and describe each of the processes in detail incurring numerous parameters. Today, interest in nitrate behaviour is environment rather than production driven: The impetus is to comply with EU legislation (refer to section 1.4). Therefore, the current focus is on the receiving environment, be it surface- or groundwater. Management models tend to have fewer input requirements and rapid simulation times, but the accuracy of predictions may suffer and outputs are considered of relative value to be used for advisory purposes. A quality assurance policy, together with adequate data used correctly, an appropriate model and properly posed problem and boundary conditions will assist in the use of the results of modelling for land and water resources management (Shaw & Falco, 1990). Use of models for regulatory purposes depends on an ability to estimate the prediction of errors (Dillon & Kelly, 1994). An uncertainty analysis and some estimation of the reliability of the attempt should always accompany modelled simulations (Van Herpe *et al.*, 2002).

The development of nitrate leaching models reflects the developers' purpose and academic background (Rodda, 1993). Historically, soil physicists attempted to plot the physical movement of solutes through the soil profile. Then, agricultural/biological scientists considered leaching as a process linked with agricultural production and the biochemical transformations within the nitrogen cycle. Hydrological scientists postulated that the hydrological cycle was the driving force from which empirical relationships could be derived to relate land-usage/agricultural practices with surface- or groundwater quality. Because of the high solubility of the nitrate ion, its transport is intimately linked with the hydrological pathways controlling nutrient transport from the land to surface and groundwater (Van Herpe *et al.*, 1999). Another purpose for modelling nitrogen cycle dynamics is simulation of the consequences of climate change (Robins, 1998). The effects of wetter winters or warmer, drier summers on the nitrogen cycle, hydrological regimes and agricultural practices may be simulated using nitrate models that require climatic data as input parameters.

Many models exist to describe nitrate movement in the soil profile but few have been developed for management planning (Khakural & Robert, 1993; Stychen & Storm, 1993). The reasons given for the plethora of nitrate-leaching modelling approaches are the growing emphasis on environmental policy and awareness and the availability and computational efficiency of modern desktop computers (Squire & Hamer, 1990). Essentially, it is now relatively easier and cheaper to develop and apply a theoretical model than carry out large-scale dedicated field experiments, which are costly, lengthy and potentially difficult (Rodda, 1993). However, a model is only as good as the field data used in development and validation (Shaffer, 1995). In general, the accuracy of model predictions cannot exceed the accuracy of the input data used in the analysis, as models can never be totally independent of measurements (Stockdale, 1999).

Soil nitrogen models have been developed for a range of applications at various spatial scales. Measurements, pedo-transfer functions and models may be used alone or in combination to predict nitrate losses (Stockdale, 1999). The scale under investigation and the purpose of the work dictates the modelling strategy employed. Throughout the last century scientists have provided many useful insights into water flow and solute transport phenomena, but a major shortcoming is the restriction of the main body of work to homogeneous soils (Feyen, 1998). Research commissioned by the EU in the early 1990's concluded that there was no immediate need to develop new nitrate leaching models (CEC, 1991). Instead, it was deemed more efficient to incorporate new modules for missing elements (such as structured soils) and improve existing descriptions (such as denitrification). Indeed, not many mechanistic (process/physically based) nitrate-leaching models have been published since the early nineties. Feyen *et al.* (1998) provide an in-depth mathematical review and discussion of recent alternative modelling approaches, which make it possible to more accurately model the flow and transport processes in heterogeneous soils, at local and field scales. They vary from dual (multi)-porosity models, stream tube models and stochastic continuum models, but the models presented require extensive validation before they can be used to solve specific environmental or management problems.

Characterisation of the groundwater response to nitrate leaching from dairy farming; a grassland crop, is the primary focus of this investigation. However, many of the nitrate leaching models are not agricultural-crop specific, grass growth simulation is merely one user specified option. Some models are grassland specific (e.g. NCYCLE, Scholefield *et al.*, 1991 & 1992) and some models are more suited to arable applications (e.g. DAISY, Hansen *et al.*, 1990; SOILN, Jansson, 1991). Catchment and regional nitrate leaching studies require consideration of multiple agricultural land-use combinations, which was achieved by Nielsen *et al.* (1991), using DAISY, and by Arheimer & Brandt (1998) using SOILN, highlighting that these models can be used for grassland simulations in a mixed agricultural catchment. Recent research focus has been on the integration of models to more comprehensively describe combined catchment resources at scales more appropriate to policy than production research (e.g. Birkinshaw & Ewen, 2000a & b; Lord & Anthony, 2000; van Herpe *et al.*, 2002). All of these mentioned models and modelling approaches, and many more, are documented in the appendices to this work.

This modelling review owes a great debt to those who have reviewed modelling techniques and issues of relevance to the realm of nitrate leaching: Addiscott & Wagenet (1985); De Willigen (1991); Bogardi *et al.* (1990); Vachaud *et al.* (1990); CEC, (1991); Addiscott, (1993 & 1996b; Addiscott *et al.* (1995); NRC, (1993); Feyen *et al.* (1998); MAFF, (1999); Stockdale, (1999); Gogu & Descargues, (2000). The majority of previous reviews discuss field-scale root-zone models, mostly confining themselves to a specific scale. This review is novel in that not only are the concepts presented and discussed but also many models' data requirements, expected outputs, and examples of practical field applications are documented in a structured fashion.

3.3. Scales Of Application

The scale at which they are applied, their purpose, their structure or even the techniques employed are all ways of classifying models. Scale is most often discussed, in recent literature, in the context of how to validly apply soil and water quality models at different spatial scales and attention is drawn to the proceedings of a dedicated conference on the issue as reported by Finke *et al.* (1998).

3.3.1. Point and Field-Scale Simulations

These models are used, most often deterministically, to assess local impacts paying great detail to individual processes at play. Various management, soil and climatic scenarios can be explored to yield quantitative results. The spatial units investigated with these models do not generally exceed individual fields or research plots. Most of the nitrogen models available in scientific literature are at this scale. GIS technology, with its layer structure and data handling capabilities, allows these smaller scale models to be applied to whole farm analyses usually by "farming by soil" methods (Shaffer, 1995). Integration of point and field scale models with GIS, to model on a regional scale, has been achieved (Petach *et al.*, 1991; Shaffer, 1995; Hutson *et al.*, 1996). However, the intensity or resolution of input data requirements is reported to make such a detailed mechanistic model unrealistic for large area applications (Petach *et al.*, 1991; Inskeep *et al.*, 1996). These 'scaling up' considerations are discussed in more detail in section 3.3.4.

3.3.2. Farm or local-Scale Simulations

Multiple fields and management enterprises are considered at this scale. This intermediary scale is most often described qualitatively using a ranking scheme (*e.g.* Shaffer *et al.*, 1991; Magette, 1998). The point scale model LEACHN (Wagenet & Hutson, 1992) was linked with a GIS to simulate nitrogen flows on two US dairy farms (Hutson and Wagenet, 1996). However, others (Addiscott, 1993; Beven, 1989; Quinn *et al.,* 1999) question the validity of this type of approach (see section 3.3.4).

3.3.3. Regional, Catchment or National Simulations

Successful modelling at this scale is most often achieved though the use of GIS and sometimes remote sensing (see Appendix A). Advanced technology is required to adequately manage the data describing spatial and temporal changes in soils, management and climate across a catchment. SLIM (Addiscott & Whitmore, 1991) is the point-scale process model used to derive simple relationships for application in larger scale modelling efforts by a number of research teams (Quinn *et al.*, 1999; Lord & Anthony, 2000; Van Herpe *et al.*, 2002). A recently released, validated, national scale nitrate model, Nitrogen Risk Assessment Model for Scotland [NIRAMS] (Dunn *et al.*, 2003a and b), successfully employs a very simple approach based on the point-scale NLEAP model (Shaffer *et al.*, 1991)

3.3.4. Discussion: Scaling-up

Rodda (1993) summarises the work of Beven (1989) and Addiscott (1993) in discussing the problems associated with scaling up physically based models for application to catchment scale, including:

1. The general inapplicability of model equations derived for small-scale homogeneous systems to field scale heterogeneity, in particular the phenomenon of preferential flow;

2. Model non-linearity with respect to its parameters, and the values given to parameters at the large scale may not be within the range for which the model was validated;

3. Major practical constraints on model validation at the larger scale.

All of the above may seriously impede applying mechanistic models at scales greater than those for which they were developed. The advantages of empirical (functional) models are that they can more easily be derived at the scale for which they are to be applied, they are less complex, require fewer inputs and are hence, more user friendly (Rodda, 1993). Dunn (1998) also reviews large scale hydrological modelling using small scale processes

Detailed research and physical experiments have led to a series of field scale detailed physical models of soil hydrology and nitrogen cycling. Quinn *et al.* (1999) suggest that these models cannot be taken in their current form and scaled-up as they cannot be statistically parameterised from existing databases. Also, the models are thought too complex to be made sufficiently robust to act as operational tools for land-use planning. Their complexity and high data input requirements may lead to problems of uncertainty and may be difficult to justify should calibration be required (Beven, 1989). However, many authors acknowledge the experimental relationships within models and their own independent validation for many soil and crop types as extremely useful (Addiscott, 1993; Quinn *et al.*, 1999; Stockdale, 1999; Van Herpe, 2002). The output of physically-based complex models can be used to develop simple functional relationships for application to larger scale studies (e.g. Lord & Anthony, 2000). Hydrological pathways and biogeochemical transformation in the aquatic system are thought to be the controls for temporal nitrate concentration variability, on a large scale (Arheimer, 1998).

The conclusions of the soil science-modelling group at Rothamsted (Addiscott & Mirza, 1998) are that:

1. No single model will be appropriate, or even usable for all purposes at all scales.
2. There is a general inverse relationship between the size of the area to be modelled and the level of complexity that is appropriate for the model [i.e. the model needs to be functional with respect to scale (Addiscott, 1993)].

Scaling up field and plot scale models is not appropriate for a catchment scale approach. Each and every catchment is specific, with unique management and hydrogeological conditions interacting in more complex levels than found at smaller scale studies. Therefore nutrient control strategies are, in many cases, non-transferable to other areas. In August 1999, the magazine of the International Water Research Association reported that the nutrient problems of the world are widely recognised and described, but the solutions are 'a long way off'. Furthermore, 'concentration on technology-based methods was expensive and unreliable'. The article correctly identifies that action required 'across society as a whole', with "persuasion, education and action by co-operation" coming to be seen as important components of nutrient management strategy in many parts of the World (IWA, 2000).

Whitmore *et al.*, (1992) showed that for large areas (e.g. England and Wales) quite simple models (empirical/functional) are most useful, but mechanistic models are needed in order to understand the behaviour of solutes.

3.4. Model Classification

3.4.1. Deterministic or Stochastic

Models can be categorised as *deterministic* or *stochastic* (Addiscott & Wagenet, 1985). Simulated output from a deterministic model will be a fixed amount, depending on the input parameters (Rodda, 1993). Such models may be classified according to the description of the physical processes as black box and conceptual (functional) or physically based (mechanistic) and may further be differentiated as lumped or distributed with regard to spatial description (Refsgaard, 1996). Thorsen (2001) suggests three typical model types as the lumped black box model, the lumped conceptual model and the distributed physically-based model. While most nitrate leaching models are point-based, for application only to the root-zone at small scales, integration with GIS has allowed distribution of the simulation to catchment scale (see Appendix A). Deterministic models generally have large input data requirements and the simulation results are often very sensitive to the assigned input parameter values (Stockdale, 1999; Lasserre *et al.*, 1999).

Stochastic models are formulated with the premise that all input parameters are inherently variable, so the output from a stochastic model is not an absolute value: a probability of occurrence or error is associated with the simulation (Stockdale, 1999). Few stochastic models have been used in the field of nitrate leaching (Rodda, 1993); deterministic models are the norm (e.g. DAISY (Hansen *et al.*, 1990); NCYCLE (Scholefield *et al.*, 1991); SLIM (Addiscott & Whitmore, 1991); LEACHN

(Wagenet & Hutson, 1992). However, it is possible to create a stochastic extension to a deterministic model: by carrying out multiple model runs, each run using a randomly chosen set of input parameters, and employing Monte Carlo simulation techniques (refer to section 3.7.2) the prediction of certain likely outcomes is possible (NRC, 1993).

3.4.2. Mechanistic or Functional

Modelling approaches can be further divided into mechanistic or functional approaches. Arheimer (1998) summarises the differences in model structure quite nicely: in physically based (mechanistic) models, the processes are identified, but guesses are made about the rate constants but in conceptual (functional) models, in contrast, the rates are identified but guesses are made about the processes.

Mechanistic models use classical physical theory, employing quantitative equations for transport simulations (e.g. solving the Richards equation for water flow and the convection-dispersion equation for solute transport). Examples of mechanistic models are DAISY (Hansen *et al.*, 1990) and LEACHN (Wagenet & Hutson, 1992). Mechanistic models use rate parameters to model the leaching process (Rodda, 1993); many of these models were derived from laboratory studies of soil columns (Jury & Fluher, 1992), though some are based on experiments using undisturbed soil monoliths (Jarvis *et al.*, 1991).

Functional (empirical) models are simpler and use fewer parameters. These models are attractive because they require relatively less data, which are usually easily accessible, but some question the predictive capability of such models due to the semi-empirical nature of the process descriptions (Thorsen *et al.*, 2001). NCYCLE (Scholefield *et al.*, 1991) is an example of a functional nitrogen cycle root-zone model. Rodda *et al.* (1995) state that is general believed that empirical models lack versatility. However, use of coefficients derived from independent process-based studies is thought by others (*e.g.* Johnes & Burt, 1993) to add versatility to empirical models. Others (Smith & Stewart, 1989; Johnes & O'Sullivan, 1989) assert that functional models can provide numerically accurate predictions about the behaviour of the system on which they are based. A tipping bucket/capacity type approach to water movement is often employed by functional models (Stockdale, 1999), water is considered to be held in reservoirs of known capacity and when that capacity is exceeded water flows within the soil [e.g. SLIM (Addiscott & Whitmore, 1991)]. Water flow simulation, in a functional model, often takes soil retention capacity into consideration

(Lasserre *et al.*, 1999). Preferential flow can be modelled, when using a functional methodology, by including reservoirs of both mobile and immobile water (Addiscott & Whitmore, 1991). Functional models are more suitable than mechanistic for field and larger scales, they require fewer input parameters and computational effort (Arheimer, 1998). De Willigen, (1991) believes that prediction of the soil water content by the mechanistic models is not better and sometimes worse than that of simpler functional models. However, Vereecken *et al.* (1991) offers that functional models are not suitable for differing geo-hydrological conditions because they assume a constant bottom boundary and mechanistic models can handle a range of bottom boundary conditions.

3.5. Modelling Data Requirements

In general, one year's data is not enough for model development because hydrological conditions can vary enormously from year to year. Three to five year's data is recommended for any serious analysis (Breeuwsma, 1991; Hopstaken & Ruijgh, 1994). As the complexity of a model, and its solution, increases so too does the level of required detail in input data.

3.5.1. Groundwater Model Requirements

A competent groundwater model may only be created from a thorough understanding of the hydrogeology of the area under investigation. The ranges of variation of basic hydrogeological parameters, such as effective porosity, transmissivity, hydraulic conductivity should be known with some certainty (Karanjac *pers. comm.*, 2000). A carefully monitored water table and reliable recharge estimations yield an understanding of recharge processes, which contributes to accurate model development (Lasserre et al, 1999). Sampling frequency should reflect the response time for the particular parameter under investigation *i.e.* the groundwater sampling interval should be based on the systems response and residence times determined from water table observations (Hopstaken & Ruijgh, 1994; Lasserre *et al.*, 1999).

The following types of data are recommended for development of models simulating the response of groundwater to nitrate loadings (Mull & Pfingsten, 1991b; Hopstaken & Ruijgh, 1994):

- Boundary conditions, both hydrogeological (climatic data, groundwater depths, the geology and geometry of the aquifer) and agricultural (e.g. crop uptake). Boundary conditions may exhibit spatial and temporal variation (Peck *et al.*, 1988).

- Nutrient inputs to the system. Measurement of initial status and fluxes of nitrogen concentrations in the soil at different depths and for different seasons, for different soils types and agricultural scenarios.

- A reliable network of groundwater monitoring stations with adequate descriptions of soil and hydrogeological conditions including time series data for groundwater nitrate concentrations. The location and rates of all abstraction points should be known.

- Water balance for the area under observation including recharge and discharge areas.

3.5.2. Nitrogen Cycle Model Requirements

Assessment of the correct input data for the modelling procedure is crucial (Hack-ten Broeke, 2000). Development of a nitrate-leaching model firstly entails determination of the dominant nitrogen cycle processes, to be considered in the simulation, and then identification of processes that can be directly measured and those that must be obtained and interpolated from literature (Messinger & Randall, 1991).

Breeuwsma (1991) discusses in detail the data sets required for modelling nitrate leaching. They categorise modelling data into three groups and recommend the extent of data required in each group:

1) Nitrogen flux data

Nitrogen cycle components, and their significance in the model format, are:

- N Inputs: fertilisation (**S**, **M**) + deposition (**S**, **L**) + fixation (**IG**)
- N Transformations: mineralisation (**C**) + nitrification (**C**)
- N Outputs: erosion/surface runoff (**IG**) + volatilisation (**S**, **L**) + uptake (**S**, **M**) + denitrification (**C**) + leaching (**S**, **M**)
- N Storage: organic N (**C**) + mineral N (**S**, **M**)

<u>Explanation of abbreviations</u>

(**S**) = forms part of the standard dataset;

(**M**) = measured;

(**L**) = estimated from literature;

(**IG**) = ignored;

(**C**) = model calculates;

[soil organic N is assumed to be at equilibrium in a long-term grassland]

2) Background data

Suggested background data were grouped as *general* (physiographic, agronomic and soil classifications), *physical* (drainage, water retention, hydraulic characterisations) and *chemical* (soil water pH, organic carbon and total nitrogen contents per soil horizon). Five years of historical land use and fertiliser management data were suggested.

3) Monitoring data

Lastly, monitoring data for all parameters varying temporally (meteorological, nitrogen flux, soil mineral nitrogen, soil moisture and groundwater, and nitrate-leachate concentrations data) were suggested for collection (Breeuwsma, 1991).

3.5.3. Implications of Natural Variability on Model Outcomes

The magnitude of a model's response to input variability depends on the specific model's sensitivity to that particular parameter (CEC, 1991). Peck *et al.* (1988) review the consequences of spatial variability in aquifer properties and data limitations for groundwater modelling practice. Incorporation of variability in soil properties into hydrologic-modelling methodology is necessary, within process-based approaches, to provide accurate representations of the uncertainty induced by soil in simulation of hydrologic response (Wu *et al.*, 1996).

Arheimer, (1998) advocates a thorough understanding of the spatial and temporal variability of nitrogen transport. However, complex, interrelated processes, associated with the carbon and nitrogen cycles, along with the spatial variability in soil types and grazing animals' waste deposition are among numerous factors influencing the spatial variability of soil residual nitrate and nitrate leaching, (Shaffer, 1995). An extensive amount of soil samples is required for representative analysis of soil nitrate concentration profiles, in grazing systems, due to the patch-wise deposition of urine and dung by animals. When a likely variance has been quantified, formulae can be used to determine the number of samples needed to represent the system but the number of samples may prove prohibitive for most projects' budgets (Stockdale, 1999). Indications of high variability of soil nitrate contents at short distances prompted a EU study to analyse spatial variability and the application of geostatistical techniques to derive optimal sampling techniques (CEC, 1991). Finke (1991) demonstrated a high variability in model outputs

(31% variation in simulated nitrate leaching) due to spatial variability in soil profile properties and lower boundary conditions alone. Another problem, when relying on this type of detailed data for physical models, is how to reduce the extensive amounts of gathered information to avoid a noisy, cumbersome methodology (Monke *et al.*, 1989).

3.5.4. Pedo Transfer Functions

To avoid high costs in field measurement, pedo transfer functions exist, or can be developed, to relate basic soil characteristics, such as clay and organic matter content, to data that are difficult to measure, such as those describing denitrification or hydraulic conductivity (Bouma & van Lanen, 1987). Bouma (1991) and Bouma & Breeuwsma (1991) discuss the derivation of pedo transfer functions and distinguishes between continuous (using organic matter or clay contents) or class (using e.g., textural classes) functions. Stockdale (1999) advocates the use of one or more measured soil properties to be used as inputs to pedo transfer functions to predict nitrate losses directly or to estimate an index of nitrate loss. The SLIM model (Addiscott & Whitmore, 1991), successfully infers model parameters from basic soil properties [the SLIM model is discussed more fully in section **3.8.3** and Appendix A].

3.5.5. Data Challenges

The error associated with the measurement/estimation of any model parameter will eventually manifest itself in the model output (Stockdale, 1999). The accuracy of the data used as inputs is of key importance in determining the error associated with a model (Heuvelink *et al.*, 1989). It was concluded by Charnock et al (1996) that sophistication of the model components themselves is less of a limitation, with respect to simulation accuracy and applicability to decision-making, than data availability and quality or capability to calibrate the approach.

The current challenge is to meet future data needs without having to expend the extraordinary efforts expended in the past (CEC, 1991). Recent national nutrient loss models for Ireland (Daly *et al.*, 2002) and the UK (Lord & Anthony, 2000) successfully rely on existing available data, in the form of well established meteorological and hydrometrical databases and agricultural census information, in conjunction with GIS and remote sensing advanced technologies. In the absence of available detailed existing groundwater data, that is required for model development in Ireland, extrapolation of already tested surface water models may be a sensible approach.

The NRC (1993) conclude that unless a vision for a national spatial data infrastructure exists and databases, policies and standards are in place to facilitate access and use of spatial data on a national scale, opportunities will be lost in the area of environmental protection and resource management.

3.5.6. Validation Data

Many of the models describing nitrate leaching have used complex mechanistic approaches (e.g. LEACHN (Hutson & Wagenet, 1991); DAISY (Hansen *et al.*, 1990) and SOIL-SOILN (Johnsson *et al.*, 1987 & Jansson, 1991). The range of processes considered incurs heavy input data requirements, which causes problems in both data collection and model validation. Vereecken *et al.* (1991) concluded that the output from detailed research based mechanistic models, such as ANIMO and DAISY, in some cases proved too detailed for validation by measured data.

In terms of model validation, the data used should have undergone some degree of quality assurance (Shaffer, 1995). When the focus of the model is prediction of groundwater quality, in general, concentration data in the soil are not reliable enough for complete model validation (Hopstaken & Ruijgh, 1994). Groundwater concentrations are usually a reliable data source for model validation once it is understood that some local variability does occur. However, Stockdale (1999) cautions that care is required when comparing observed groundwater quality data with model predictions. Spatial and temporal variations in nitrate loadings, inadequate borehole construction and hydrogeological information (NRC, 1993), delays, transformations in the soil and inadequate monitoring programmes (Lord *et al.*, 1993) may all result in discrepancies between simulated and observed groundwater nitrate concentrations.

3.5.7. Challenges For Modelling

Vachaud *et al.* (1990) (cited in Hopstaken & Ruijgh, 1994) comprehensively outline the common challenges of modelling to be as follows:

1) Adequate definition of the microbial transformations;
2) How best to deal with preferential water flow and transport;
3) How best to account for effects of spatial and temporal variability of soil hydraulic parameters on solute transport;
4) How to efficiently couple multi-species geochemical submodels with unsaturated-saturated flow models;
5) How to improve field methods for estimating vadose zone transport parameters, and the relevant scale at which they apply, and
6) How to predict the-ong term consequences of short-term management decisions.

Feyen *et al.* (1998) have reviewed recent water flow and solute transport modelling concepts, based on the same mathematical concepts and physical laws as classical approaches, which attempt to deal with soil micro- and macro-heterogeneity and macropore flow. Preferential solute transport through heterogeneous soils is described using the dual porosity concept and a statistical model of spatial variability represents the macro-heterogeneity of the soil, with the statistical parameters subsequently used to derive the parameters of flow and transport variables at the field scale. However, these proposed modelling techniques require validation before application and are, as such, still theoretical (de Vos *et al.*, 2000).

3.6. Modelling Techniques

The techniques employed for modelling nitrate-leaching fall into four groups: 1) process-based models, 2) mass balance approaches 3) statistical techniques, and 4) overlay and index methods.

3.6.1. Process-based Models

Many models are based on mathematical equations that approximate substance behaviour and transport in the subsurface; the equations represent coupled processes governing contaminant transport (NRC, 1993). These mathematical methods are generally termed 'process-based' models and can be further classified as either mechanistic or functional [section 3.4.2]. Although many different models appear in the literature, often the basic equations are rather similar within a specific model category (Arheimer, 1998), while interfaces and routines for data handling may be considerably different.

Process-based models are generally only used at small scales, such as point or field scales, applied to a one-dimensional soil profile in areas with good data availability. Even so the relevance of such an approach is often questioned because of the perceived uncertainty related to model simulations (Thorsen *et al.*, 2001). These models are generally not relevant or applicable to scales other than those used in development (Stockdale, 1999). For example, the LEACHM suite of models (Wagenet & Hutson, 1992) can incur serious errors if attempts are made to simulate deeper than the design root zone depth (NRC, 1993). Despite these cautions, LEACHN was applied, by its developers, to a farm scale study (Hutson & Wagenet, 1996) with reported success (see section 3.3.2).

Biochemical, physical and microbial processes are all significant in nitrogen cycle dynamics and hence require some consideration in the modelling process. Most root-zone models, which are process-based, rely on comprehensive descriptions of the carbon and nitrogen cycles in the soil (Stockdale, 1999) and hence demand comprehensive descriptions of the soil nitrogen and carbon contents and the environmental controls on cycle activity (temperature and moisture). Most of these parameters are not easily obtained or determined. In addition, this type of model must be calibrated for each unique site and crop variety to which it is applied (Hanson *et al.*, 1999). Recent research by Mc Lay *et al.* (2001) found no direct relationship between typical-model soil properties (total carbon and nitrogen, potentially mineralisable nitrogen and denitrifying enzyme assay) and groundwater nitrate concentrations.

Soil organic matter is usually considered as more than one pool of material in process-based simulations (Jarvis *et al.*, 1996). Examples include DAISY (Hansen *et al.*, 1990), RZWQM (USDA, 1992, 1995), ANIMO (Ritjema *et al.*, 1995), SOIL-SOILN (Jansson, 1991) and LEACHN (Wagenet & Hutson, 1992). Given the strong dependency, during model development, on carbon and organic matter controls on nitrate leaching, it would seem sensible to investigate whether a proposed model is appropriate for the relatively high organic matter contents of Irish soils (approximately 8% O.M., Gardiner & Radford, 1980). For example, the model NLEAP has not yet been developed for organic soils (USDA, 1996b).

With process-based models, nitrate leached from the root-zone is usually calculated as a product of the flux of nitrate concentration in pore water and estimates of soil water flux (De Willigen, 1991). Alternatively, the transport of solutes is computed as a weighted average of current concentration and incoming concentration (Addiscott, 1993). Therefore, these models have two elements that are usually integrated; soil nitrate production and soil water movement (Stockdale, 1999). These two elements are dictated by agricultural, climatic and soil physical characteristics. The effects of dispersion and diffusion are accounted for by the introduction of appropriate coefficients (source and sink terms) into the solute transport equations (Shaffer, 1995). Modelling approaches from the Netherlands (Vereecken *et al.*, 1991; Hopstaken & Riujgh, 1994; Hack-ten Broeke, 2000) advocate use of an external water balance model, usually SWATRE (Belmans *et al.*, 1983), prior to the application of a dedicated nutrient process model.

Process-based models attempt to provide predictions in both space and time (Stockdale, 1999). Each of the models mentioned above, and many others, consider one-dimensional transport in the root-zone and predict solute concentration with depth, at discrete time intervals, before, during and after a nutrient is applied to the surface (NRC, 1993). While they attempt to incorporate more complex descriptions of all processes affecting contaminant transport, they may not necessarily provide more accurate results (De Willigen, 1991; Stockdale, 1999). It is possible to create simpler (functional) process-based models (e.g. SLIM – Addiscott & Whitmore, 1991) by including most of the major processes but represented in a less sophisticated way. This loss in scientific rigour and conceptual detail is rewarded by a reduction in computational time and greater ease of use (NRC, 1993).

Most models in this class are based on an assumption of local sorption equilibrium (between the soil and chemical), which is not likely under natural conditions; transport non-equilibrium arising from some degree of preferential flow is probably more significant (NRC, 1993). Preferential flow can be the dominant transport phenomenon under certain circumstances, even in soils that exhibit no identifiable macrostructure (Ghodrati & Jury, 1990; Roth *et al.*, 1991). The inability of most process-based models to deal with the complexities of flow is a serious limitation (NRC, 1993). Complex models that explicitly account for certain types of preferential flow in structured soils are available (e.g. Jarvis et al, 1991; Feyen *et al.*, 1998). However, the required information on spatial distribution of preferential flow paths is practically impossible to determine and these models remain virtually untested in any practical sense (Beven, 1991; Feyen *et al.*, 1998).

Perhaps the popularity of process-based methods in the US can be explained by the extensive nature of national environmental databases (climatic, soils and agronomic). Many US models, such as NLEAP (Shaffer *et al.*, 1991), GLEAMS (Leonard *et al.*, 1987) and SWAT (Arnold *et al.*, 1994 & 1997), are based on the US SOILS S/6 and Pedon databases (Shaffer, 1995). These databases contain extensive information on soil properties such as texture, drainage class, hydrologic group, bulk density, pH, plant available water-holding capacity, percentages of organic matter and coarse fragments. In addition, the Pedon databases contain more detailed information on soil properties such as water retention relationships and soil chemistry. This level of soils information does not exist in Ireland.

Mc Lay *et al.* (2001) determine that many process-based leaching models, constrained by the need to satisfy stringent boundary conditions, do not cope well with non-uniform strata and the numerous biological and chemical processes that influence nitrate concentrations in soil and underlying aquifers.

3.6.2. Mass Balance Approaches

A model of this nature is essentially a quantification of all inputs to and outputs from the system under investigation. The balance between nitrogen inputs (fertilisers and feedstuffs) and outputs (grass and products) dictates loss to the environment. This means that the nitrate concentration at a point of abstraction depends on the overall balance of agriculture in the catchment (Archer & Thompson, 1993) or the efficiency of agricultural systems in a catchment. Therefore, a strategy for modelling nitrate leaching to groundwater may take a mass balance approach. Scholefield *et al.* (1991) summarise the use of mass balance approaches, and report that they have been adopted widely. Hauck & Tanji (1982) described the advantages and disadvantages of the balance method. Mass balance calculations have been recognised as providing a basis for both model development and validation (Long & Hall, 1987) for quite a while. Mass balance data has been used to develop models for grazed grassland systems nitrogen fluxes by Field & Ball (1982), Van de Ven (1989) and more recently by Scholefield *et al.* (1991) in the NCYCLE model. Models for evaluating the fate and transport of nitrogen into surface water (Quinn, *pers. comm.*, 2000) and groundwater (Short, 2000a) have been prepared in the Microsoft EXCEL spreadsheet package following a balance type approach with factors added relating inputs and transformations occurring.

Chemical fertiliser nitrogen, manures, biological nitrogen fixation, atmospheric deposition, net mineralisation of soil organic nitrogen, and nitrogen in concentrates fed to animals can be summed as inputs to the system. Outputs are considered as the nitrogen removed in animal product (milk and meat), uptake by plants/crops, immobilisation, denitrification and losses to the air (volatilisation) and water environments. In climatic areas where winter rainfall normally exceeds evapotranspiration sufficiently to ensure that nitrate is leached, as is experienced in the UK and Ireland, the assumption of balance, with no appreciable difference in soil inorganic nitrogen between the beginning and end of the growing season, is valid (Scholefield *et al.*, 1991). Outputs from this modelling technique are general and can be used to indicate relative problem areas and policy issues requiring further research (NRC, 1993).

A national nitrogen balance sheet for Irish agriculture (Sherwood & Tunney, 1991) highlighted that only 16% of total inputs were represented in the total nitrogen output as products. A further 12% was attributed to immobilisation in soil, which means that 72% of nitrogen inputs are not recovered in soil or animal product. Lee *et al.* (1994) conclude that the 72% of nitrogen inputs, not recovered, must be lost to water and the atmosphere, representing a financial loss to the farmer and potential damage to the environment.

The same balance principles can be applied at farm level. On Irish dairy farms output in product represents about 20% of the input for nitrogen, which begs improved nutrient management in the interest of sustainability (Lee et al, 1994). Farm-level balances in Ireland (Richards, 1999), Northern Ireland (Watson *et al.*, 1992) and England (Jarvis, 1993) yield the same results; approximately 20% of nitrogen inputs are accounted for in product outputs. Nitrogen balance quantifications for the conventional and organic dairy farms at Teagasc, Johnstown Castle, attributes 14-20% of all nitrogen inputs to be lost to water (Lee *et al.*, 1995; Cosgrave, 2000). However, this figure may be higher if other 'unaccounted for' portions of the nitrogen cycle are re-evaluated. The term 'unaccounted for' often appears in nutrient balances (e.g. Jarvis, 1993; Sherwood & Tunney, 1991). In the farm level balance analysis completed by Jarvis (1993), 46% of the total nitrogen input was *estimated* to have been lost to the environment and 34% was 'unaccounted for'. One must question how the distinction between environmental loss and 'unaccounted for' nitrogen is quantified. Some nitrogen is stored on the farm, in animals and silage, and some is immobilised in the soil (Richards, 1999) but how is, say, immobilisation quantified?

Bechmann *et al.* (1998) evaluated the relations between nitrogen surface balances (mass balance considering nitrogen additions to, and removal from, the land's surface) and nitrogen leaching. They found a low linear correlation (R^2=0.15) between nitrogen surface balances and nitrogen leaching for all study catchments and years. However, the linear correlation between nitrogen leaching in autumn and nitrogen surface balances was good (R^2=0.95), when only catchments with similar soil properties and years with similar weather conditions were included. They conclude that although nitrogen balances can be convenient tools for reducing nitrogen leaching they are not a direct measure for nitrogen leaching in any specific catchment.

Nutrient Management Planning (NMP), provided for in the Irish Waste Management Act (DELG, 1996), is a form of nutrient balancing in that it attempts to create an accounting system for nutrients. The objective of NMP is to minimise nutrient applications consistent with achieving optimum production targets while, at the same time, avoiding nutrient loss to waters (DELG, 1998b). Nutrient budgeting is also enshrined in Netherlands' government policy: MINAS (MINerals Accounting System) [Anon, 1995] requires all farmers to account for the nitrogen and phosphorus entering and leaving the farm gate. There are charged and levy-free surpluses available to farmers, which will steadily be decreased until 2008 (Oenema *et al.*, 1998). A simple mass balance model, relying on detailed databases, was employed to predict mean national groundwater nitrate concentrations for the full implementation of MINAS in 2015. Oenema *et al.* (1998) give full details of the mass balance model/balance equation and environmental databases employed by the Dutch and results obtained at national level. Their mass balance equation for simulating future groundwater nitrate concentrations is as follows:

$$[NO_3] = \{(N_{sur.} + N_{dep.} + N_{fix.}) - (N_{vol.} + N_{deni.} + N_{run.} + N_{immob.}) / V_{gw}\} \text{ x } F_{NO}^{3} \text{ x } 62/14 \qquad \text{(Eqn. 3.1)}$$

where

NO_3 = nitrate concentration in the groundwater (mg/l);
$N_{sur.}$ = levy-free N surplus following MINAS (kg/ha);
$N_{dep.}$ = N input through atmospheric deposition (kg/ha);
$N_{fix.}$ = N fixation through biological N_2 fixation (kg/ha):
$N_{vol.}$ = N losses through ammonia volatilisation (kg/ha);
$N_{deni.}$ = N losses through denitrification (kg/ha);
$N_{run.}$ = N losses through runoff and drainage (kg/ha);

$N_{immob.}$= net storage in the soil (kg/ha)

V_{gw} = groundwater recharge (10^3 m^3 /ha/yr.)

$F_{NO}{}^3$ = fraction of nitrate in N recharge (dimensionless)

62/14 = conversion factor of N to nitrate-N (dimensionless)

The European Environment Agency (EEA, 2000) reports that the results of a mass balance analysis highlights a nearly constant nitrogen surplus in the period 1990-1995 for the twelve EU countries. An initial downward trend (recently reversed) in the use of inorganic nitrogen fertiliser was attributed not to environmental awareness but to use of manures as nutrient supplements. Eurostat calculated Ireland's nitrogen surplus to range from 200,000 tonnes in 1990 to over 260,000 tonnes in 1995. Surplus nitrogen - a source of pollution – remained constant at 7.2-7.4 million tonnes/year from the combined fifteen EU member states, yielding the conclusion that agriculture is the main source of nitrate pollution (EEA, 2000).

3.6.3. Statistical Techniques

Examples of statistical methods include simple and multiple regression for single and multivariate variables, linear discriminant analysis, analysis of variance, correlation analysis, cluster analysis, geostatistical analysis [e.g. kriging] and time series (Reilly, 1997). These models do not attempt to define processes. Riley *et al.* (1990) state that "water quality is a multi-variate concept not defined by any single constituent", which prompts the NRC (1993) to conclude that multivariate statistical techniques are suited to the analysis of water quality and influencing physiographic and management data. If two parameters, or events, can be statistically related or correlated and scientifically justified then the resulting probability can be justified (Bauder *et al.*, 1993). Statistical methods can be used to evaluate, determine and quantify the associations between measurements of contaminant concentrations and various types of information that are thought to be related to the contamination (NRC, 1993).

Statistical methods incorporate data on known areal contaminant distributions and provide characterisations of contaminant potential for the specific geographic area from which data were drawn (Davis, 1986). Good regional databases are necessary for statistical model development.

The issue of scale, so often a problem in the reapplication of models based on physical relationships, is more easily overcome when applying a statistical model (NRC, 1993).

Examples of statistical models for hydrogeological applications are not prolific in the literature. Seyan *et al.* (1985) firstly used traditional hydrogeological techniques to identify partitioning in a dolomitic reef aquifer and then successfully employed multivariate cluster analysis to support earlier conclusions. Pedroli (1990) identified sixteen classes of shallow groundwater within a 20km^2 area using cluster and discriminant analysis of hydrochemical data. The variations in groundwater quality were found to be associated with landscape features, farm fertilisers, infiltrating and discharging water components. Bauder *et al.* (1993) developed a statistically supported probabilistic model to relate physiographic and land use characteristics to nitrate concentration in groundwater. It was found that soil groups and land slope were the two most significant factors affecting groundwater nitrate concentrations in that study. Ratha & Venkataraman (1997) successfully studied seasonal variation in the concentration levels of chemical and physical soil and groundwater parameters using linear discriminant analysis and partial correlation analysis. D'Agostino *et al.* (1998) used geostatistics to describe the spatial and temporal behaviour of nitrate concentration in an Italian Aquifer, and also to quantify the uncertainty of the analysis, by applying co-kriging using temporal subsets of data.

In Ireland, modelling nitrate concentrations, whether in groundwater or surface water, has not yet been attempted at any scales larger than point- or field scale. However, Daly *et al.* (2002) successfully modelled Irish river's P concentrations, using empirical methods employing statistical techniques, namely multiple regression and correlations, to derive relationships between catchment characteristics and water quality. GIS technology was employed and the data sets used included land use, climate, soil type and soil-P. This framework has potential for national scale nitrogen loss modelling, if such a task is deemed necessary. The importance of including more than one catchment characteristic in any relational analysis is stressed (Bauder *et al.*, 1993; Gerten & Krysanova, 1998; Arheimer, 1998).

3.6.4. Overlay and Index Methods

These methods combine various physical attributes in a simple form to give a qualitative or semi-quantitative analysis of an area's vulnerability to contamination (NRC, 1993). The capabilities of

GIS technology have encouraged the use of overlay methods, especially as their structure is to overlay layers of information in map form (Engel *et al.*, 1996).

Overlay and index methods can be used to assess intrinsic (related to actual physical characteristics) or specific (referring to a specific contaminant) vulnerability. The saturated zone is the reference location for most models in this class (Gogu & Dassargues, 2000). DRASTIC (Aller *et al.*, 1987) is an overlay methodology developed for wide-scale application [described fully in Appendix A]. Mc Lay *et al.* (2001) compared three approaches (dominant land use at or surrounding groundwater sampling sites, topsoil properties which reflect nitrogen cycling and the DRASTIC risk assessment model) and found that DRASTIC gave the best correlation with actual groundwater nitrate concentrations. They suggest that models such as DRASTIC that assess the risk of solute leaching to groundwater at a site, perhaps with a land management index included, are more useful for predicting areas for more intensive monitoring of groundwater. The general approach taken in the use of all overlay or index methods is that they help identify problem areas, which can then be further investigated using a more detailed approach to investigate the processes controlling contamination. Although the overlay process is less precise, less detailed information is required in order to obtain results.

Variables used in overlay maps include topographic information, unsaturated and saturated zone properties, depth to water table, recharge mechanisms and land use data. The relative importance of the physical attributes influencing the processes at play, the natural variability in the attributes used and the availability and spatial resolution of the available data are all important considerations when employing overlay and index methods (NRC, 1993). It is important that the assessment method be appropriate for the specific situation and that the weightings reflect the reality of the situation.

Coulter *et al.* (1993) employed an overlay procedure to create a series of 'aquifer vulnerability to nitrate' maps for each county at the request of Irish local authorities, detailing aquifer vulnerability to nitrate for each county. These risk maps were derived purely from soil classifications and nitrate loading (estimated for each DED using Central Statistics Office data). The soil vulnerability classification was based on the General Soil Map of Ireland, 2nd Edition (Gardiner and Radford 1980), agricultural census information and aquifer maps, published by the EC, reproduced on a county basis. Soil cover was hypothesised to be an important factor in deciding if an aquifer is vulnerable to increases in nitrates due to leaching. More recently, at far greater level of detail, the

GSI have prepared aquifer vulnerability maps for approximately 50% of the Ireland's area. These maps are referred to as groundwater protection schemes (DELG *et al.*, 1999) and many are available on the GSI web page (www.gsi.ie).

Index methods apply numerical rankings to those processes considered influential to loss of nutrients to the environment. Most methods use an annual, average, single value for a specific point location, but attributes can vary both spatially and temporally (NRC, 1993). Magette (1998) developed a weighted ranking scheme for Irish conditions. This system considers the factors affecting loss of nutrients from agriculture and their subsequent transport to receiving waters, to aid in decision making at both farm and field level. The weights and relative risks of nutrient loss were derived from professional judgement, like most other ranking schemes, as virtually no site-specific data exists from which to develop definitive relationships. The two stated considerations in assigning weights to each factor were the overall importance compared to other factors and the degree of control that an individual could exercise in influencing that factor.

Gogu & Dassargues (2000) reviewed current trends and future challenges in groundwater vulnerability assessment using overlay and index methods. Fritch *et al.* (2000) developed a predictive modelling approach for assessing aquifer pollution susceptibility using weighted available data variables (e.g. land use/land cover, soil permeability, depth to water table, aquifer hydraulic conductivity and topography). Corniello *et al.* (1997) compared four overlay methods to the same research zone using the same data. They showed that the relatively simple methods could provide similar results to the complex ones, which has been suggested before (De Willigen, 1991; Stockdale, 1999), in respect to all model types.

3.7. Uncertainty

Given that a model is a *representation* of reality (Addiscott, 1993) based on a perception of understanding of the details of a system, uncertainty regarding both the model and its outputs must be seriously considered. Although not widely discussed in the literature that details specific model applications, the issue of uncertainty in simulation outputs has been reviewed quite comprehensively (Beck, 1987; CAMASE, 1995; NRC, 1993; Stockdale, 1999). Peck *et al.* (1988) review the sensitivity of groundwater models to unrepresentative data (e.g., aquifer parameters varying with depth and errors in assumed boundary conditions or aquifer recharge).

3.7.1. Sources of Uncertainty

Uncertainties, inherent in all approaches, may derive from either

- **inaccurate model development** - e.g. incorrect model assumptions, inappropriate choice of equations, misrepresentation of processes, incorrect solving of model equations, scale effects or the incorrect determination of boundary conditions, or

- **data related errors** - e.g. errors incurred from the monitoring network design, sampling strategy or sample collection, laboratory analyses errors, errors due to natural spatial and temporal variability (e.g. soil physical characteristics), extrapolation, interpolation or averaging errors, data processing and handling errors.

Imperfect models and data are the norm rather than the exception (NRC, 1993). Most nitrate leaching models assume a homogeneous porous medium; the discrepancy between this assumption and the observed natural heterogeneity in field soils is a major problem in modelling water flow and solute transport (Feyen *et al.*, 1998). Soil variables may vary spatially and temporally. The error associated with either measuring, estimating or interpolating basic soil characteristics (e.g. by kriging) will express itself in a model (Vereecken *et al.*, 1992).

Even if the nitrate leaching model chosen is deemed perfect for a particular application, uncertainty resulting from data related errors is likely (Loague & Green, 1991). Predictions of nitrate losses should therefore be accompanied by information about the reliability of estimates, if they are to be used as part of a decision making process (Bouma *et al.*, 1996a & b). Uncertainties in adequate representation of micro-heterogeneity, occurring in structured, cracked or macroporous soils, and macro-heterogeneity, due to the inherent spatial variability of soil properties, have a distinct effect on water flow and solute transport simulations.

3.7.2. Uncertainty Analysis

Uncertainty estimates encourage realistic, and more justifiable, land use management and environmental policy processes (Stockdale, 1999; Van Herpe *et al.*, 2002). Brandstetter & Buxton (1989), cited in NRC (1993) grouped methods for evaluating uncertainty into five categories:

1. Classical statistical variance component analysis, which can be used to partition the total observed variance in the output to contributing factors.
2. First-order uncertainty analysis (FOUA) based on Taylor series expansion of the function (model) to evaluate variance of the output as a function of the variance in input parameters.
3. Statistical sampling methods that utilise a range of likely values for input parameters to assess the probable range of output parameters. Examples given are Monte Carlo simulation, Latin hypercube sampling, discrete-event simulation, and boot-strapping methods.
4. Stochastic modelling approaches that directly incorporate the parameter or process uncertainties in the model itself and provide direct uncertainty estimates of model outputs.
5. Bayesian methods when uncertainties in input parameters can be specified by either expert judgement or estimated from existing databases from which input parameter values have been obtained.

Examples of FOUA and Monte Carlo methods are provided in Peck *et al.* (1988). The NRC (1993) also report examples (e.g. Small & Mular, 1987; Jury & Gruber, 1989) of stochastic modelling approaches to evaluate uncertainty associated with climatic and soil variability in assessments of groundwater vulnerability

3.7.3. Discussion

Van Herpe *et al.* (2002), whilst pondering the conundrum of whether complex physical models or simple empirical models are a better approach, advocate an approach with as simple a structure as possible so that the impacts of parameter uncertainty (significant in even a simple model) can be assessed. Using the GLUE (Generalised Likelihood Uncertainty Estimation) procedure (Beven, 1991), to analyse each model parameter in turn and evaluate its sensitivity, their overall analysis concluded that uncertainty in their model was high but the procedure also highlighted the remedial steps required to reduce the model uncertainty.

Consideration of variances, as well as means, is required in giving information on reliability of model estimates (Addiscott, 1996b). The sampling variance of a measurement has been used as a criterion of its reliability since the beginning of statistics (Kendall & Stuart, 1973). However, applying statistical formulae to determine a reliable sampling strategy often results in a sample number far exceeding a viable option (Stockdale, 1999). Data challenges have already been discussed in section **3.5.5**.

The issue of scale also incurs uncertainty. Using models at scales other than those for which they were designed is not advised (see section **3.3.4**). Changing the scale of a model may result in changes in its scope, input values and data requirements (Stockdale, 1999). Models whose parameters are not too variable in space and are linear with respect to their parameters are required for modelling on a grid basis with validly averaged parameters (Addiscott, 1993). Thorsen *et al.* (2001) consider the scale issue in relation to assessing uncertainty in simulation of nitrate leaching to aquifers at catchment scale. It appeared that the magnitude of the uncertainty depends significantly on the considered temporal and spatial scale. Their simulations of flux concentrations leaving the root zone at grid level were associated with large uncertainties, whereas uncertainties in simulated concentrations at aquifer level on a catchment/aquifer scale were much smaller. They argue that the results of simulations at point/grid scale have such large uncertainties as to render point-scale process-based models of minor practical use. However, the duality of their scale-research findings implies that the subsequent reduction of uncertainty when reaching the catchment (aquifer) scale makes the simulated output useful again in practice. In conclusion they encourage definition of the type of simulation result, in terms of spatial and temporal scale, when discussing model uncertainty.

Peck *et al.* (1988) conclude that a staged development strategy with appropriate monitoring and periodic model improvement is the most common and practical approach for reducing uncertainty in groundwater model output.

3.8. Modelling Subsurface Zones

Various zones (subsystems) divide the subsurface. Contaminants, applied at the surface, or stored in the shallow subsurface, are lost from the system through plant uptake, volatilisation, and escape to the atmosphere, or leaching downwards to the water table. Leaching represents mass flow of a chemical constituent and is the product of water flux and dissolved chemical concentration (van der Heijde, 1994). Mass flow is dependent on the amount of applied water, the intensity of applied water, the saturated hydraulic conductivity of the soil, the chemical concentration, the soil's adsorption capacity, and, indirectly, temperature (Jury & Valentine, 1986). The presence of electrically charged clay minerals and organic matter, in association with the large surface area of the minerals and humus, can act to adsorb chemicals and thus remove them from chemical mass subject to flux (van der Heijde, 1994). Nitrogen forms such as ammonium are readily adsorbed to the clay minerals. However, nitrate is easily leached (refer to section 2.3). In order to model nitrate leaching to groundwater, the total path of the nitrate ions from their origin at the surface to their appearance in the aquifer can be divided into three distinct zones: the root zone, unsaturated zone and saturated zone or aquifer (Singh & Sekhon, 1978/1979). Each zone plays an important role in determining the amount of nitrate reaching the aquifer.

3.8.1. The Root Zone

3.8.1.1. Modelling Considerations for the Root Zone

The root zone is the upper part of the unsaturated zone where plant growth is supported. The root zone is the interaction area between the surface and subsurface. It is well aerated, has a network of roots, a higher organic matter content than deeper soil zones and has as its upper boundary the ground surface for all applied nutrients.

Nitrogen is applied, in organic or inorganic forms, and is transformed into plant-usable forms of nitrogen by microbes in the soil. The nitrogen cycle dynamics in the root zone are complex (as discussed in chapter 2) and so this zone is usually modelled as a distinct zone of the unsaturated subsystem. The typical nitrogen transformations considered in a root zone model have been shown in figure 2.1. Nitrate can be taken up by the crop from the soil solution in the root zone, incorporated into the soil organic matter, denitrified and leached to deeper soil and groundwater zones (Addiscott, 1996a).

Nitrate in the root zone, in excess of plant requirements, and the vertical movement of water are necessary for nitrate leaching (Addiscott *et al.*, 1991). Excess rainfall (rainfall minus evapotranspiration) patterns and antecedent moisture conditions influence nitrate leaching and groundwater concentrations (Burt & Trudgill, 1993). Nitrate leaving the root zone will then undergo transformation in the deeper unsaturated zone and upper aquifer that will influence the observed nitrate concentrations in groundwater.

The root zone's bottom boundary is the maximum depth that the roots can penetrate. The thickness of the root zone, measured from the ground surface, depends on the kind of crop, soil and climate, but can be considered constant for a particular crop in an area (Singh & Sekon, 1978/79). Perusal of Irish Soil Survey information suggests grassland root zones typically less than 100mm. In Ireland, the roots beneath grassland rarely extend 150mm below the ground surface (Culleton, *pers. comm.*, 2001).

3.8.1.2. Root-Zone Models Reviewed

Point and field-scale nitrogen process models provide an estimation of nitrate leaving the root zone and examination of control processes. In this review the following root zone models have been considered:

- NCYCLE (Scholefield *et al.*, 1991);
- NLEAP (Shaffer *et al.*, 1991);
- RZWQM (USDA, 1992, 1995);
- CREAMS (Knisel, 1980);
- EPIC (Williams *et al.*, 1983);
- AGNPS (Young *et al.*, 1987, 1989).

Details for each of these models can be found in Appendix A: model structure, assumptions used in model development, tabulated data requirements and analysis of field applications are documented for each individual model. This author completed these individual model reviews so as to inform selection of a model appropriate to both the posed research question and Irish data and resource availability. Section 3.9 provides details regarding the complete strategy adopted for modelling nitrate leaching through the subsurface to the groundwater body, as deemed appropriate for this work.

3.8.2. The Unsaturated Zone

3.8.2.1. Modelling Considerations for the Unsaturated Zone

Solutes leaving the root zone travel through the unsaturated zone to the saturated zone. The various processes occurring in this region play a major role determining both the quality and quantity of (soil) water recharging the saturated zone (Feyen *et al.*, 1998).

Three main factors are stated to govern nitrate concentration in the unsaturated zone: the difference between nitrogen inputs and crop removal; drainage volume; and soil profile characteristics (Singh & Sekhon, 1978/1979). The dominant parameter affecting flow and contaminant transport in the unsaturated zone is hydraulic conductivity (van der Heijde, 1994). Before modelling of nitrogen dynamics can start, the water flow in the unsaturated zone has to be modelled with sufficient accuracy (Hack-ten Broeke, 2000).

The majority of unsaturated zone models conceptualise the soil system as a layered one-dimensional soil column. Water flow, with a calculated nitrate concentration, is simulated using mathematical equations. Many (process-based) models employ Richard's equation to describe unsaturated flow. Richards' equation is derived by combining the mass balance principle with the equation of motion, Darcy's law, ignoring compressibility effects of matrix, fluid and air (van der Heijde, 1994). For modelling unsaturated zone water flow, and hence nitrate transport, accurate representation of the physical soil properties is crucial for all physically based (mechanistic/process based) models (Monke *et al.*, 1989; Hack-ten Broeke, 2000) (refer to section 3.6.1 for more detailed discussion of process-based model's simulation). However, Addiscott & Whitmore (1991) created a functional model, SLIM, whose input parameters can be estimated from the percentages of clay and other soil components.

Because of dispersive and diffusive mechanisms, nitrate movement through the zone of aeration (root zone and unsaturated zone) is conceptualised to be slower than bulk fluid movement, as a result of water movement at different rates through pores of different sizes (Bigar & Nielsen, 1967). However, in soils when the rainfall rate exceeds the infiltration rate of the soil matrix, excess water and solutes may move quickly down through the soil profile using, or sometimes creating, structural voids (or 'macropores') even though the matrix remains unsaturated (Burt & Trudgill, 1993). Feyen *et al.* (1998) distinguish between micro-heterogeneity, occurring in structured, cracked or macroporous soils, and macro-heterogeneity, due to the inherent spatial variability of soil properties, both having a distinct effect on water flow and solute transport processes.

Van der Heijde (1994 & 1996) presents a technical review of modelling in the unsaturated zone and associated analytical and numerical solutions. Performance of a model can be evaluated by comparing time series of measured and simulated values, but the complexities of site-specific process interactions may make comparisons difficult (Engelke & Fabrewitz, 1991a &b).

3.8.2.2. Unsaturated Zone Models Reviewed

The unsaturated zone nitrate leaching models discussed and tabulated in this review are:

- LEACHN (Hutson & Wagenet, 1991);
- SLIM (Addiscott & Whitmore, 1991);
- DAISY (Hansen *et al.*, 1990);
- SOIL-SOILN (Johnsson *et al.*, 1987 & Jansson, 1991), and
- RENLEM (Kragt & de Vries, 1987, Kragt & Hack-ten Broeke, 1991).

Again, details for each of these models can be found in Appendix A: model structure, assumptions used in model development, tabulated data requirements and analysis of field applications are documented for each individual model. This author completed these individual model reviews so as to inform selection of a model appropriate to both the posed research question and Irish data and resource availability. Section 3.9 provides details regarding the complete strategy adopted for modelling nitrate leaching through the subsurface to the groundwater body, as deemed appropriate for this work.

Two unsaturated zone models were also found, in the literature, which continued the simulation to the saturated zone:

- ANIMO (Berghuijs *et al.*, 1985 & Ritjema *et al.*, 1995), and

- SWMS_2D (Simunek *et al.* (1995, 1996).

These models are also presented in Appendix A because the distinction between subsurface flow in deep soils and in shallow aquifers is sometimes hard to make; Burt & Trudgill (1993) count the division between 'soil water' and 'groundwater' as necessarily somewhat arbitrary.

3.8.3. The Saturated Zone (Groundwater)

3.8.3.1. General Groundwater Concepts

Water soaks into the ground to collect within pores in soil and rock. The amount of water held in a rock depends on its porosity: This is the proportion of the volume of the rock that contains of pores, and is usually expressed as a percentage of the total rock mass (Brassington, 1998). When all the pores are full the zone is described as saturated and its upper boundary is termed the water table. In Ireland the water table may be in the subsoil or rock. Water below the water table, *i.e.* in the saturated zone, is called groundwater. Generally, a water table mirrors topography in a subdued way, so it is deeper beneath hills and shallower beneath valleys; it may even coincide with the ground surface where wet marshy ground, ponds, springs or rivers are surface expressions (Price, 1996). However, groundwater in karstified environments behaves differently, see section 3.8.4.2 below.

The rate and direction of groundwater movement depends on the hydraulic and transmissive characteristics of the basin sediments and on the hydraulic gradient (Singh & Sekhon, 1978/1979). Many discuss the governing equations for water and solute flow in groundwater bodies (e.g. Hermance, 1998; Peck *et al.*, 1988; Anderson & Woessner, 1992; van der Heijde & Elnaway, 1993). Burt & Trudgill (1993) present the most extensive review of nitrate in groundwater and the sources and pathways of nitrate in groundwater are shown in Figure 3.1. Further discussion regarding hydraulic characteristics of the subsurface, and how they were measured in this study, can be found in chapter five.

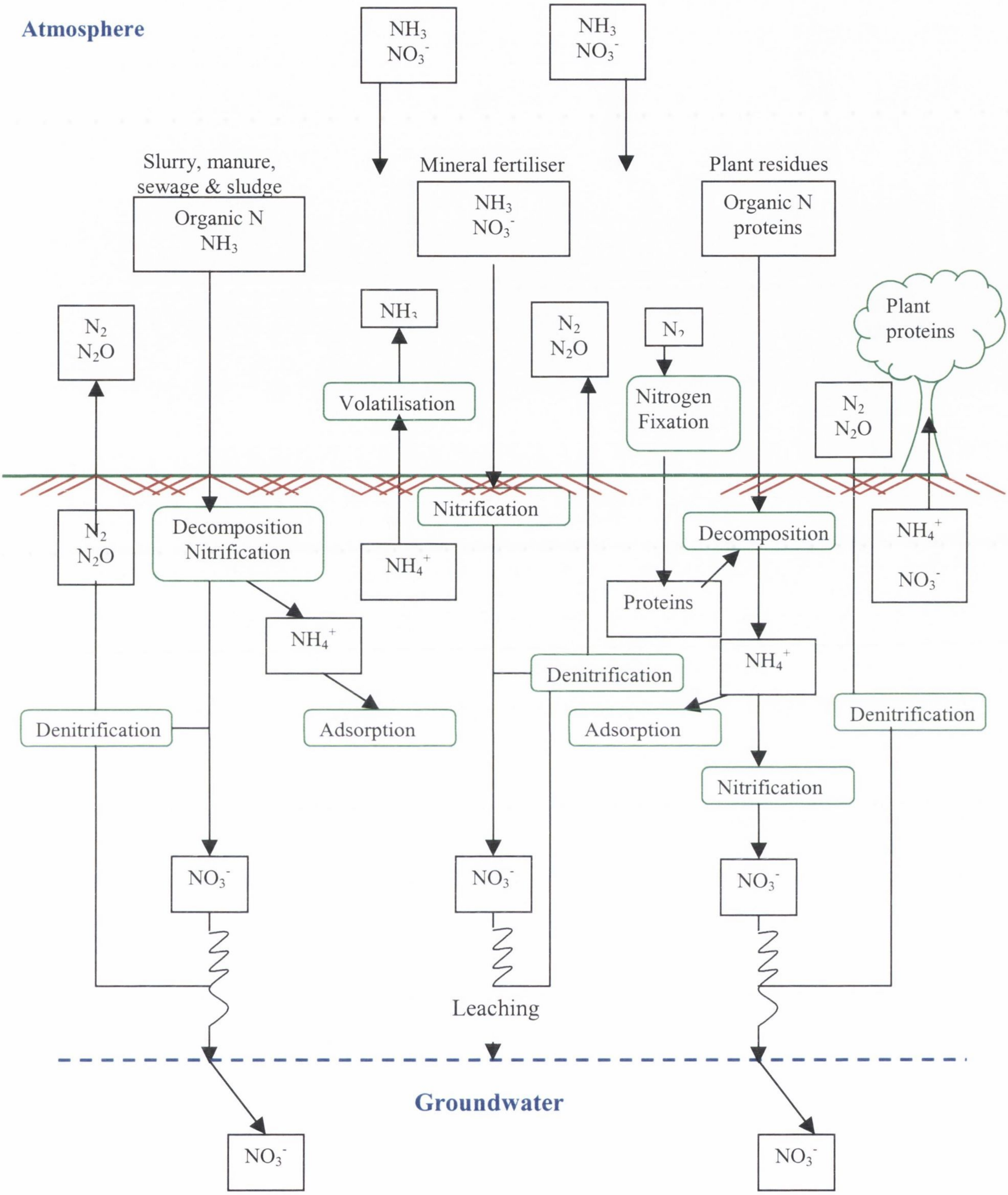


Figure 3.1 Sources and pathways of nitrate in groundwater (redrawn from Burt & Trudgill, 1993, source: Freeze & Cherry, 1979).

3.8.3.2. Karstic Groundwater Environments

Widespread fracturing in Irelands bedrock has resulted in aquifers that are characterised by groundwater flow in fissures. Karstified limestone underlies approximately 50% of the country and this limestone is the main groundwater source and resource in the country (Coxon & Drew, 2000). Karstified aquifers are characterised by rapid conduit flow that requires different modelling considerations to those typically discussed in the literature.

Modelling karstic systems is complex because of the interaction of different flow mechanisms. Modelling nitrate transport when preferential flow occurs, in the context of unsaturated zone contaminant transport, is of some significance here also in the context of dual transport phenomenon. Karst geology is associated with shallow soils and rapid preferential flow down sinkholes and cracks (Mc Lay *et al.*, 2001). Richards *et al.* (1996) report higher nitrate concentrations in a karst region than the rest of their study district.

Groundwater, within a karst limestone aquifer, is thought to flow in three main hydrogeological regimes (Kelly & Motherway, 2000):

1. An upper, shallow, highly karstified weathered zone, known as the epikarst, in which water flow is quick through solutionally enlarged channels, which rapidly respond to rainfall.

2. Cave systems and large, interconnected, solutionally enlarged channels form a deeper zone of flow, which has high velocities.

3. A slower, dispersed flow also occurs in smaller fracture and joint systems outside the principal flow system.

3.8.3.2.1. Modelling Karst Systems

Adams & Parkin (2001) further developed the established SHETRAN model (Birkinshaw & Ewen, 2000a & b) for flow in karstic hydrogeological conditions. The intended use of the model is to predict the effects of different catchment management strategies on water supplies, and also the effects of climate change on water resources. Flow processes requiring consideration when modelling karst systems are shown in Figure 3.2.

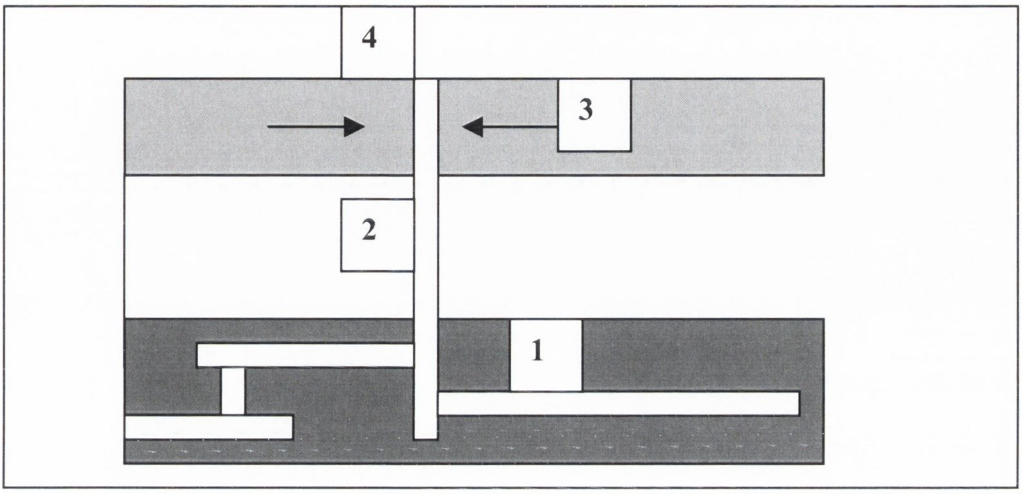


Figure 3.2 Karstic flow processes modelled in SHETRAN (from Adams & Parkin, 2001).

(1) Flow in a sub-horizontal cave network in the saturated zone
(2) Shafts
(3) Epikarst bypass flow generation
(4) Interactions with surface flows

The modifications made to SHETRAN to simulate karstic aquifers were as follows (Adams & Parkin, 2001):

1) The addition of a preferential "bypass" flow mechanism to represent vertical infiltration through a high conductivity epikarst zone;
2) The coupling of a pipe network model to a variably-saturated three-dimensional groundwater component to simulate flow under pressure in saturated conduits;
3) The coupling of karst surface features to the conduit system. Also, a particle tracking routine was added to trace the path of hypothetical particles with matrix and pipe flow to discharge points such as springs. The particle tracking

routine enables use of the model in defining groundwater protection zones around a source in catchments that are vulnerable to diffuse source pollution.

Clemens *et al.* (1996) are reported by Adams & Parkin (2001) to have used a similar modelling approach, by adding conduits to an existing porous media groundwater flow model (MODFLOW) to simulate the formation of a cave system through calcite dissolution. However, both of these approaches (Clemens *et al.*, 1996; Adams & Parkin, 2001) consider groundwater flow only and SHETRAN and MODFLOW require so much site-specific information that their application in an Irish context is unrealistic given Irish data availability. Therefore, other strategies will be considered in this review.

In an Irish context, the hydrogeology of a lowland karst area was successfully modelled by application of a pipe-network model HYDROWORKS (Johnston & Peach, 2000). Because the conduit system was well defined and the size of fissures reasonably well understood, the network/conduit representation was successfully represented with what is essentially a hydraulic pipe network model. The St. Venant equations were used to simulate the flows in pipes, open channels and storage elements. However, this approach requires a high level of conduit characterisation, which is not readily available for most Irish karst aquifers.

3.8.3.3. Modelling Considerations for Simulating Nitrate leaching to Groundwater

For any given soil type, the amount of annual fertilisation and precipitation are the main readily quantifiable factors influencing groundwater recharges nitrate concentrations (Mull & Pfingsten, 1991a), with crop cover and fertiliser type designated as nominal factors. The two principal loading terms requiring quantification are therefore nitrogen application sources and precipitation. Given constant fertilisation the variance in the yearly nitrate concentration in the groundwater recharge (percolating water) is mainly a function of the weather (CEC, 1991).

Denitrification, dilution, advection, dispersion and mixing in the groundwater body, aquifer side-flows, nitrogen uptake by deep rooted riparian vegetation, travel times, and other factors are important processes that impact groundwater nitrate concentrations (Shaffer, 1995). It is generally accepted that convection, diffusion and denitrification are the most significant mechanisms in the transport of nitrate in the saturated zone (Wuttke *et al.*, 1991).

Reliable predictions of contaminant movement can only be made if the processes controlling convective transport, hydrodynamic dispersion, and chemical reactions affecting dissolved chemicals in groundwater are well understood (Konikow, 1976). Even in static water, solutes diffuse along the concentration gradient from high to low concentration and if the water is moving convection also occurs: that is the mass transport of water, and any solute dissolved in it, from one location to another (Burt & Trudgill, 1993). The combined movement of convection and diffusion is referred to as dispersion (more formally as hydrodynamic dispersion). A dilution of local loadings in flowing groundwater is attributed to hydrodynamic dispersion (Zahn & Grimm, 1993).

Dispersion causes a zone of mixing to develop between a fluid of one composition that is adjacent to or being displaced by a fluid of another composition (Domenico & Schwartz, 1990). Convective transport and hydrodynamic dispersion are both mechanisms that can be modelled on their strong dependence on groundwater flows (Wuttke *et al.*, 1991). The convective-dispersion equation must be solved to interpret time of travel information (Oakes, 1988). Kazmann (1987) airs concerns about problems with dispersivity that are commonly ignored, particularly that dispersivity seems to possess obscure properties that do not enter equations in a manner that breeds confidence in the results of the simulation. A further complication in a porous medium is that some portions of water, and its' solutes, travel faster than others, through large pores or by more direct routes (Burt & Trudgill, 1985).

Denitrification is a process whereby nitrate-nitrogen (NO_3-N) is reduced microbiologically to nitrous oxide (N_2O) and/or dinitrogen (N_2) under reduced or anaerobic conditions; therefore denitrification may be modelled as a sink term (Wuttke *et al.*, 1991). The findings of Stychen & Storm (1993) [Appendix A] are instructive in modelling the influence of denitrification in the groundwater layer at the redoxcline (the zone where groundwater condition changes from oxidised to reduced). However, the karstified hydrogeological environment under investigation in this study is unlikely to support long residency times or reduced conditions.

Altman *et al.* (1995) discuss the dilution of non-point source nitrate in groundwater. They prove that comparison of nitrate and chloride concentrations as an effective method of determining whether nitrate concentrations decrease due to dilution. Because chloride behaves conservatively in groundwater decreases in its concentration with depth, in the direction of groundwater flow, must be caused by dilution (Altman *et al.*, 1995).

Two trends have been identified in groundwater modelling (CEC, 1991), as follows:

1) Trend towards more sophisticated models describing complex biochemical and physical reactions of chemicals/contaminants.

2) Trend towards use of more simple models that are incorporated into information systems (e.g. GIS).

Modelling nitrate leaching through the subsoil profile to an aquifer can be conceptualised in a very simple, qualitative way using the same basic assumptions, concerning a generic contaminant, employed by the DRASTIC methodology (Aller *et al.*, 1987). Those assumptions are as follows:

(a) Material introduced at the land surface, as a soluble solid or liquid, travels to the aquifer with recharge waters derived from precipitation;
(b) The mobility of a contaminant is assumed to be equal to that of the groundwater;
(c) Attenuation processes are assumed to go on in the soil, vadose zone and aquifer.

3.8.3.4. Groundwater Models Reviewed

In terms of fate and transport in groundwater bodies, nitrate models are few and far between. Few model applications regarding groundwater modelling of nitrate transport were found. Kinzelbach *et al.* (1990) discussed groundwater quality models and their application in agricultural problems but that review is dated now.

The following groundwater models were reviewed (those groundwater applications that did not assign a specific name to their model are identified, in this review, by author's name):

- Stychen & Storm (1993);

- Lasserre *et al.* (1999);

- GLEAMS (Leonard *et al.*, 1987, Knisel, 1993);
- DRASTIC (Aller *et al.*, 1987);
- MODFLOW (Harbaugh and McDonald, 1996) & MT3D (Zheng, 1990);
- RAM (ESI, 2000).

Again, details for each of these models can be found in Appendix A: model structure, assumptions used in model development, tabulated data requirements and analysis of field applications are documented for each individual model. This author completed these individual model reviews so as to inform selection of a model appropriate to both the posed research question and Irish data and resource availability. Section 3.9 provides details regarding the complete strategy adopted for modelling nitrate leaching through the subsurface to the groundwater body, as deemed appropriate for this work.

3.8.3.4.1. Other Models Reviewed

These models are not strictly groundwater models but they were investigated to see if any could be adapted for use in this study. Most of these models, listed below, were developed as catchment scale models that either considered surface water only or, in some cases, combined catchment resources. The modelling approaches reviewed are as follows (again, those model applications that did not assign a specific name to their model are identified, in this review, by author's name):

- Jordan *et al.* (1994);
- MAGPIE (Lord & Anthony, 2000);
- INCA (Whitehead *et al.*, 1998);
- NCATCH (Scholefield & Rodda, 1992);
- Van Herpe *et al.*(1998; 1999; 2002);

- Arheimer & Brandt (1998).

While further development of these models was not necessary for this work, model details and tabulated data requirements have also been included in Appendix A, in the same format as all other models reviewed. The concepts employed in these models might be useful, in the future, for work associated with implementation of Water Framework Directive (EC, 2000) or in future research in the area of nutrient mobilisation at catchment- or national-scales.

3.9. Discussion - Simulating Nitrate Leaching To Groundwater

Groundwater flow models (e.g. MODFLOW, detailed in Appendix A) could be used to model nitrate behaviour in the saturated zone but their use is complicated, especially their calibration. Initial and boundary conditions must be set in order to solve the transient flow equation. Data related to initial conditions and change in storage are necessary only when transient effects are to be investigated (Peck *et al.*, 1988). Steady state models require less data but would not show annual patterns of nitrate loss. Initial conditions for saturated flow systems are given by values for the piezometric head throughout the area to be modelled. Boundary conditions are specified on the periphery of the model domain, either at the border or at locations within the system where system responses can be quantified (e.g. surface water levels, well abstractions). Boundary conditions for flow simulation must be of three types: specified head, specified flux, and head-dependant flux conditions (van der Heijde & Elnaway, 1993). Because of uncertain nitrate input concentrations in space and time, variations in groundwater flow patterns and difficulties in quantifying denitrification processes; the use of groundwater flow models for nitrate applications incurs heavy uncertainty (Meier, 1989). Mull & Pfingsten (1991b) suggest that if groundwater flow models are to be used, the model should be calibrated for the area first and then the transport model is applied to predict nitrate migration in the aquifer. Further, calibration of the transport model will allow future predictions of nitrate leaching in the area. Kazmann (1987) concludes that predictions of even elaborate models will do nothing that could not be done using gradients and computed travel times, both methods having the same degree of accuracy. The above discussions again highlight the uncertainty inherent in any attempt to model a system by quantitative representation and description of processes in a systematic model.

Models are a tool to be used in the evaluation and solution of real contamination threats and problems. However, threats to groundwater and other elements of the environment exist at scales larger than those many existing models were intended for. There is an extensive array of existing models describing nitrate leaching from agriculture, but few have been designed to simulate leaching to a groundwater receptor. Many of existing models describe the leaching process at plot or field scale. The National Research Council (1993) urges, "for comprehensive evaluation of a regional vulnerability assessment model, application at field-plot scale should be based on the same type of detail as exists at the regional scale".

Considering the large number of models and techniques presented in this review, those who advocate model-minimalism speak volumes to those acutely aware of Irelands lack of comprehensive databases required for model development (e.g. soil hydrological characteristics) and subsequent validation (e.g. comprehensive temporal and spatial trends of groundwater nitrate concentrations). The simpler functional approaches (e.g. NCYCLE: Scholefield *et al.*, 1991) are advocated by model reviewers (De Willigen, 1991 and Stockdale, 1999), and are more appropriate for policy-focussed research and land-use management.

Data availability is an issue when considering use of a process-based model (data challenges have been discussed in section 3.3.5). It is often not possible to collect the entire field data required for input to data-hungry models (Stockdale, 1999). Estimation of input parameters, or approximation and interpolation from existing data, for process-based models renders the method no better, yet far more complex and labour intensive, than qualitative approaches such as index or overlay methods (e.g. Magette, 1998). Selection of an appropriate national modelling strategy for simulation of nitrate leaching from dairy farming to groundwater requires full consideration of Ireland's available data. Relatively little research has been carried out on nitrates in groundwater in Ireland. In addition, inconsistencies in monitoring result's reporting and monitoring intervals complicate data usage. In 1997 the EPA completed a 'Nitrate Report' for each county. However, these data are limited due to the fact that they are collected for monitoring not modelling (the EPA groundwater-monitoring network is sampled twice yearly only). Local Authority data, for specific counties, may be more useful but the applicability of public-supply boreholes to environmental assessments has already been questioned (Evers, *pers comm.*, 1999).

Often the individually quantified process outputs from a complex, high maintenance model cannot be measured in the field (model validation) with true confidence or certainty (Vereecken *et al.*, 1991). An EU detailed evaluation and implementation of five process based models found that the leaching models showed less variation in estimation of leaching than the 'substantial' differences obtained, between models, in the estimation of actual transpiration, net mineralisation, plant uptake and denitrification (CEC, 1991). Short (2000b) highlights that the main problem with any mechanistic model is to correctly determine the land area load of nitrogen from agricultural use, atmospheric fallout in rain, fixation by clovers where necessary, removal by crops and removal/alteration of form in both soil and groundwater processes. Pierce *et al.* (1991) used nitrogen budgets in association with a percolation index to estimate nitrate leaching. Nutrient budgets have been used in the implementation of groundwater- nitrates reduction policy and groundwater-nitrates future scenario modelling in the Netherlands (Oenema *et al.*, 1998). Mull & Pfingsten (1991a) stress that input variations at the surface are only important in the vicinity of the input and not on a global scale.

For groundwater simulations, when contaminant transport is the issue, a contaminant loading must be calculated previous to flow simulations. Point- and field-scale nitrogen models can be used to determine nutrient loading leaving the root zone. This loading is then usually applied as a recharge rate with a given contaminant concentration (e.g. Lasserre *et al.*, 1999; Jordan *et al.*, 1994). Transport of the concentration with flow must be simulated with a contaminant transport model. Saturated contaminant transport modelling without accounting for dispersion is simply particle tracking simulating advective transport (e.g. MODPATH) and this has been a common approach in the environmental industry because of its expediency and the usual lack of data to support more sophisticated fate-and-transport analysis.

3.9.1.1. Selection of Appropriate Root Zone Model

Of all models reviewed, NCYCLE (Scholefield *et al.*, 1991) is the root-zone model of most relevance to the factors influencing nitrate leaching and available environmental databases in Ireland. It is a simple, mass balance, model that is already under further development for Irish climatic conditions by the original UK team of model developers and Teagasc, Johnstown Castle, within the same EPA research contract that funded this research project (refer to section 1.5.1 for details). The NCYCLE model will be employed in this work to simulate nitrate available to leaching from each different agricultural treatment in operation on a typical Irish dairy farm. The simulated leaching rate, outputted from NCYCLE, will then act as the source term for simulation of nitrate leaching to groundwater.

Mass balance models were discussed in section 3.6.2. NCYCLE's successful application in the UK is attributed to the mineralisation sub-model that takes into account soil texture, sward age, previous cropping history and the climatic zone. NCYCLE requires that a climatic zone be specified, thereby referencing altitude and latitude, primarily concerning itself with temperature as the main climatic influence on mineralisation with moisture supply deemed to have a lesser effect (Scholefield *et al.*, 1991). It must be highlighted that there is no hydrological component within NCYCLE; the model provides a loading of nitrogen that is available to leaching from the root zone. This load will essentially be applied as the nitrogen source term for an appropriate hydrological/ hydrogeological model. Also of note, NCYCLE is capable of simulating nitrogen cycling, and consequent nitrogen available to leaching, on an annual time-step only. Full details for NCYCLE, and all other reviewed models, can be found Appendix A.

Neither NLEAP, RZWQM nor CREAMS were selected because they are all USDA models, which have been developed to rely on particularly detailed databases that are not available here in Ireland. NLEAP has recently been successfully employed within the national scale nitrogen risk assessment model, NIRAMS (Dunn *et al.*, 2003a & b), developed in Scotland (see section 3.8.4.4). However, the successful Scottish application of NLEAP relied heavily on the HOST (Boorman *et al.*, 1995) soil hydrological classification system but, again, this database resource does not exist in Ireland.

NLEAP is essentially a screening tool but Magette (1998) has developed a weighted ranking scheme, specifically for Irish conditions, that considers the factors affecting loss of nutrients from agriculture and their subsequent transport to receiving waters, to aid in decision making at both farm and field level [see section 3.6.4]. Although NLEAP is more subsoil and process orientated than Magette's subjective methodology, the current phase of EPA research funds further development and application of the Magette ranking scheme and it would be more logical that if a ranking scheme was to be chosen, it should be one that Magette has developed for Irish conditions. However, for the purposes of this investigation a quantitative model was required, which ruled out Magette's scheme.

Another reason for not selecting RZWQM is that it is an arable simulation tool with specific emphasis on pesticide dynamics for US applications. In order to use a model for a grassland application it must have a grass growth component in which all the relevant mechanisms such as nitrogen uptake, root development and nitrogen fixation are simulated. RZWQM has been used for grassland simulations in a limited way but does not have a detailed mechanistic grass-growth model (Ahuja, pers. comm, 2000). The model does have a quick plant routine that allows grass growth in a simple way, for the purpose of taking up water and nitrogen, in this way, the movement of water and nutrient balances can be simulated for agricultural application.

CREAMS was designed as a scenario tool for long-term simulation of different agricultural management scenarios and as such is not entirely relevant to this work.

3.9.1.2. Strategy for Modelling the Unsaturated Zone

None of the reviewed models were selected as appropriate in the development of a strategy for modelling nitrate leaching from dairy farming to groundwater. The decision to not model the nitrate load as it migrates from the bottom of the root zone to groundwater was based on many reasons, some of which are outlined for specific reviewed models below. However, the opinions of Mull & Pfingsten (1991b) most succinctly convey the general reasoning: if the aim of an investigation is saturated zone characterisation, and the nitrate loading can be quantified, there is no necessity to investigate the total flux of nitrogen from the soil surface through the subsurface regime, it is sufficient to investigate the saturated zone for groundwater quality modelling. This was one of the conclusions of one element of a multi-faceted research project concerning modelling nitrate leaching to groundwater from agricultural soils under the EU Fourth Framework Environmental Research Programme (CEC, 1991).

The country of origin of a model is also an important consideration. In the Netherlands it is relatively easier to model/link unsaturated and saturated zones: The modelled output from the root zone can acceptably be considered the input to the saturated zone, as the groundwater table is often found at <200cm below ground level (e.g., ANIMO and SWMS_2D). Also, given the importance of subsoil carbon and organic matter contents in controlling nitrogen cycle activity, the sandy soils of the Netherlands or the lower organic matter contents of US subsoils, are sure to influence model development, equations and hence outputs. Climatic differences are another important issue. SOIL-SOILN and DAISY are heavily mechanistic models developed in countries that have severe winters. These countries do not share our experience of some springtime peaks of nitrate leaching (Neil, 1989), which is attributed to temperate winter conditions allowing mineralisation to occur throughout the winter. Therefore, none of these models are recommended as appropriate for further development in the context of an Irish strategy to model nitrate leaching to groundwater.

LEACHN is an unsaturated zone nitrate leaching model that has already been applied in an Irish research project (Mulqueen *et al.*, 1999). However, it is not a model advocated by this reviewer. It is heavily mechanistic; a trait shared with many of the other unsaturated zone models reviewed. The range of processes considered incurs heavy input data requirements, which causes problems in both data collection and model validation (refer to sections 3.5.3 & 3.5.6). Estimated data in a large detailed model, with many parameters, will give less reliable results than few measured data in a simple model, so long as both adequately describe the system (Bouma *et al.*, 1996a). For these, and all the other arguments presented, in this literature review, regarding model complexity, scaling-up, model errors and inherent uncertainties, it would seem more sensible to use a simpler modelling approach.

SLIM is a functional model, which relies on fewer input parameters that are not overly sensitive to variability so model performance is not hampered. Extensive validation of SLIM in the UK might add to SLIM's attractiveness for application here in Ireland, if modelling the unsaturated zone was thought appropriate. Both SLIM and NCYCLE are components of the UK national modelling framework MAGPIE (Lord & Anthony, 2000). However, a national scale nutrient modelling framework already exists for Ireland (Daly *et al.*, 2002), albeit relating to P, which has received considerable investment from the EPA. It is suggested that for the purposes of policy-focussed research, existing Irish approaches should be further developed rather than effort invested in process-based unsaturated zone modelling.

3.9.1.3. Selected Strategy for Modelling Nitrate Leaching to the Saturated Zone

Only one model demonstrated a utility capable of easy representation of karstified systems in association with an easily accessible model framework and low data demands: the RAM (ESI, 2000) model was therefore selected as the most appropriate hydrogeological model for this study. The RAM model was originally developed for risk assessment simulations. Full model details can be found in Appendix A. Given that low data demands and model simplicity were paramount considerations and that the intended model should be compatible with the risk framework currently adopted by the GSI in their vulnerability assessment methodology, it seemed appropriate to select a risk model that has been developed within the source-pathway-target framework.

The source-pathway-target model of risk has already been accepted in an Irish context (e.g. GSI groundwater protection schemes (DELG *et al.*, 1999)). Misstear *et al.* (1998) detail the theory of risk as it is applied in Irish hydrogeology: the GSI groundwater vulnerability assessment methodology is essentially based on the concept of risk (see section 5.3.4 for more details and section 6.1.1.5 for the vulnerability assessments carried out in this work). With reference to the source-pathway-target model and nitrate leaching, the source would be the residual nitrate in the root zone at the beginning of the leaching season; the pathway would be the subsoil and unsaturated zone and the target is the groundwater body. Within the RAM model (ESI, 2000), impact on the target (groundwater) is assessed using the appropriate water quality standards, which are selected by the user.

The work of Johnston & Peach (2000) informed selection of the RAM model. Their application of a network model to a karstified hydrogeological environment demonstrated that models that have been developed for other purposes could merit attention for potential solution of the problem under current consideration.

Short (2000c) suggested a personal computer spreadsheet approach to modelling nitrate leaching to groundwater, employing a black box methodology with boxes linked by simply defined relationships. He assumed that the nitrogen forms leaching into the water table (ammonium and nitrate) are well mixed in the top one metre depth only; this mixing is a function of aquifer porosity, particle-size and groundwater flow velocity. The simple principles advocated by Short (2000c) were found in the RAM model (ESI, 2000). As previously stated, simulation output from NCYCLE will be used to provide the source leaching rate for simulation of nitrate leaching to groundwater.

The limitation of the selected modelling approach is that only annual simulations are possible. Temporal dynamics of loss is linked to hydro-meteorological impact, especially biochemical seasonality and antecedent hydrological conditions (Arheimer, 1998). Many models have been discussed which have been proven to predict total loss of nitrate from the system, for any given year. However, it is the timing of nitrate loss that even complex models find difficult to predict (Stockdale, 1999). Future Irish work in this area will require more resources and GIS expertise.

The necessity for using GIS systems in this type of modelling work is well documented in the literature (see Appendix A). Lasserre *et al.* (1999) used GIS to link an nitrogen model and a groundwater flow model. Observations and predictions of nitrate concentrations in groundwater matched well. Wendland *et al.* (1998) combined submodels, within a GIS environment, relating to nitrogen balance, groundwater recharge, groundwater flow and nitrate degradation to form a comprehensive model describing the flow of nitrate in the soil and groundwater of Germany. The model was not constructed to calculate actual concentrations in space and time, but to provide comparative analysis of potential nitrate hazard areas. They used their model on a supraregional scale to evaluate the impact of various nitrogen reduction strategies on the nitrate pollution of soil and groundwater in Germany. Wuttke *et al.* (1991) made partial use of GIS to complete an agro-ecosytem model, employing EPIC as the nitrogen model. Poor validation of their predicted results would suggest that it is better to use an established groundwater flow model (e.g. MODFLOW) rather than attempt a complex approach tailor-made for a particular system. Stychen and Storm (1993) achieved an integrated approach with the DAISY/MIKE-SHE modelling approach, which successfully modelled catchment loads and surface and groundwater nitrate concentrations. The NIRAMS model Dunn *et al.* (2003a & b) also requires a GIS environment. This model warrants further attention for Irish application towards modelling temporal nitrate-nitrogen trends (see discussion in section 6.6.5), towards identifying critical periods of loss. The selected strategy adopted in my work operates on an annual scale, which is relevant to policy such as the Nitrate Directive (EEC, 1991a).

3.10. Conclusion: A strategy for Modelling Nitrate Leaching from Dairy Farming to Groundwater

The NCYCLE model (Scholefield *et al.*, 1991) has been selected to simulate nitrate leaching from a typical Irish intensive dairy farm. NCYCLE is a root-zone model. Nitrate leaching through the unsaturated zone will not be simulated using a specific unsaturated zone model. Instead, the hydrogeological risk assessment model RAM will be employed for unsaturated and saturated zone modelling. The NCYCLE model will provide the leachable nitrate source data to RAM (ESI, 2000). The RAM model was been selected for the following reasons:

- Within RAM the prediction of contaminant transport and fate is based on the source-pathway-receptor approach enshrined in the vulnerability assessment methodology already adopted by the GSI (Fitzsimons *et al.*, 2003) and groundwater protection schemes (DELG *et al.*, 1999);

- data input requirements are substantially less than those of any other model reviewed and are also more available for extension of this model for application for Nitrate Directive policy-making on a national scale;

- the software utilises the familiar Microsoft Excel environment, with standard editing and calculation facilities, which ensures great model transferability and ease of use;

- both deterministic or stochastic simulations are possible;

- if stochastic simulations are chosen, Monte Carlo uncertainty analysis (section 3.7.2) is possible within software that is associated with RAM.;

- modelling of a karstified environment is possible because the model is flexible and allows customisation to meet site specific requirements.

CHAPTER FOUR Details of Study Areas

4.1. Introduction to this Chapter

This chapter presents background information on the two study areas investigated. The principal farm-site for investigation of nitrate responses in the groundwater body was Curtin's farm, county Cork. Information on the farm location, soils and subsoils, geology, hydrogeology, recharge and available groundwater quality data is presented for Curtin's farm in section 4.2. This general information was gathered through desk study prior to site instrumentation. The results of my field investigations yielded more detailed information and this is presented in section 6.1. Investigation methodologies are presented in chapter five, where subsurface characterisation strategies are presented in section 5.2.

Information for an additional farm-site, Johnstown Castle, county Wexford, is also presented and discussed in this chapter in section 4.3. My work on Curtin's farm (2000-2003) represents the major field and analysis endeavour of the thesis. My prior work at the Johnstown Castle site (1998-2000) might have been considered a pilot study for instrumentation methods employed at Curtin's farm. However, the relevance of the Johnstown Castle work to the results of the investigation at Curtin's Farm, with respect to learnt vulnerability concepts, was later realised. It is for this reason that study area details for the Johnstown Castle site are also presented in this chapter. The function of section 4.3 is to provide physical details for the Johnstown Castle farms, which can be compared with those found in the Curtin's farm study. In addition, I decided to present groundwater nitrate status at Johnstown Castle here, in section, 4.3.9, and not in chapter six, essentially the results chapter, for these reasons:

a) The Curtin's farm work is the primary focus of this dissertation, therefore the results chapter will provide results for Curtin's farm exclusively;

b) The hydrological and nitrogen loading data for Johnstown Castle provides context for loadings data presented for Curtin's farm in the next chapter, in section 5.5;

c) Groundwater nitrate status at Johnstown Castle provides context for the groundwater nitrate response at Curtin's farm, a farm that practices similar dairy farming practice in a contrasting hydrogeological environment. This is discussed more fully in section 6.1.1.5 where the application of the GSI vulnerability assessment methodology (Fitzsimons *et al.*, 2003) to Curtin's farm is presented.

4.2. Curtin's Farm Details

4.2.1. Curtin's Farm

The farm is owned by Teagasc and managed by the Moorepark research centre. Curtin's covers a land area of 50ha and is a relatively intensive dairy farm carrying a stocking density of ~2.4 LU/ha. The land is good farming land that is characterised by freely draining sandstone till, which forms the subsoil overlying a karstified-limestone bedrock aquifer. However, the nature of the subsoils in combination with the aquifer characteristics creates a vulnerable groundwater environment. The nature of karst aquifers was introduced in chapter one, section 1.5.2, and discussed in chapter three, section 3.8.3.2.

The farm, in accordance with usual Irish dairy farming practices, has dedicated areas for grazing, dirty water application, first cut silage and second cut silage. Dairy farming practice on Curtin's farm was introduced in a general way in chapter one, section 1.5.2, and more specific information regarding all nitrogen loading rates can be found in chapter five, section 5.5.2.

4.2.2. Curtin's Farm Location

Curtin's Farm is located in north Cork, approximately 35km northeast of Cork city. It is about 2km north of Fermoy on the N8 national primary route, which separates the Moorepark research centre's buildings from the study farm. The national grid co-ordinates are R813 008 and sheet number 74 of the OS, Discovery Series, covers the area with a 1:50,000-scale map. Figure 4.1 shows the farm's location within county Cork and its position nationally. Dairy and pig farmers intensively farm this area of north Cork. It is close to the region known as the Golden Vale and large dairy food processors operate in the region.

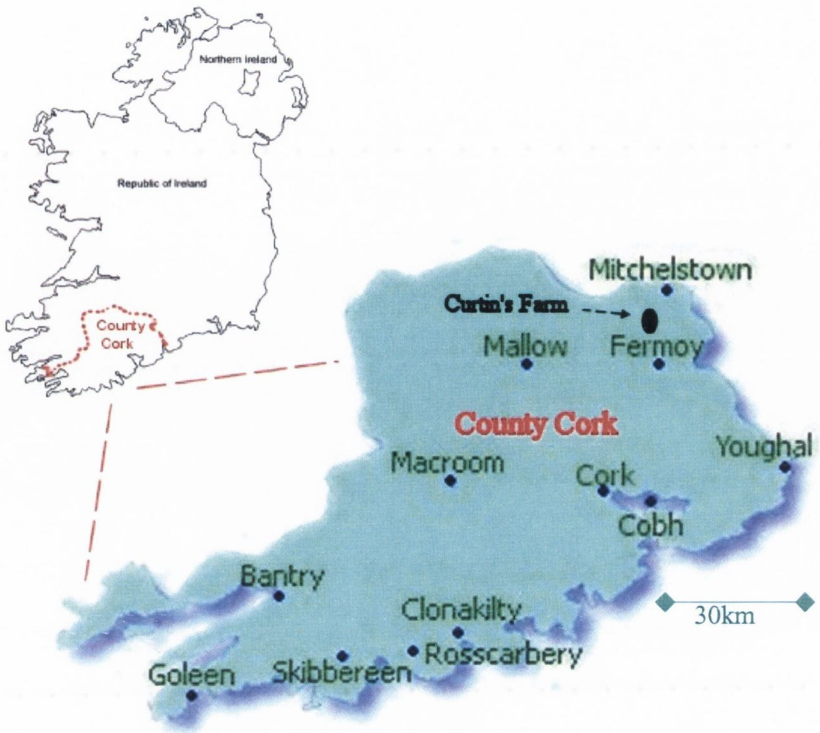


Figure 4.1 Study farm location, Curtin's Farm, within the region and also its position nationally.

The farm sits on a plateau, 50m AOD, with the River Funshion approximately 1.5km to the northeast and the River Blackwater just under 2km to the south. The two rivers join at a distance of about 2km to the east of the study farm, where riverbed elevation is approximately 20m AOD. The land is characterised as well drained with few surface water and drainage features. Regionally, topography is gently undulating where underlain by limestone and generally the high ground is underlain by sandstone (Motherway, 1999). However, steep inclines lead to and from Curtin's farm's plateau, along the N8 national primary route. The mountain ranges in the vicinity of the study farm are the Kilworth Mountains to the north (930m AOD) and the Knockmealdon Mountains to the northeast, both across the River Funshion (see Figure 4.5).

4.2.3. Soils & Subsoils of the Curtin's Farm Region

Field measurement in one farm plot revealed a 250mm/day surface infiltration capacity (Gibbons *et al.*, 2003), which is high.

In this context 'subsoils' refer to the Quaternary deposits that cover bedrock and provide the soil parent material. More than 90% of the bedrock geology of Ireland is covered by sediments of the Quaternary period (Sleeman & McConnell, 1995). The north Cork region is characterised by thin glacial deposits, with Quaternary deposits seldom more than 3-4m thick and bedrock outcrops abound (Sleeman & McConnell, 1995).

There is no detailed soils map for the north Cork area. According to the General Soil Map of Ireland (Gardiner & Radford, 1980) the soils of Curtin's farm are described as soil association 13, which describes an acid brown earth derived from mixed sandstone and limestone till with 70% acid brown earth and 30% grey brown podzolics. Another soil type in the region is soil association 15, which are mostly brown podzolics, parent material sandstone, and lower Avonian shale glacial till. These two soils 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 & Radford, 1980).

The Forestry Inventory Planning Service (FIPS) project, currently being undertaken by Teagasc's Kinsealy research centre, is deriving soil-parent material maps for many parts of the country. Their techniques (GIS, aerial photography, GSI maps, field investigation, interpolation) have yielded a first draft picture of the area, which is quite straightforward. They report that the majority of the soils in the Fermoy area are derived from sandstone till with some areas derived from till dominated by limestone, yet even these deposits have a high percentage of sandstone within them (Meehan, *pers comm.*, 2001).

An extensive GSI geophysics and subsoil augering programme (Kelly & Motherway, 2000) in the area surrounding the Downing's Bridge public supply borehole (see Figure 4.5), north-east of Curtin's farm, concluded that:

- The subsoils comprise a mixture of coarse and fine-grained materials, namely till;
- The underlying limestone bedrock directly influences the soils;
- Limestone fragments tend to dominate the till which varies from silty sand with frequent/abundant gravels to angular sandy gravels with clay.

4.2.3.1. Nutrient Status of Curtin's Farm's Topsoil

In the course of soil fertility investigations for agronomic purposes a technician sampled the topsoil's of Curtin's farm. Topsoil samples were collected in January 2002 from representative plots for each of the four agricultural treatments. No fertiliser had been applied to the lands surface for at least four months. Potassium (K) levels in the topsoil's of Curtin's farm were observed to be approximately 80 mg/l K in the grazing and silage areas, but in the dirty water disposal area topsoil potassium levels measured 200-300 mg/l K (see Figure 4.2). Results from the standard soil phosphorus (P) test (Morgans extractable P) by the soils laboratory in Johnstown Castle revealed alarmingly high concentrations in the dirty water treatment area (see Figure 4.3). Soil phosphorus concentrations of 20 mg P/l were observed in the topsoil of the dirty water area, where >10 is considered very high, and at 10 mg P/l soil phosphorus test Teagasc recommends that no phosphorus fertiliser be applied. Soil phosphorus tests in the grazing and silage areas were 12mg/l, on average, with values of 14 mg P/l observed in the two-cut silage area. Teagasc does not routinely test soils for nitrogen levels as part of soil fertility assessment. However, the variance in soil phosphorus and potassium levels is a measure of relative agricultural impact in different areas of Curtin's farm, and it is for that reason these maps are presented here.

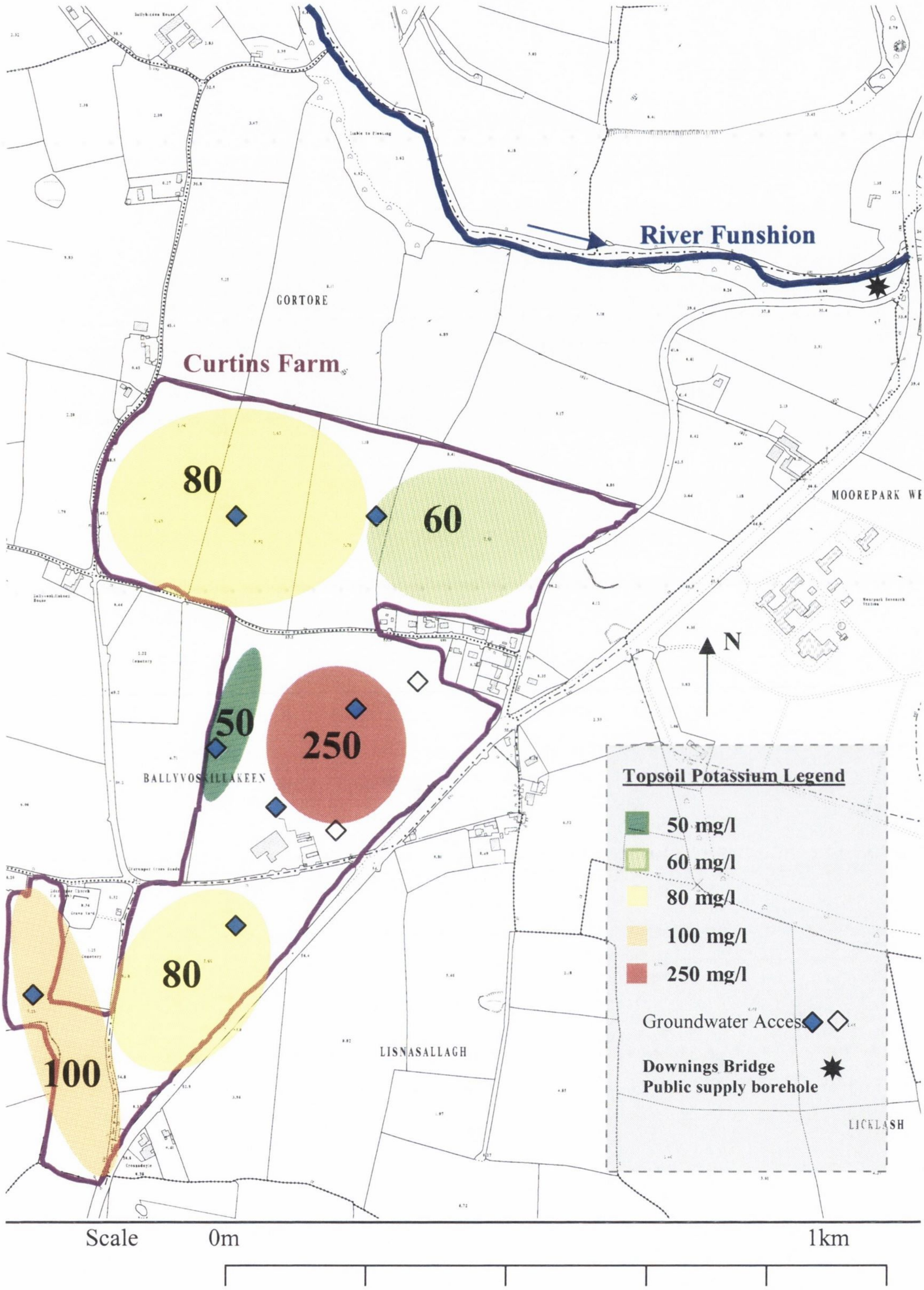


Figure 4.2 Topsoil potassium (K) levels at Curtin's farm (January 2002).

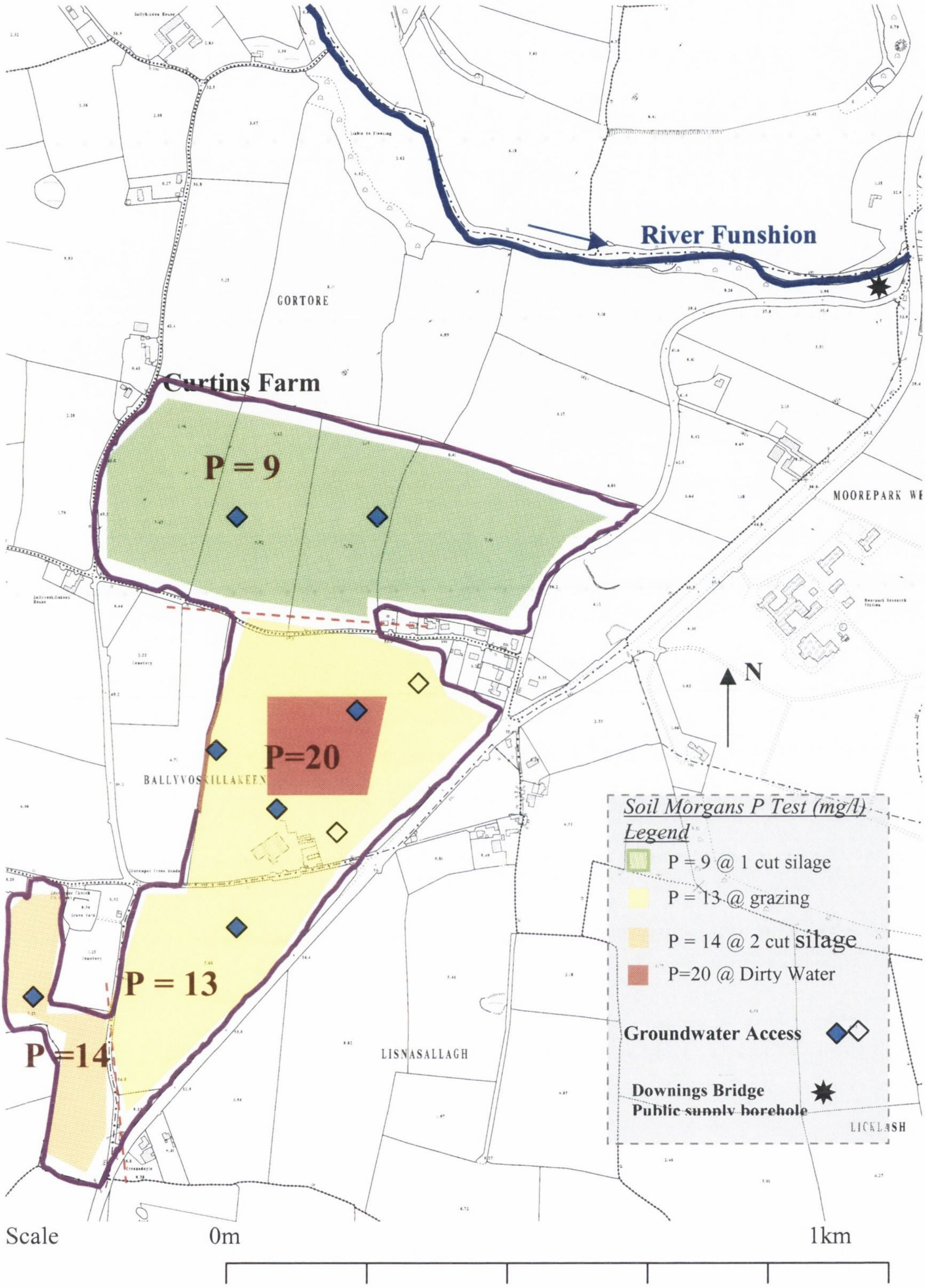


Figure 4.3 Topsoil phosphorus (Morgans P) levels at Curtin's farm (January 2002).

4.2.4. Geology of North Cork

The geology of the study region is described by Sleeman & McConnell (1995) in a report accompanying the published 1:100,000 scale geological map series, sheet number 22. Carboniferous Limestone, underlain by Devonian Old Red Sandstone and Silurian Shale, dominates the geology of north Cork (Shearley, 1988). The rocks are the result of sediments deposited during Carboniferous times (over 300 million years ago). A GSI map showing the simplified geology of the region is shown in Figure 4.4. The borehole stratigraphy for the farm, obtained as part of this doctoral research investigation, is presented in section 6.1 and Appendix B.

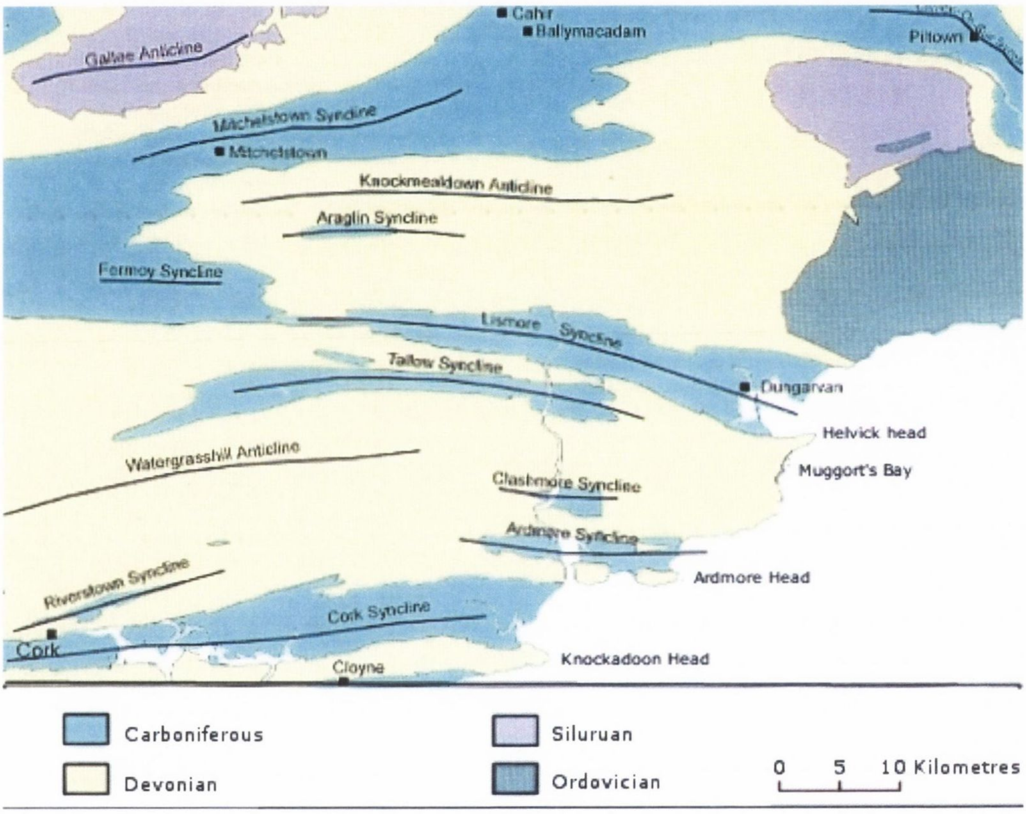


Figure 4.4 Simplified Geology of East Cork and Waterford (Sleeman & McConnell, 1995).

The stratigraphy is Waulsortian Limestone, 500-700m thick, underlain by Ballysteen Limestone, 75m thick, underlain by Devonian Sandstones, 500-2000m thick. The major structural control in north Cork is the Fermoy Syncline and the Knockmealdown Anticline to the north. Both these structures plunge gently to the east (Motherway, 1999).

Waulsortian Limestone (WA) dominates the geology of the Curtin's farm area. This rock unit is described as a pale grey massive unbedded lime-mud stone with abundant spar-filled cavities (Sleeman & McConnell, 1995). The study area is in the middle of the Fermoy Syncline, a major east-west trending fold (Shearley, 1988). Minor folds occur with similar orientations. Two major fault sets are widespread across the region: east west trending [strike faults] and north-south trending [cross faults] (Kelly & Motherway, 2000). Several minor antiforms and synforms run through the area and these are parasitic to the Fermoy syncline (Motherway, 1999).

Although no karst features are noted by the GSI karst database for the area, regional terrain is hummocky with many small depressions (collapsed or solutional features) visible on the OS Discovery series maps (Motherway, 1999). Local well-drilling contractors refer to many unpredictable gravel filled cavities in the limestone. GSI geophysical investigations have also reported the limestone to be inhomogenous and the hydraulic properties of the aquifer support this with suggestions of variations in the nature/quality of the bedrock (Motherway, 1999).

A very recent geophysical survey by Kevin Barton (NUIG) on Curtin's farm has yet to be processed and reported in full. However, preliminary field-derived assessments of the soils suggests that the bedrock mirrors topography, with many slight collapses and at least three obvious ridges where bedrock is either evident at the surface or inferred from summer drought damage in localised patches. The rock outcrops appear to be weathered limestone and the soils in these areas show signs of being geophysically different from those in depressions or sunken features on the farm. The soils on the ridges have much greater resistivities suggesting less water content, perhaps less clay, more gravelly, and hence better drained. The rock appears to be much closer to the surface in and around these slight elevations than in the even slightly sunken features. In one case there was evidence of perhaps a cliff-like fall off in bedrock with only a very slight manifestation at the ground surface. GSI resistivity surveys for the Gortore townland, immediately north of the study area, suggest subsurface infilled cavities that have no surface expression (Motherway, 1999).

4.2.5. Local & Regional Hydrogeology of Curtin's Farm

Groundwater flow in this Waulsortian limestone bedrock unit is characterised by fissure flow. Predominant groundwater flow occurs through shallow interconnected solutionally enlarged fracture zones and along fractures and joints outside the main fracture system (Kelly & Motherway, 2000).

An upward trend in groundwater nitrate concentrations at the Downing's Bridge public supply borehole was introduced briefly in chapter one (more details follow in section 4.2.9). The abstraction rate from the Downing's Bridge public supply borehole is currently ~140,000 gals/day (~$0.009m^3/s$). North Cork County Council commissioned the GSI to delineate a 'Source Protection Zone' (SPZ) for the Downing's Bridge borehole. It was determined that a significant portion of Curtin's farm lies within the Downing's Bridge SPZ. The supply source is described as a regionally important karstified aquifer (Rk), located in the Waulsortian limestone unit. The area around the supply is described as highly, or extremely, vulnerable to contamination. The SPZ for Downing's Bridge public supply borehole, delineated by the GSI (Kelly & Motherway, 2000), is shown in Figure 4.5. I have added a general demarcation of Curtin's farm and other features for purposes of clarity in the discussions presented herein. The topography over karstified limestone is reported not to provide a reliable means of delineating groundwater divides. According to GSI source protection reports for the area (Kelly & Motherway, 2000) the groundwater divide is assumed to lie between the Rivers Funshion and Blackwater, although they do not mark this divide. I, purely for indicative reasons, show a possible groundwater divide on Figure 4.5.

Hydraulic gradients in the area are low, and comparable with the gradients in Irish karstified limestones, typically 1:2000 to 1:500 (Motherway, 1999). There were no wells on Curtin's farm prior to those installed in the course of this investigation in 2001. Local domestic water supply, and that of Curtin's farm, is from the mains supplied by Fermoy urban district council. Therefore, there are few wells in the area and only four wells could be found to survey in Motherway's work (1999). These wells included the Downing's Bridge public supply borehole and three Moorepark wells, located on the main grounds of the research centre (see Figure 4.5 for indication of the location of the Moorepark wells).

Motherway (1999) reports his aquifer pumping tests on the Moorepark wells and previous tests on the Downing's Bridge well as follows:

- The hydraulic gradient was found to be 1:2334;

- The Moorepark wells reveal transmissivities of $424m^2/day$ (MPL) and 212 m^2/day (MPU), both wells are shown on Figure 4.3;

- The Downing's Bridge well was tested in 1983 to have a calculated transmissivity of 3405 m^2/day. The driller's log notes gravel filled cavities. The hydraulic conductivity of the screened layer (at 3.9m) was calculated from the transmissivity to be 873m/day. This exceptionally high value was substantiated by a very small pumping test drawdown of 1.14m at a pumping rate of 2257m^3/day;

- Permeabilities in the Moorepark wells are in the 10 to 200m/d range. Porosity is considered to be about 0.025. Velocities are estimated to be about 30m/d in the vicinity of the borehole. In general, velocities range from 4-2500m/d within the Waulsortian Limestone.

On a regional scale, groundwater and surface water are flowing towards the Blackwater River (Kelly & Motherway, 2000). On a local scale, however, groundwater close to the river will flow and discharge to the Funshion River. It is assumed that the Funshion River represents the true groundwater elevation, as it is the lowest surface water feature in the vicinity. Electrical conductivities of the river are high (600μS/cm on 20/8/99) indicating that groundwater forms a high proportion of the summer river water flow (Kelly & Motherway, 2000). The gradient of the Funshion River, about 1:1000 to 1:2000, is similar to that of the groundwater.

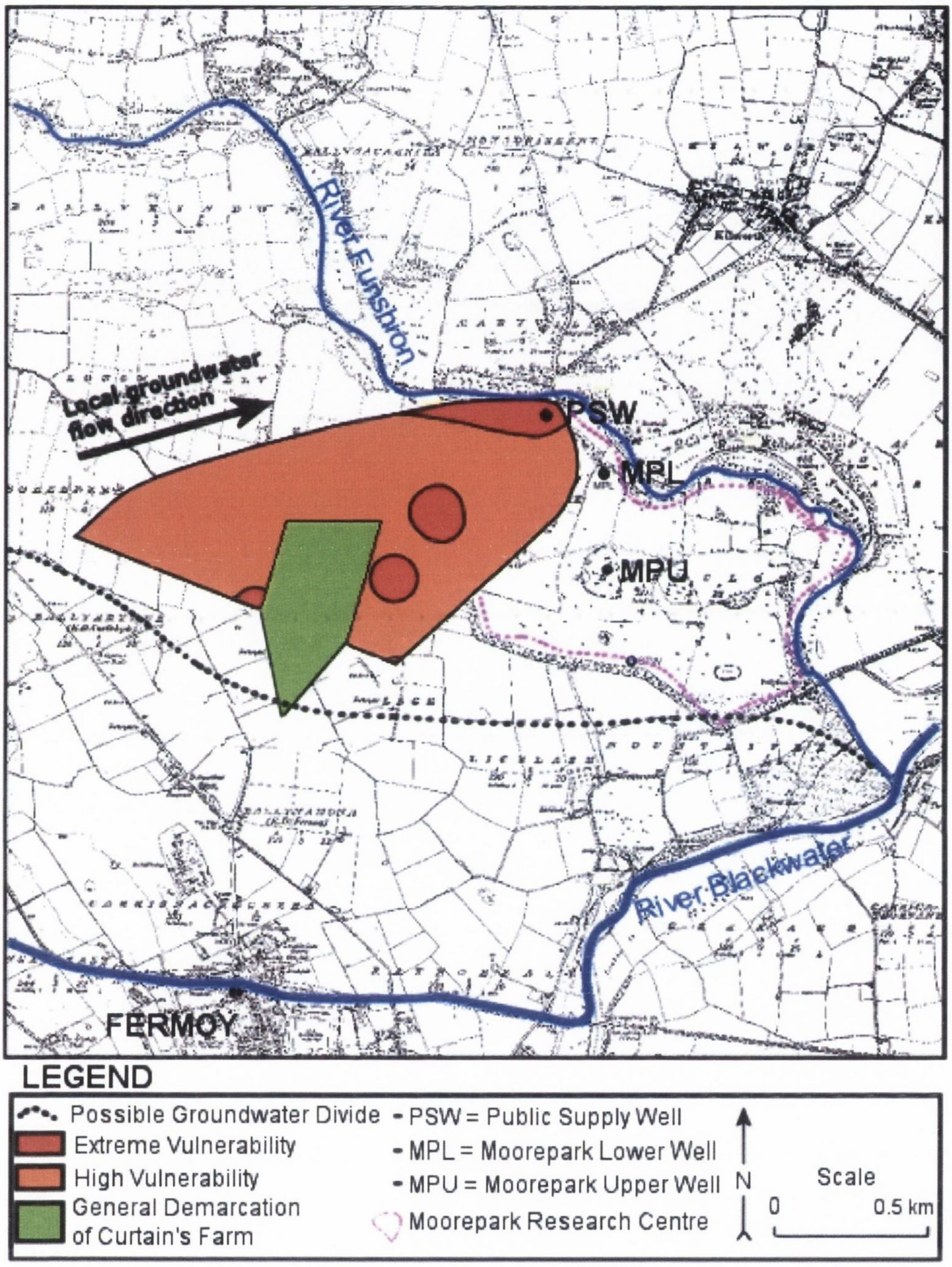


Figure 4.5 The GSI SPZ for the Downing's Bridge public supply well (PSW) (Kelly and Motherway, 2000). General demarcations for Curtin's farm, a possible groundwater divide, and other features have been added, for the purposes of clarity, in the course of this work.

A groundwater sample from beneath a particular investigation site is not only a function of the leachate concentrations migrating vertically from the unsaturated zone to the saturated zone, but also of the concentration of the incoming groundwater flow (Burt & Trudgill, 1993). The groundwater coming from up gradient may have higher or lower nitrate concentrations than the leachate, causing supplementation or dilution to take place. Curtin's farm is an ideal study site because:

- It sits on a plateau. Therefore, it is reasonable to assume that nitrate concentrations, in the underlying groundwater, mostly reflect the influence of recharge percolating vertically through the subsoils of Curtin's farm;

- Previous work (Kelly & Motherway, 2000) suggested that inflowing groundwater comes from the southwestern border of the farm. Therefore, this study can place piezometer instrumentation with due consideration of monitoring nitrate concentrations in groundwater flowing into the farm area. Hydrogeological data collected in the course of the present study are presented in section 6.2.

4.2.6. Surface Hydrology at Curtin's Farm

The region shows a distinct lack of surface drainage or surface recharge features apart from some sharp depressions, presumed to be infilled dolines or swallow holes. Therefore groundwater recharge is likely to be predominantly from diffuse precipitation. The River Funshion is located approximately 1.5km to the north of the farmyard at Curtins farm. However, the ground surface is relatively flat on the farm. The banks of the River Funshion are very steep and so land runoff to the River does not feature in the immediate farm area.

4.2.7. Preliminary Meteorology & Recharge Data

Preliminary information on the meteorology of the area, Table 4.1, was obtained in a GSI report (Kelly & Motherway, 2000). Detailed recharge calculations generated in the present study are presented in section 5.5.1. Despite runoff estimations presented in Table 4.1, it is unlikely that runoff is a transport phenomenon on Curtin's farm, due to the topography and freely-draining soils.

Table 4.1 Preliminary local area meteorological data (Kelly & Motherway, 2000).

Average annual rainfall, R.	1034mm
Estimated Evapotranspiration (E_t)	434mm
Potential recharge ($R - E_t$)	600mm
Runoff losses	30mm
Estimated Actual Recharge	570mm

4.2.8. Natural Groundwater Hydrochemistry

The natural hydrochemistry of four different aquifer types in Ireland were presented in a recent EPA publication (EPA, 2003a) and details for a Carboniferous Limestone aquifer are reproduced in Table 4.2. The data were obtained from the Carboniferous Limestone aquifer at Ballaghdereen, Roscommon.

Table 4.2 Natural Hydrochemistry – Irish Carboniferous Limestone Aquifer (EPA, 2003a).

Parameter	**Carboniferous Limestone Aquifer Natural Groundwater concentration (mg/l)**
Ammonia as Ammonium	0.13
Nitrate-Nitrogen*	0.2
Calcium	102
Hardness as $CaCO_3$	307
Magnesium	12.9
Potassium	3.0
Sodium	8.8

*The EPA report (2003a) reports this parameter as 0.9mg/l NO_3^- but I have taken the liberty of reporting it in the NO_3-N format to allow easy comparison with values reported in this work.

4.2.9. Local Area Groundwater Quality And Nitrates

EPA monitoring data shows that the Rivers Funshion and Blackwater in the vicinity of the Curtin's farm study area are classified as unpolluted (Lucey, et al., 1999). The freely draining nature of the soil and subsoil means there is low tendency for runoff. The land generally lends itself towards higher river water quality than groundwater quality. In this geographical region, moderately polluted rivers tend only to occur in the Mitchelstown area, 10km north of the study farm.

The only long-term groundwater quality data available is that of the Downing's Bridge public supply borehole (Cork County Council, 1998 & 2003) and this is reproduced in Figure 4.6. A linear relationship line has been added to illustrate the upward trend (Original data is provided in Appendix C).

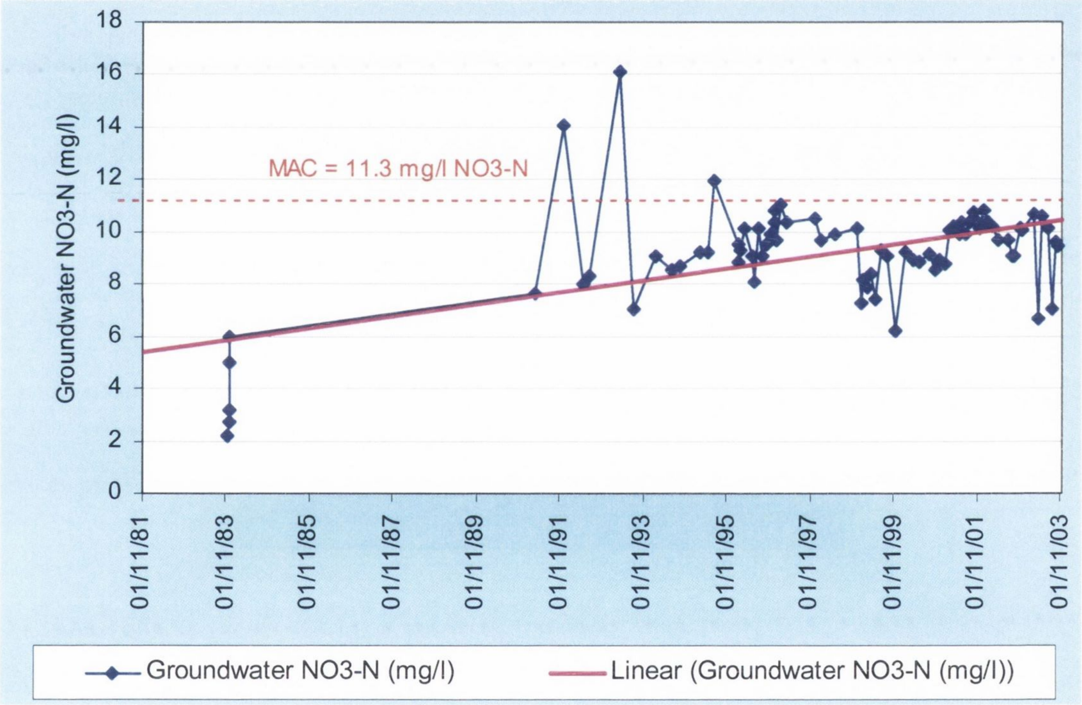


Figure 4.6 Groundwater nitrate-nitrogen (NO_3-N) concentrations in the Downing's Bridge public supply borehole recorded over the last twenty years. Data supplied by Cork County Council (1998 & 2003). Raw data is provided in Appendix C.

As can be seen from Figure 4.6, records for Downing's Bridge public supply borehole show an upward trend in groundwater nitrate-nitrogen concentration over the last twenty years. Initially, in the early 1980's, concentrations were below the Drinking Water Directive (EC, 1998) guide level (GL = 5.6 mg/l NO_3-N) but today's concentrations consistently hover around the maximum admissible concentration (MAC = 11.3mg/l NO_3-N). The MAC was exceeded on three occasions (19/11/91, 30/3/93 & 10/7/95) and approached the limit on 16/4/98 with a concentration of 11 mg/l NO_3-N. Nitrate concentrations ranged from 2 to 16.1 mg/l as NO_3-N, (39 samples: 1983-2000), with and average of 9 mg/l NO_3-N. The multi-seasonal nature of all the serious contamination incidences suggest both point and diffuse sources of pollution may be to blame (Kelly & Motherway, 2000). However, others might postulate that the surge type response of groundwater nitrate concentrations is characteristic of the nature of fissure flow in karstified bedrock. While all the houses in the study area are supplied by mains water, sanitary disposal is by means of private septic tanks. However, the area up gradient of Curtin's farm is very sparsely populated.

For the purposes of collecting preliminary information for this study I sampled the two Moorepark production wells (refer to Figure 4.5) on the 14/12/00 finding concentrations of 10.17 mg/l NO_3-N (Dairy Production Centre-MPL well) and 15.37 mg/l NO_3-N (Dairy Research Centre-MPU well). A professional laboratory had previously analysed groundwater from the MPU well on the 16/8/00, at the request of Moorepark, showing a mean concentration of 14.92 mg/l NO_3-N (Consult Us Laboratories, pers. comm., 2000).

Richards (1999) provided other groundwater quality data for the north Cork region. He studied groundwater nitrate concentrations beneath another Teagasc farm, Ballyderown, approximately 4km east of Curtin's farm. The bedrock beneath the Ballyderown farm consists of Lower Carboniferous Limestone of the Ballysteen Formation. The soils of Ballyderown farm were very shallow, reported to be 200cm at most with many areas of even shallower soils. Soil depths on Curtin's farm ranged from 0 to 4m (more details are presented in section 6.1). The majority of groundwater samples from Ballyderown had nitrate concentrations ranging from 20 to 30 mg/l as NO_3-N, which far exceeds the EU MAC (EC, 1998). Mineralisation of soil organic matter, dirty water irrigation and other agricultural management factors were implicated as serious contributors to groundwater nitrate concentrations in Richards' work (1999).

Another facet of Richards' work (1999) was a regional scale groundwater-sampling programme in the wider north Cork region. More than 50 private wells that supplied individual dwellings were sampled. The area investigated covered 180 km^2. Groundwater nitrate concentrations ranged from 0.5 to 20.5 mg/l with the mean concentration being 7.9 mg/l. Over 70% of the wells sampled had nitrate concentrations less than the MAC (11.3 mg/l NO_3-N) and groundwater nitrate concentrations less than GL (5.6 mg/l NO_3-N) were observed in 41% of the total number of wells sampled (Richards, 1999).

The National Federation of Group Water Schemes (NFGWS) supplied other data regarding regional groundwater quality. Groundwater quality information for 15 sources, for the monitoring period November 2000 – November 2001, was supplied (O'Connell, 2003). These 15 supplies are the total NFGWS data set for the region. Data sheets supplied by the NFGWS (O'Connell, 2003) are provided in Appendix D. Groundwater nitrate-nitrogen data are represented in Figure 4.7 to show regional groundwater quality at the start of the Curtin's farm investigation that is described in this thesis. The group water scheme data reveal that:

- Generally groundwater nitrate-nitrogen concentrations were low;
- 40% of the sources consistently returned samples less than, or equal to, the guide level (GL = 5.6 mg/l NO_3-N);
- 53% of the sources consistently returned samples less than the maximum allowable concentration (MAC = 11.3 mg/l NO_3-N); and
- Only one sample greater than MAC was returned (of a total annual sample number of 150).

The NFGWS data and the results of Richard's (1999) regional monitoring programme delivers the same message, a generally low groundwater nitrate status in the wider north cork area.

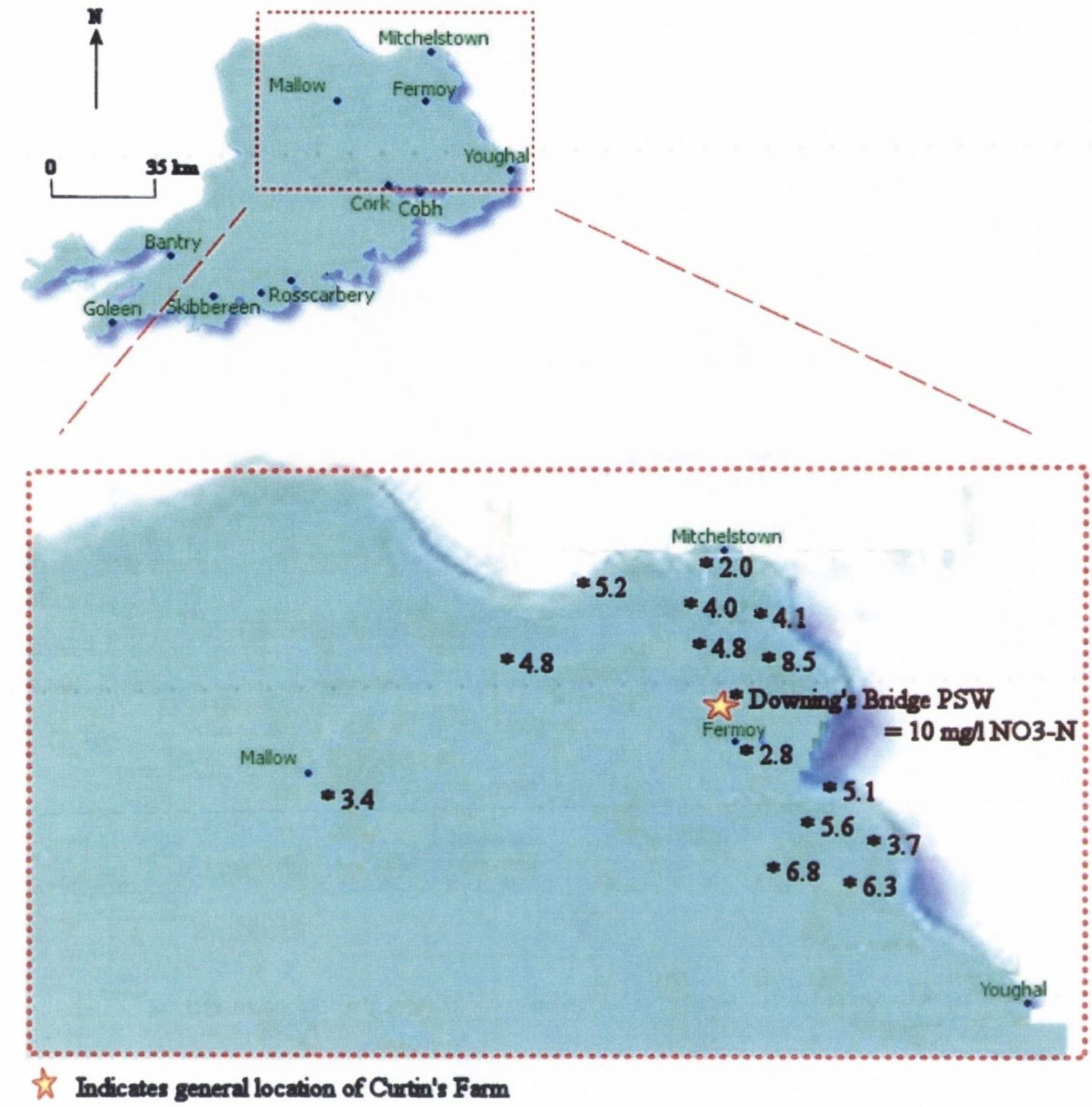


Figure 4.7 Regional groundwater nitrate-nitrogen concentrations (mg/l NO_3-N) in north Cork, 2000-2001. (Cork County Council supplied the Downing's Bridge data (Cork County Council, 2003). All other data relates to private wells in the National Federation of Group Water Schemes (O'Connell, 2003). These data are presented in full in Appendices C and D).

4.3. The Johnstown Castle Study

This section presents details of the pilot project at Johnstown Castle, county Wexford, which took place prior to the Curtin's farm investigation. Two farms were instrumented at Johnstown Castle: the conventional dairy farm and the organic dairy farm. Both groundwater quality and piezometer water levels (WL) were monitored bi-weekly over an 18-month period (February 1999 to November 2000). Ancillary details for the Johnstown Castle work such as borehole instrumentation and groundwater-monitoring methods can be found in Appendix E.

The Teagasc research centre at Johnstown Castle (grid reference T302 118) is located 6km southwest of Wexford and covers a total area of about 400ha of low-lying land (40m-100 AOD). Figure 4.8 indicates the location of Johnstown Castle.

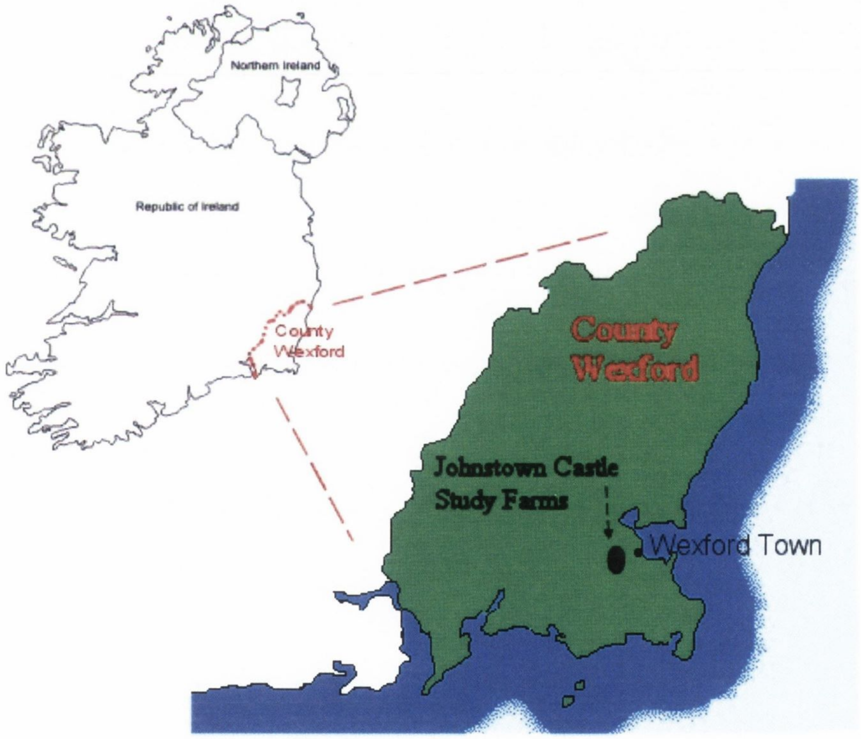


Figure 4.8 Location of Johnstown Castle within the region and its position nationally.

There are three artificial lakes on the Johnstown castle estate, covering a total area of just over 8ha, fed by diversions from the Kildavin River, which flows through the organic farm and along the western boundaries of the estate. The landform is gently undulating, typical of a glacial outwash plain. Of the total area, the ornamental gardens, woods and parkland of the original estate comprise approximately 210ha, the remainder being devoted to agricultural research. There are three distinct experimental farms on the estate: conventional dairy, beef production and organic dairy systems operate at different locations.

4.3.1. Site Instrumentation at Johnstown Castle

Site selection for piezometer installation was a function of similarities in soil type, geology, farming practices, topography and water table elevations. In all, five study sites were chosen. Three study sites are located on the conventional dairy farm (DF1, DF2 & DF3) and two on the organic dairy farm (ORG1 & ORG2), as shown in Figure 4.9. At four of the five sites, piezometers were installed in a group of three to target successively deeper zones within the groundwater body[1]. Nested piezometry was possible at Johnstown Castle because there is a saturated zone in the subsoil as well as in the consolidated (bedrock) zone. Installation details are more fully explained in Appendix E. The site conditions at Johnstown Castle vary greatly from the karstified hydrogeological environment at Curtin's farm.

4.3.2. Soils & Subsoils at Johnstown Castle

The pattern of distribution of the soils at Johnstown Castle is complex. This is a reflection of the intricate nature of the drift deposits from which the soils are derived.

The predominant soil type on the dairy farm is fine loam, consisting of a loam surface, 15-40cm deep, overlying a loam to clay loam subsurface soil (Culleton & Diamond, in press). The structure of the soil is generally poor at the surface with many cracks, which may have been caused by historical permafrost or other more recent phenomena. Ryan (1998b) demonstrated with the use of

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[1] At one site (DF1), drilling for bedrock was abandoned after 20m of difficult clayey overburden. Therefore, at DF1 there is only a single piezometer installed.

dyes that preferential flow does occur through the soil profile on the conventional dairy farm at Johnstown Castle.

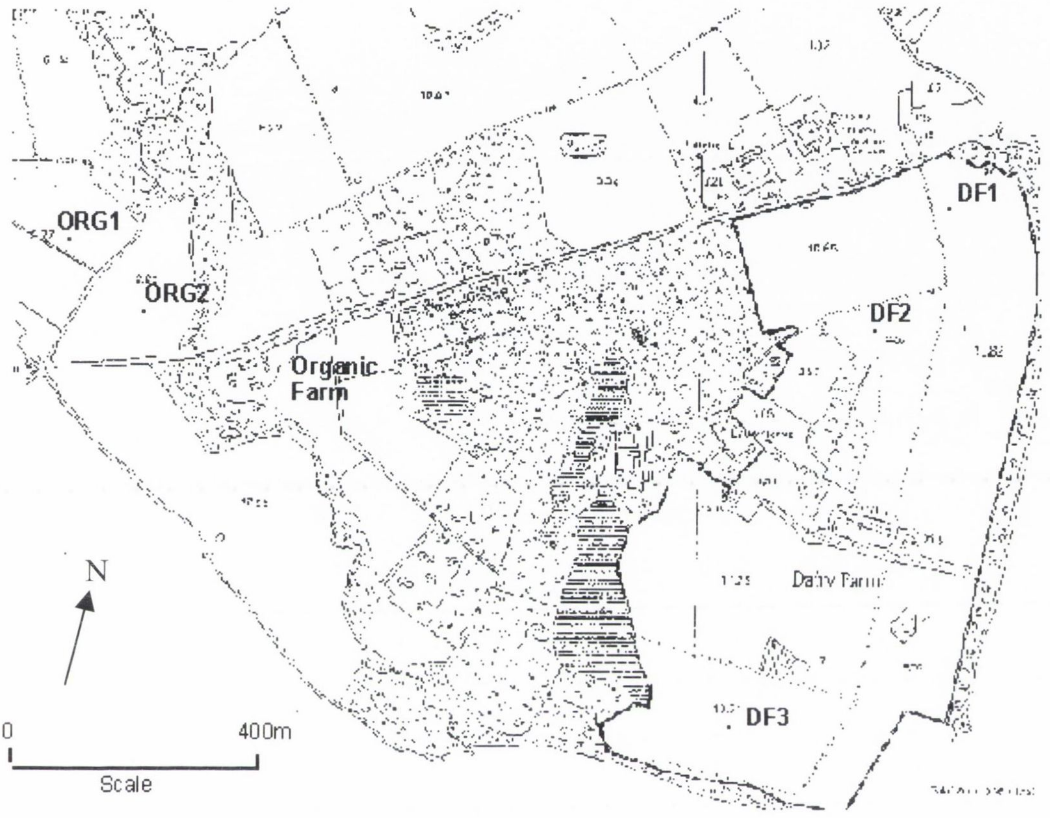

Figure 4.9 Instrumentation locations at the Johnstown Castle dairy farms

A mantle of drift of Irish Sea provenance covers the bedrock. This varies in depth throughout the estate from 1-20m (areas of higher elevation having thicker cover). Field investigations in several areas have uncovered area where the till is covered by a layer of sand of varying thickness from a few centimetres to over a metre. The absence of bedding, the relative immobility of the sand and the occurrence of sand layers generally throughout the till indicate that it is probably an ablation deposit (Culleton & Diamond, in press).

Information about subsoil type, depth and geology for each instrumented site is presented in Table 4.3. Disturbed subsoil samples were collected during drilling for piezometer installation. They were analysed by this author in the soils laboratory of Trinity College. Subsoil descriptions were determined using B.S. 1377 (1990). All soil types were similar with the exception of those found at DF2 on the conventional dairy farm, adjacent to the Bog Wood. All bedrock is shale except for that at the southern end of the conventional dairy farm (DF3), which is sandstone.

Table 4.3 Soil type and depth to rock (subsoil depth) at each sampling location.

Site Location	**Soil Description**	**Water Strike** +	**Depth to Rock**	**Bedrock Type**
DF1	Brown sandy CLAY	7m	>20m	Green grey shales*
DF2	Silty/clayey/gravely SAND	6m	12m	Green grey shales*
DF3	Brown sandy CLAY	6m	12m	Red-grey sandstones^
ORG 1	Brown sandy CLAY	8m	12m	Green grey shales*
ORG 2	Brown sandy CLAY	6m	10m	Green grey shales*

+ December 1998 water strike (metres below ground level)
*Cullenstown Formation of Cambrian age
^Duncormick Formation of Carboniferous age.

4.3.3. Geology of South Wexford

The geology of the study region is described by Tietzsch-Tyler & Sleeman (1994) in a report that accompanies the published 1:100,000 scale geological map series, sheet number 23. A map showing the simplified geology of the region is shown in Figure 4.10.

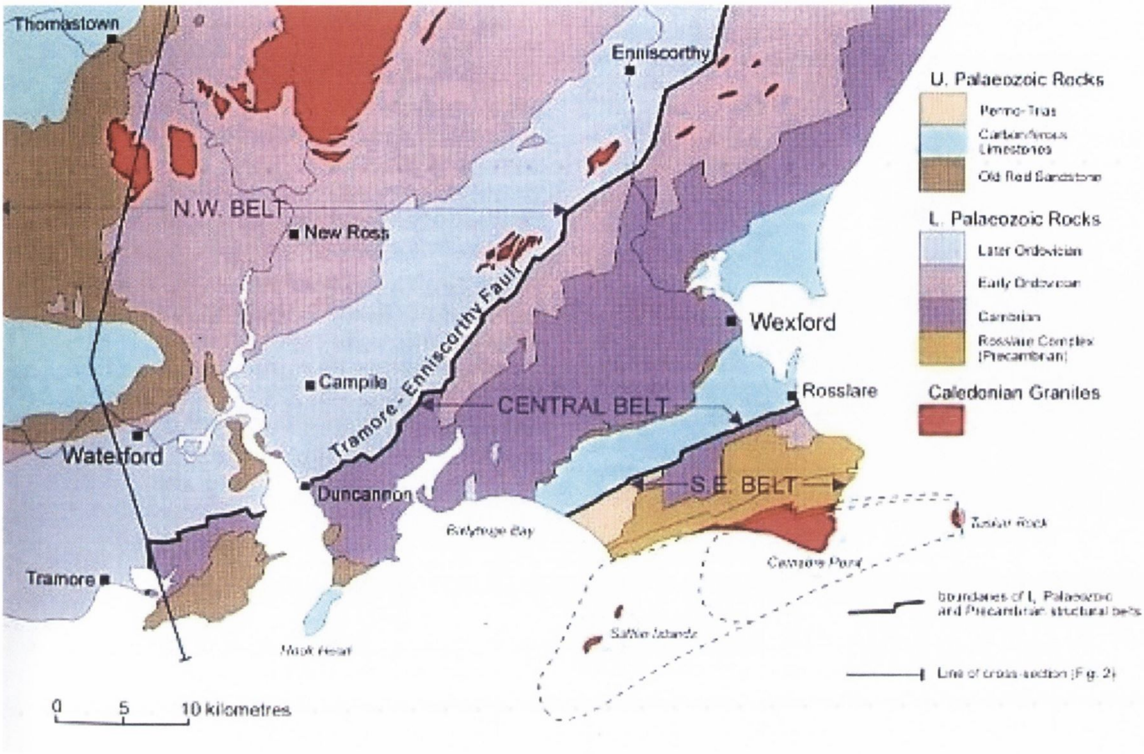

Figure 4.10 Simplified Geology of South Wexford (Tietzsch-Tyler & Sleeman (1994).

The rocks underlying the Johnstown Castle farms belong to the Pre-Cambrian and Lower Carboniferous era and can be divided into four main rock types (Daly & Hudson, pers. comm., 1995):

- Green grey shales (Cullenstown Formation of Cambrian age) underlie all of the organic farm and most of the conventional dairy farm.

- To the south-east of these shales the bedrock consists of red-grey sandstones and conglomerates (Duncormick Formation of Carboniferous age).

- Minor parts of the estate to the extreme north-west and south-east are underlain by the Shelmalier Formation (white-purple quartzites and slates) and the Porters Gate Formation (sandstones and thin limestones) respectively, both of Carboniferous age.

The shale bedrock is believed to be significantly fractured. There are two faults running in an approximately N-S direction through the estate and an unconformity traverses the conventional dairy farm in an approximate NE-SW direction.

Quartzite outcrops on the west of the estate and highly weathered shales have been noted in places where cover is thin (Culleton & Diamond, in press). Rock exposures of schist and sandy shale have been observed in the banks of the Kildavin River, which flows through the organic farm along the western boundaries of the estate.

4.3.4. Hydrogeology of Johnstown Castle

A GSI assessment of the Johnstown Castle farm area reported that the grey green shales (underlying both the conventional and organic dairy farms under investigation) are relatively impermeable as are the quartzites and slates to the northwest of the estate (Daly & Hudson, pers. comm., 1995). The aquifer classification of these rocks is uncertain - probably poor with higher permeabilities only in local zones. Cullen (pers. comm., 1982) suggests that it would be possible to drill into the bedrock at any site on the estate and expect a yield in the 0.5-2m^3/hr range. Because of the nature of the bedrock it is probable that most of the groundwater is in the upper few metres (Cullen, pers. comm., 1982).

A water table contour map for the conventional dairy farm (Bartley, 1996) suggests that the predominant groundwater flow is southwards until the dairy unit buildings, mirroring surface topography (see Appendix E). There is a little deflection of groundwater towards the Bog Wood stream on the dairy farm. The dairy unit buildings mark the region where the farm lake begins to dominate the groundwater flow. The DF3 site is the only study site that is affected by the lakes (refer to Figure 4.9). The water level in the farm lake is higher than groundwater levels in the vicinity of the lake. Ordinarily, surface water features act as sinks for groundwater flow but on the estate the artificial lakes contribute the groundwater regime. There is a general confluence of groundwater flow in the south-south western part of conventional dairy farm. It is therefore concluded that the water table beneath the Johnstown estate is influenced by, and mirrors surface topography, generally flowing south-south westerly. With respect to the organic dairy farm on Johnstown Castle, groundwater flows towards the adjacent Kildavin River.

4.3.5. Surface Hydrology at Johnstown Castle

The hydrology of the organic farm area is relatively simple in that the Kildavin River, and its associated subtle valley, naturally drains the land so there is no need for artificial land drains.

The conventional dairy farm is underlain by a complex pattern of land drains consisting of old box-drains and more conventional agricultural pipe drainage, at an average depth of 90cm. The hydrology of the conventional dairy farm is made even more complex by the extension of land and road drains from the beef farm area to a natural Bog Wood on the dairy farm. The beef farm is situated to the north-west and separated from the dairy farm by a third class national road. No written record of drain installation exists at Johnstown Castle, as much of the drainage network predates Teagasc's stewardship of the land, but Kurz (pers. comm., 1996) provided a general indication of land drains on the dairy farm. The fact that a low flow of water is sustained throughout the summer months suggests that these land drains also drain natural groundwater springs. A small stream emerges from the southern end of the 'bog wood' and flows over ground for approximately 200m until it is directed to another drain, which returns it underground to convey it off the estate. Johnstown's drains and surface water features are sampled regularly for water quality analysis but no significant nitrate concentrations have been recorded.

4.3.6. Meteorology & Recharge at Johnstown Castle

The mean annual rainfall (R) at Johnstown Castle is approximately 1000mm. There is a meteorological station at the research centre where daily rainfall is recorded and potential evapotranspiration (P.E.) is calculated. Long term P.E. data has not been compiled for the study area but a five-year average yields a value of 530mm (1992-1996). At Johnstown Castle, actual evapotranspiration (A.E.) is calculated by taking 90% of the P.E. value to allow for soil moisture deficits, so A.E. is estimated as 477mm/yr. Therefore, the potential recharge (R – A.E.) is taken to be approximately 530mm/yr. Johnstown Castle meteorological data was collated in a previous study (Bartley, 1996) and is presented in Table 4.4. On the conventional dairy farm a significant portion of this potential recharge is intercepted by the extensive under-drainage system. On the organic dairy farm there is little or no artificial under-drainage but runoff losses are higher, estimated at about 15% of potential recharge.

Table 4.4 Recharge Estimations for the Johnstown Castle Farm Sites (Bartley, 1996).

	Conventional Dairy Farm	Organic Dairy Farm
Potential Recharge	530 mm/yr	530 mm/yr
Surface Runoff	@ 8% = 43 mm/yr	@ 15% = 80 mm/yr
Drainage Interception	@ ~30% = 150mm/yr	Nil
Recharge	337 mm/yr	~470 mm/yr

4.3.7. Johnstown Castle Dairy Farming Practice

The Johnstown Castle conventional dairy farm covers a total area of 61ha over a varied soils pattern, varying from Brown Earths to Gleys with a localised sandy area. The land is not naturally free draining and, as discussed above, is extensively drained by subsurface agricultural drains. The average stocking rate is 2.5 LU/ha. The spring calving herd consists of 118 cows. The yearly herd replacement rate is 20% of calves from the herd. Other animals on the farm include the 28 heifer calves (born in year), 28 heifers (from the previous year) and 2 bulls. The 2001 average milk yield for the herd was 5900 litres/cow, similar to yield at Curtin's farm. Generally, the conventional dairy farm at Johnstown Castle and Curtin's farm operate similar stocking rates and farming practices.

4.3.7.1. Comparisons Between Johnstown and Curtin's Farm

Outdoor grazing management is similar at both Johnstown and Curtin's farms. The main diet of the animals is grazed grass and grass silage (dairy ration is also used to supplement silage during the winter housing period). The animal's annual grazing cycle is as follows:

- Day-time grazing only from the end of February to mid April (silage–fed at night);
- Day and night-time grazing until the end of October; and then

- Day-time grazing only, again, until mid-November when they are winter-housed until the end of the following February.

More freely-draining land at Curtin's farm extends their grazing season by one month more than that at Johnstown Castle. This month is divided, two weeks at the beginning of the grazing season and two at the end (see chapter five, section 5.5.2.4 for Curtin's farm details).

Silage growing practice is similar on Johnstown Castle's conventional dairy farm and Curtin's farm. At Johnstown Castle 45% of the farm area is devoted to first cut silage, cut at the end of May or early June. 27% of the farm area is then reserved for second cut silage, which is cut approximately 8 weeks later. Dairy cows graze areas that are not being used for silage production and from early August the entire farm is available for grazing.

Fertiliser application rates vary spatially on Johnstown Castle's conventional dairy farm. Nitrogen fertiliser is applied at an annual rate of 320kg/ha in some areas and 90kg/ha in the REPS treatments. Applied nitrogen fertiliser is applied in the urea form early in the growing season, usually in February, at a rate of 50kg N/ha on all plots. The areas devoted to silage receive a further 74kg N/ha at the end of March. CAN is used over the remainder of the growing season to a total rate of approximately 230kg N/ha, usually 5-7 applications of equal amounts, in relevant plots.

Approximately 1060m^3 of slurry is produced annually on the Johnstown Castle conventional dairy farm. The slurry is agitated before removal from the tanks and was spread using the splash plate method until 2001 but now the band-spread technique is used. This slurry is spread on the silage area in March at a rate of 30m^3/ha. Any excess slurry is stored for spreading on the second-cut silage area after the first cut has been taken, usually at the end of May. Dirty water produced on the farm is spread over 12ha. Approximately 10,000 l/day is produced, resulting in an additional N loading equivalent to ~50kg TN/ha/yr spread in a localised area of the farm (Bartley, 1996).

For many years previous to 1989 a legume-based experiment (white clover) compared herbage yield with conventional fertiliser applications for grass growth, which resulted in 50% of the farm receiving little or no fertiliser N. Maize was grown on approximately 9ha of the farm in 1993.

The stocking rate on the organic dairy farm was 1.5 cows/ha and the area received no artificial fertiliser. Clover, fixation and farmyard manures, in association with more frequent ploughing and reseeding, are the sources of nitrogen in organic systems.

4.3.8. Johnstown Castle Groundwater Nitrate Status

Summary groundwater nitrate-nitrogen concentrations for each piezometer are shown in Tables 4.5 and 4.6 (for the monitoring period February 1999 to November 2000). There are three instrumented study locations on the conventional dairy farm (DF 1, DF2 and DF3) and two locations instrumented on the organic farm (ORG 1 and ORG2). These sites have been indicated on Figure 4.9. All hydrochemical analysis was carried out at the Johnstown Castle water analysis laboratory and the results are presented in Appendix E. The target depth of the piezometer screen is stated for the purpose of demonstrating the pattern of nitrate-nitrogen travelling through the groundwater profile. The water level (WL) range in each piezometer is also shown. The elevation of the wellheads at each sampling location is shown for the purpose of highlighting relative groundwater flow directions to the sampling points of each farm (bearing in mind that the water table mirrors surface topography, refer to section 4.3.5).

Table 4.5 Piezometer details and range of groundwater nitrate-nitrogen concentrations (mg/l) at the Johnstown Castle conventional dairy farm (1999-2000).

Piezometer Reference	**Target Depth**	**Mean NO_3-N (mg/l)**	**Maximum NO_3-N (mg/l)** (& month)	**Minimum NO_3-N (mg/l)** (& month)	**WL range (m bgl)**	**Wellhead (m AOD)**
DF1	7.0m	0.8	1.1 (Nov/Jan)	0.5 (Sept/Oct)	0.5 - 2.7	60.47
DF2A	6.5m	1.6	2.4 (April)	0.1 (Mar)	0.3 – 2.4	54.27
DF2 B	12.0m	3.2	4.1 (Sept)	2.7 (May)	0.7 – 3.3	54.38
DF2 C	16.5m	2.7	3.7 (Oct)	1.7 (Apr)	0.9 – 2.8	"
DF3 A	6.0 m	0.9	2.0 (Mar)	1 (Oct)	1.9 – 2.7	33.46
DF3 B	12.0m	<0.3	1.4 (Dec)	<0.3	1.9 – 2.6	33.48
DF3 C	17.0m	<0.3	<0.3	<0.3	1.3 – 2.6	"

Table 4.6 Piezometer details and range of groundwater nitrate-nitrogen concentrations (mg/l) at the Johnstown Castle organic dairy farm (1999-2000).

Piezometer Reference	Target **Depth**	**Mean NO_3-N (mg/l)**	**Maximum NO_3-N (mg/l)** (& month)	**Minimum NO_3-N (mg/l)** (& month)	**WL range (m bgl)**	**Wellhead (m AOD)**
ORG1 A	9.5m	2.0	7.4 (Sept)	0.3 (Mar/Apr)	1.2 – 9.4	60.46
ORG1 B	12.0m	3.6	4.0 (Jan)	3.3 (Feb)	8.1 – 12.1	60.36
ORG1 C	16.5m	4.8	6.0 (Oct)	3.1 (Feb)	9.6 – 14.8	"
ORG2 A	6.5m	<0.3	<0.3 (Oct)	<0.3 (Aug)	1.8 – 3.8	52.43
ORG2 B	11.0m	0.9	1.8 (Mar)	0.3 (July)	7.2 – 9.1	52.09
ORG2 C	15.0m	2.4	3.0 (Oct)	2.0 (Feb/Jun)	6.8 – 9.1	"

The instrumented grazing area, at DF1, supports a stocking rate of 2.5 LU/ha and receives 325 kg N/ha in mineral fertiliser and a loading of 213 kg N/ha in the form of organic nitrogen. The mitigating factors for the very low nitrate concentrations (almost consistently <1mg/l) here in the saturated soil zone at 7m below ground level (bgl) are the poorly drained clay soil with a low permeability that ensures ponded surface conditions, and hence supersaturated soils with anaerobic conditions, for a few months each winter.

The highest groundwater nitrate concentrations were observed in DF2, which has a more freely draining soil, but is under REPS nitrogen management and so receives the least amount of bagged fertiliser loading. Although this instrumented one cut silage and grazing area (DF2) reveals the highest nitrate concentrations observed on the conventional dairy farm, they are still consistently below the EU GL of 5.6mg/l NO_3-N (EC, 1998). This is area is under REPS management and so receives only 90 kg N/ha in mineral fertiliser form and 167kg N/ha in organic nitrogen form. The stocking rate is relatively low at 1.96 LU/ha. However, clover cover is extremely good in this plot. Clover naturally fixes nitrogen from the atmosphere but a disadvantage is that the release of nitrogen from clover to the soil system is uncontrollable and therefore not timed to grass growth requirements. The subsoil at this site is described as a 'Silty clayey gravelly SAND' (using B.S. 1377, 1990) whereas the four other sites have 'Brown sandy CLAY' cover. Therefore, the significance of subsoil classification, and soil permeability is further illustrated. Soil at DF2 is more freely-draining than at any other of the instrumented sites.

The DF3 plot is a two-cut silage area, which means that it received the highest nitrogen loading of all instrumented plots (330 Kg N/ha bagged fertiliser N in addition to 213 kg/ha organic N). Table 4.5 shows that groundwater abstracted from the two deeper piezometers (B & C) have lower nitrate concentrations than the shallow piezometer at this location. Dilution, either by the deeper groundwater body or from the farm lake, is a possible explanation. These two deeper piezometers respond instantaneously to pumping, showing very little draw-down in water levels, unlike any other sampling locations on either farm. The water levels recorded in the three piezometers at this site suggest an upward gradient from the deeper groundwater body. Therefore results from the two deeper piezometers, B and C, most likely do not relate to the farming practices in the plot. The 'Brown sandy CLAY' cover (B.S. 1377, 1990) appears to delay the onset of autumn leached nitrate at the 6m sampling depth, until late December, compared to results observed at the DF2 site.

In conclusion, on the conventional dairy farm, groundwater nitrate concentrations are low and have not been recorded to even approach the EU GL of 5.6mg/l NO_3-N (EC, 1998). Little seasonal differences or trends were observed.

There are fifteen surface-water monitoring stations on the Johnstown Castle estate. Four of these concern the dairy farm drains. While surface-water monitoring reveals generally low nitrate concentrations on the estate, the dairy farm drains demonstrate the highest levels. However, the nitrate levels in the monitored drains hover around the EU GL (EC, 1998) throughout the year and only once breached 5.6 mg/l NO_3-N (1998-2000).

On the organic farm, groundwater nitrate concentrations are consistently higher than those beneath the conventional dairy farm but again concentrations are always less than the EU GL of 5.6mg/l NO_3-N (EC, 1998). No bagged nitrogen fertiliser is permitted in the organic farming system. The only sources of nitrogen are atmospheric fixation by clover, farmyard manures, grazing-animal urine and dung deposition and nitrogen cycle activity. The stocking rate is relatively low at 1.4 LU/ha. There is virtually no artificial under-drainage on this organic farm. Ploughing is a necessary feature of all organic farming systems; both fields under investigation have active recent ploughing records (both have been ploughed twice within the last ten years).

CHAPTER FIVE INVESTIGATION STRATEGIES AT CURTIN'S FARM

Characterisation of the hydrogeology of an area involves studying hydrology, subsoils, geology and groundwater hydraulics; therefore study of the groundwater hydraulics can itself be properly achieved only by employing a variety of techniques (Price, 1996).

5.1. SITE INSTRUMENTATION

5.1.1. Borehole Locations

Four specific agricultural management practices are used on a typical Irish dairy farm: grazing pasture; grazing and dirty water treatment; one-cut silage and grazing, and two-cut silage and grazing. Generally, these four distinct agricultural managements are grouped spatially on Curtin's farm, as shown in Figure 5.1 (refer to section 5.5.2 for more detail on agronomic loadings and spatial zone designation). The original intention was to target each of the four managements with three replicate piezometer installations, which would have resulted in twelve fields on the study farm having a piezometer targeting the groundwater body. However, difficult drilling conditions in association with budget constraints, and the developing conceptual groundwater flow model, necessitated the boreholes to be located with less emphasis on the agricultural managements in the immediate vicinity of the borehole. Drilling a hole into bedrock did not guarantee a water-strike and seventeen bores were attempted, which resulted in nine successful bores striking water (Figure 5.2 shows all drilling locations). The eventual nine operational project boreholes may be classified by spatial location and with reference to the conceptual groundwater flow model as shown in Table 5.1. Borehole logs for each drilling location shown in Figure 5.2 are presented in Appendix B.

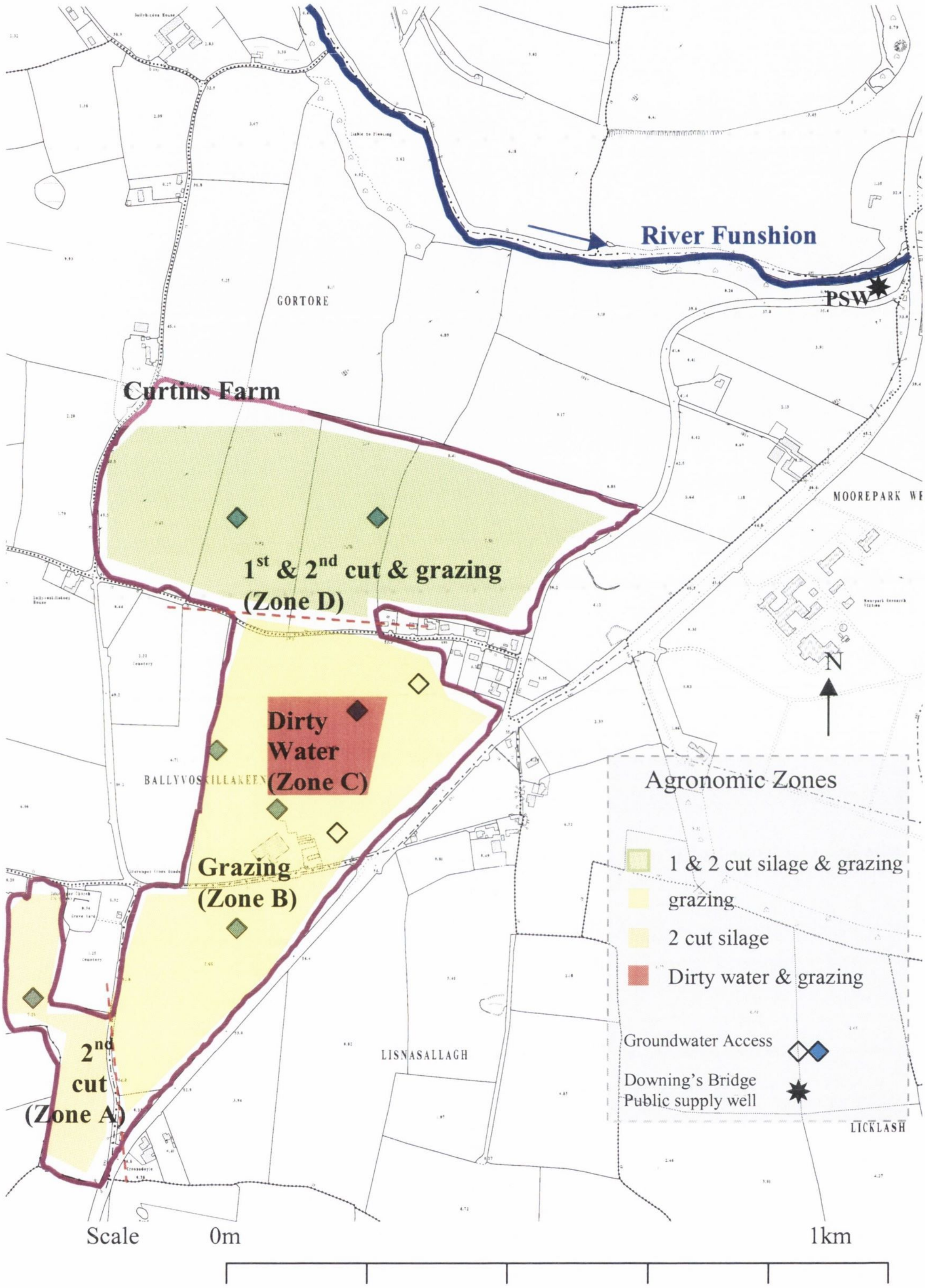

Figure 5.1 Agronomic management zones on Curtin's farm.

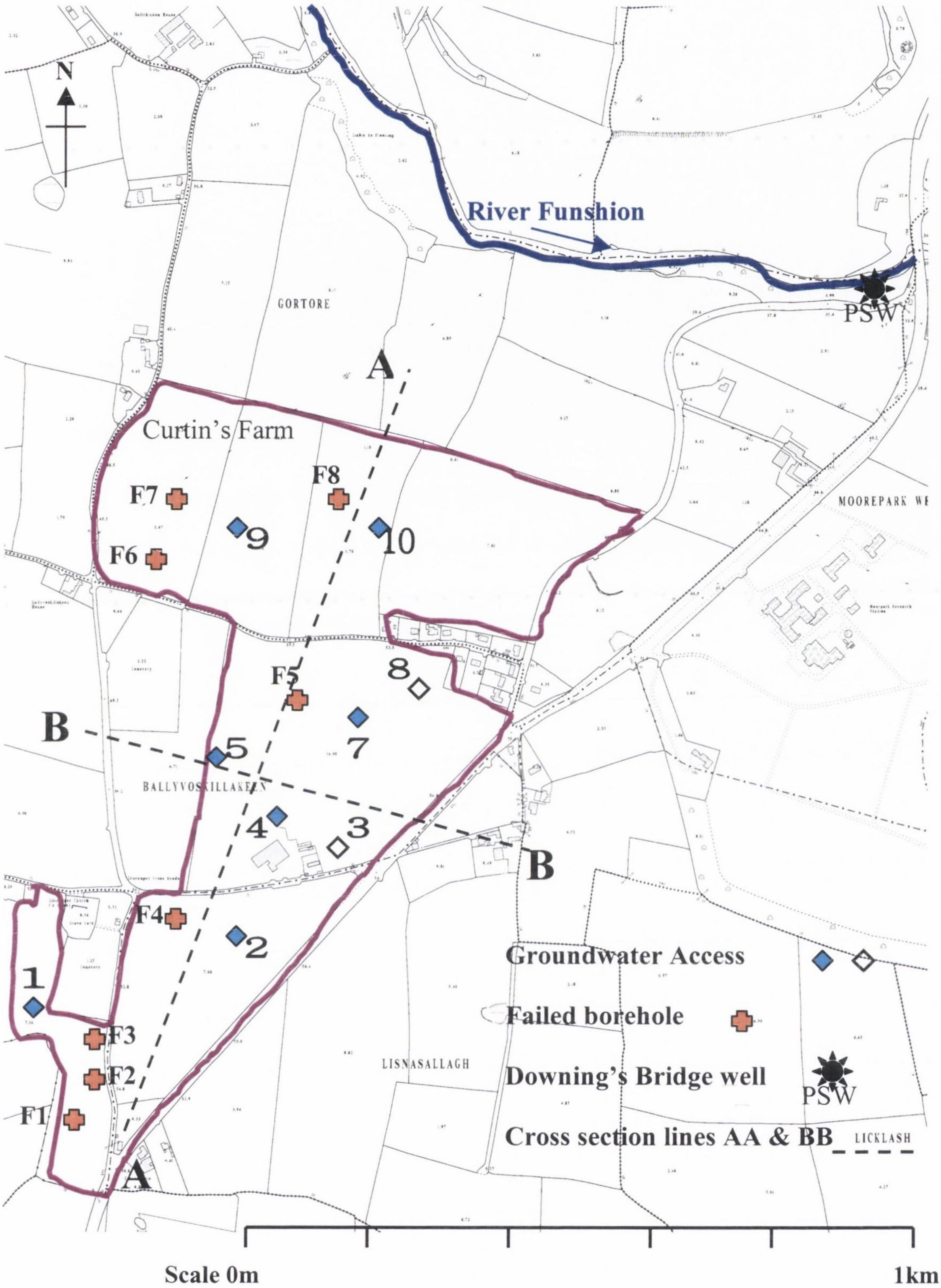

Figure 5.2 All drilling locations, showing both failed (e.g. **F1**) and successful boreholes (e.g. **1** on this figure refers to the usual project borehole notation BHC.1, *etc.*).

Table 5.1 Operational Project Boreholes: Location and Classification.

Borehole I.D.	**Location** **With reference to Groundwater Flow**	**Agricultural Management in Vicinity of Bore** **(Spatial Zone as indicated on Figure 5.1)**
BHC.1	Upgradient of all other bores and farm loadings	Two-Cut Silage & Grazing (Zone A)
BHC.2	Upgradient of farmyard and all bores except BHC.1	Grazing only (Zone B)
BHC.3	Central farm area – influenced by recharge area at BHC.7	Grazing only (Zone B)
BHC.4	Central farm area – influenced by recharge area at BHC.7	Dirty water & grazing (Zone C)
BHC.5	Central farm area – influenced by recharge area at BHC.7	Experimental plot, no nitrogen applied (Zone B)
BHC.7	Central farm area	Dirty water & grazing (Zone C)
BHC.8	Central farm area	Grazing only (Zone B)
BHC.9	Down-gradient of central farm area	One-Cut Silage & Grazing (Zone D)
BHC.10	Down-gradient of central farm area, close to River Funshion	One-Cut Silage & Grazing (Zone D)

Note: BHC.3 & BHC.8: drilled by mineral exploration company as 50mm diameter bores, and therefore do not contain piezometry.

Note: BHC.4 struck a large cavern, which prevented fixing of a piezometer.

5.1.2. Borehole Design - Piezometry

The purpose of the piezometers is to access the groundwater body for pressure-head monitoring, sample collection and groundwater quality analysis (with specific regard to nitrate concentrations) hydrogeological testing and analysis of flow directions. Holes were drilled using compressed air boring methods: the drilling rig created a 150mm diameter borehole to house a 50mm diameter piezometer. Figure 5.3 shows a drilling rig in operation at Curtin's farm.

Figure 5.3 Borehole drilling at Curtin's farm.

Drilling of initial bores demonstrated significant bedrock instability and it was necessary to install piezometers immediately after withdrawal of the drilling rods, otherwise borehole collapse necessitated re-drilling of the bore. For this reason, it was not possible to carry out pumping tests on the open bores. Instead, falling head response tests were used to test groundwater hydraulic conductivity (refer to chapter 6, section 6.1.1.3 for test results).

Each piezometer had a 3m sump and a fixed bottom cap at its base, then a 3m-screened interval to target the water-bearing region in the limestone. The annulus between the piezometer and the bore walls was filled with gravel around the sump and screened interval and a one-metre bentonite seal was placed above the gravel to isolate the screened-sampling interval. The remaining annulus was then backfilled with cement and rock-spoil waste from the drilling procedure to the epikarst region (weathered top of bedrock). A second 1m deep bentonite seal was installed at the top of the bedrock to ensure no direct contamination from leaching from the subsoil zone. Each piezometer was covered at ground level with a lockable well cap set in concrete. Figure 5.4 provides detail of the piezometer installations that were installed, where feasible, at each borehole. In the cases of BHC.3 & BHC.8, these bores were drilled by a mineral exploration company whose drilling rig created only a 50mm diameter annulus. It was not possible install a piezometer in the 50mm bores. The installation of a grouted protective sleeve prevented possible contamination of the groundwater from the subsoil at BHC.3 & BHC.8. At BHC.4 water-strike was within a subsurface cavern (refer to Appendix B for borehole logs), which prevented fixing of a piezometer and so access to groundwater here was by open 150mm bore. The borehole stratigraphy is discussed in chapter 6.1.2.2.

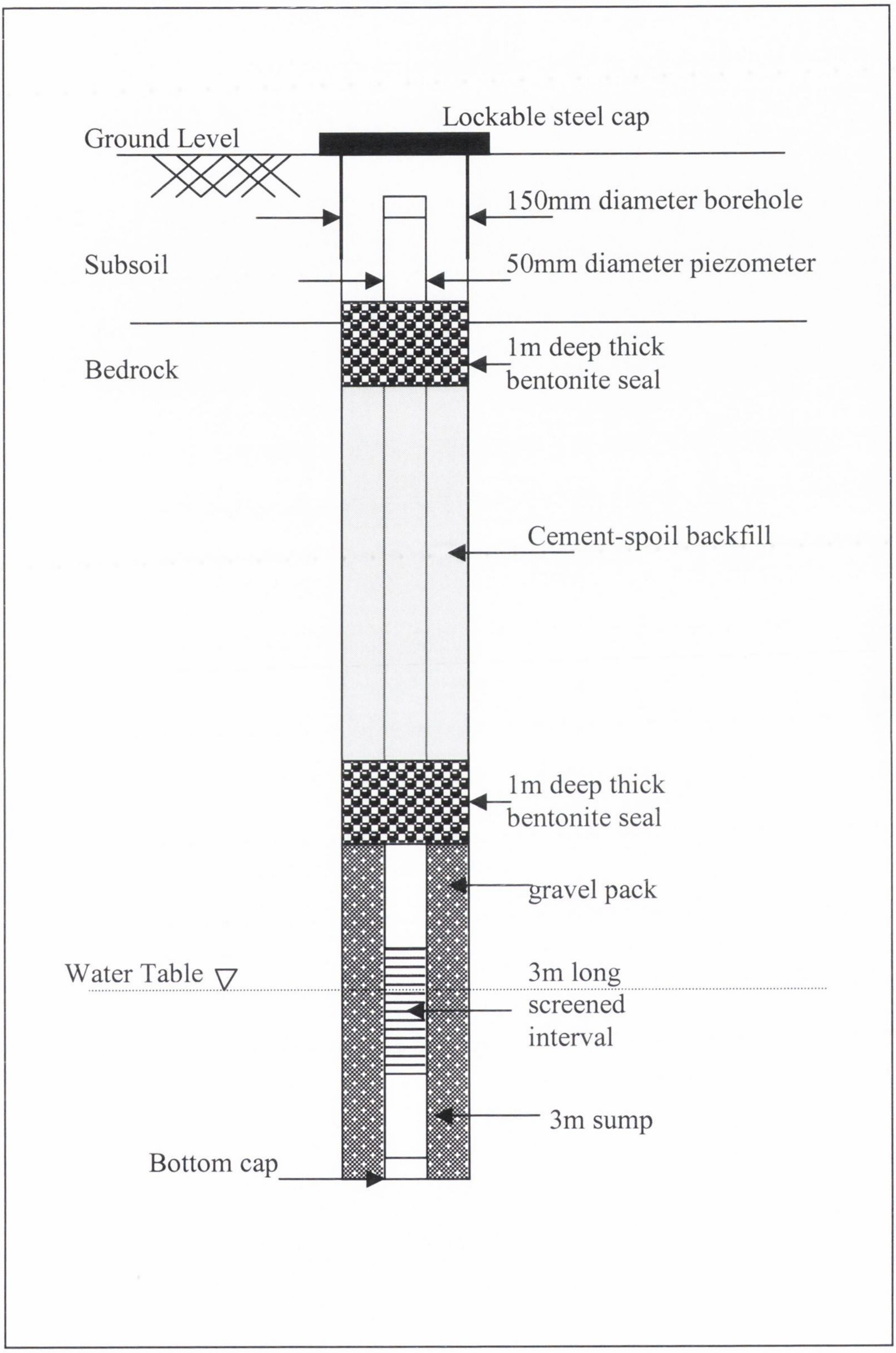

Figure 5.4 Schematic detail of piezometer installations (not to scale).

5.2. SUBSURFACE CHARACTERISATION

5.2.1. Subsoil Characterisation

The subsoil is important because it is effectively the first control that water percolating through the topsoil, and out of the root zone, meets when it starts to enter the ground (Price, 1996). The relative ease with which water moves into and through the soil influences the extent to which leaching (nitrogen losses) and runoff (P losses) occur, and thereby the potential for ground and surface water pollution respectively (Magette & Carton, 1997). The subsoils, therefore, provide a physical layer of protection within which chemical and biochemical activities act to enhance or retard nutrient loss.

The depth to bedrock encountered during drilling on the farm was 2.5m on average but undulated in depth from zero where outcrop occurs to 4.5m, which is consistent with karst terrain. Depths to bedrock results are presented in chapter six, Figure 6.1, and Appendix B. Disturbed topsoil and subsoil (collectively termed overburden) samples were collected at appropriate vertical intervals during drilling at ten of the seventeen drilling locations. These samples were later analysed in order to determine particle size distribution (textural analysis) in the soils laboratory at Trinity College. The significance of these tests, and others, are discussed in the following sections.

5.2.1.1. Laboratory Analysis – Particle Size Distribution

Physically, the subsoil's ability to accept water and then transmit it to groundwater can be described in many ways. The composition/texture of the soil can be described using the British Standard guide (B.S. 1377, 1990), which apportions the percentages of silt, sand, clay and gravel composites in a disturbed subsoil sample taken from the field to the laboratory. The general ability of the subsoil to transmit water can be inferred from the textural description (particle size distribution) yielded by B.S. 1377 because soil texture and hydraulic conductivity are related. A soil with a relatively high sand content is described as coarse textured and is known to have higher hydraulic conductivity and lower water retention capacity than a fine textured soil, which would have high silt and clay fractions (Kiely, 1997).

Wet sieve analysis, following B.S. 1377 (1990) was carried out on 25 subsoil samples collected during borehole drilling. The samples were collected at 0.5m intervals from the spoils of borehole drilling at ten different locations. Further laboratory analysis was carried out on a representative subset of all samples: Pipette analysis (sedimentation tests), also described in B.S. 1377 (1990), allowed further differentiation of the actual proportions of silt and clay. Sedimentation tests were carried out on samples taken from 1m-depth bgl. It was only feasible to carry out the time-consuming sedimentation tests on a representative subset of the original 25 samples and the 1m-depth was chosen. Full results of the particle soil analysis, the associated subsoil grading curves and classification of soil types are presented in Appendix F. Summary results are shown in association with field test results for hydraulic conductivity in section 6.1.

There are many other laboratory tests, such as bulk density and volumetric water content, that may be carried out on samples returned from the field in order to examine the potential of water to move through a soil. Price (1996) summarises the differences between laboratory and field measurements of hydrogeological mediums. He suggests that while laboratory tests permit accurate measurements to be made on disturbed material that is unrepresentative of insitu conditions; field methods provide somewhat inaccurate measurements on what was representative material only before the test boreholes were drilled through it. However, he also highlights the truth that field conditions are so variable, and measurement methods so imprecise and beset with complications, that unless one resorts to 'crystal ball technology' the current best available methods must be employed in an attempt to provide reality-based technical predictions for real problems. Rightly, Price (1996) and others after (e.g. Stockdale, 1999) conclude that although field studies are expensive and their results open to non-unique interpretation, the isolation of samples tested in the laboratory can never fully account for the spatial anisotropy of subsoils and aquifers. Ideally, Price (1996) recommends a combination of the two – laboratory and field-testing.

5.2.1.2. Field Testing of Soils & Subsoils- Hydraulic Conductivity

Field-testing of soils and subsoils usually focuses the investigation on the most pertinent issues of infiltration capacity and hydraulic conductivity, both a function of soil structure. Infiltration is the movement of water from the soil surface into the soil. The rate at which water moves through the subsurface is termed hydraulic conductivity. Hydraulic conductivity (K) is the constant in Darcy's law of liquid movement through porous media and expresses the readiness of the media, be it soil or bedrock, to allow flow at any particular hydraulic gradient. Knowing K enhances the conceptual model developed for water flow (leachate) and will improve the ability to numerically model water and solute transport through any system. The hydraulic conductivity is the most important soil property controlling water and solute movement in soils but it is also the most variable and uncertain of soil properties (Powlson, 1993).

In the course of this study hydraulic conductivity was investigated at 0.5m depth intervals, in the subsoil profile, in five different farm-field plots, each of which contained groundwater-monitoring piezometers. During this testing period the water table was approximately 25m bgl. The site details are shown in Table 5.2, below. Surface infiltration capacities were measured, by another work-group to be 250mm/day (Gibbons *et al.*, 2003).

Table 5.2 Site details for subsoil hydraulic conductivity investigations (refer to Figure 5.2 and Table 5.1 for borehole locations).

Plot I.D.	Borehole I.D.	Number of Auger Holes	Targeted Depths
15BLUE	BHC.1	4	0.5; 1; 1.5 and 2m bgl
17BLUE	BHC.2	4	0.5; 1; 1.5 and 2m bgl
NUIG plot	BHC.5	4	0.5; 1; 1.5 and 2m bgl
12BLUE	BHC.7	5	0.5; 1; 1.3; 1.5 and 2m bgl
3BLUE	BHC.9	5	0.5; 1; 1.2; 1.3 and 2m bgl

The auger hole method is a well-documented method (Bouwer, 1978; Ritzema, 1994; Domenico & Schwartz, 1998; and Schwartz & Zhang, 2003) for measuring saturated hydraulic conductivity (K_{sat}) in subsoils. It is important to make every attempt to measure hydraulic conductivity for the saturated soil condition, as the ease at which a soil conducts water is dependent on the water content of the soil (Bouwer, 1978). With increasing water content more pores fill, and the rate of downward water movement increases (Fetter, 2001). Given that for any volume of a mineral soil there is an equal proportion of solids and pore spaces (Kiely, 1997), in unsaturated subsoil parts of the pore channels are filled with air, which physically obstructs water movement (Bouwer, 1978). Measurement of K in pore-saturated conditions returns a maximum value of the rate of leachate migration in the winter season, which is the worst-case/fastest-movement scenario, with respect to nitrate leaching. When the soil is saturated the K values obtained from successive tests will be replicable. Unsaturated hydraulic conductivity is not constant and, in fact, demonstrates a high degree of hysteresis.

The auger hole method is based on the principle that if a hole bored into the subsoil is repeatedly filled with water until the area is practically saturated, the infiltration rate will be constant and K is the saturated hydraulic conductivity of the wetted subsoil (Ritzema, 1994). The hole is drilled to the required depth in the subsoil using an auger or other method; the 'Giddings' mechanical small-bore drill was used in this investigation. The diameter of the test-holes for the auger hole method is relatively small, 5 to 10cm, by design. The holes drilled with the 'Giddings' had a diameter of 8cm, on average. The auger hole technique enables measurement of K that reflects mostly the hydraulic conductivity in a horizontal direction except when the head of water is relatively small (Bouwer, 1978).

In each of the five plots the subsoil stratigraphy was investigated for K_{sat} at 0.5m depth intervals. Each auger hole was spaced approximately 10m apart to avoid interference between test bores. The auger holes were repeatedly filled ('fill-period') with water over a two-day period: sometimes requiring filling only three times before a steady infiltration rate was achieved but in some highly permeable zones over ten consecutive fills were required.

During the actual tests, which were replicated up to three times, a head of less than 0.5m was applied in order to ensure that the hydraulic conductivity would be determined for a specific stratum only, at the base of the auger hole, and that the head of water would not influence the test. The water level in the auger hole was monitored using a dipmeter and a sufficiently intensive time interval for the rate of water infiltration. During the saturation period, when holes were repeatedly filled with water, the response of the water level over times in the holes was recorded at a less intensive time interval for indicative purposes. Generally, two or three plots/sites were being tested simultaneously and the tests took two and a half days to replicate. The recorded water level responses over time were converted to infiltration rates per hour in order to effectively determine steady state conditions. In some cases it was very difficult to create saturated conditions, which was manifested in tests that were difficult to replicate. In these particular cases, one can only infer very permeable conditions. Results from 2m bgl at the BHC.1, NUIG and BHC.9 plots were difficult to replicate due to either sandy or gravelly lenses, possibly boulders or epikarst region. The occurrence of these highly permeable lenses was not always obvious from returns from the subsoil drilling. On completion of the tests, the holes were filled with bentonite pellets to within 10cm of ground level, wetted and then filled to ground level with the soil spoil retained from drilling. The hole was then recovered with the original sod.

5.2.1.2.1. Data Analysis for Hydraulic Conductivity Determination

During these field experiments conducted on Curtin's farm it was observed that infiltration rate was positively correlated with the head of water, as indicated by Bouwer (1978). Therefore, the K_{sat} value was usually calculated from observations at the end of the test, when the head was 0.2m or less. Schwartz and Zhang (2003) explain that the classical work by Hvorslev (1951) showed the behaviour of the water level to be exponential; the change per unit time starts out relatively large and slows down. The time required to return to equilibrium depends on the hydraulic conductivity (K); in high K units the water level return to pre-test levels will be seconds or minutes, while in low K units the recovery might take months.

Saturated hydraulic conductivity was determined by calculation using equation 5.1, as presented by Ritzema (1994).

$$K = 1.15*r *[\{\log (h_o+0.5r) - \log(h_t+0.5r)\}/(t_t - t_o)] \qquad \text{(Equation 5.1)}$$

where:

r = radius of auger hole (cm)
h_o = standing height of water at start time t_o (cm)
h_t = standing height of water at time t_t (cm)
t_t = time after start for measurement of h_t (seconds)
t_o = start time (seconds)

Other equations, such as those presented by Bouwer (1978) and numerous methods presented by Schwartz & Zheng (2003), were also considered but all assumed a water table in the subsoil and this was not our field environment. Richards (1999) successfully employed equation 5.1 to determine subsoil hydraulic conductivity in an investigation in the same geographic region as Curtin's farm. For each of the twenty-two tests carried out on the farm, data were structured to create four graphs (shown in Appendix G):

1. Top Water Level (m below ground level) versus Time (seconds).
2. Head above the base of the auger hole (m) versus Time (seconds)
3. H/H_o (ratio of head at any time over initial head) versus Time (seconds).
4. Log H/H_o versus Time (seconds).

The graphs were used to demonstrate the straight-line response behaviour required for application of equation 5.1. Originally graphs 3 and 4 were prepared for application of the Hvorslev method (1951) and even though this method was not applied, the graphs were not redundant because they aided identification of a test period that was appropriate for application of equation 5.1.

For solution of K; two particular head (cm) values and their associated times (seconds), for a straight-line portion in the latter stages of a test, were substituted in equation 5.1, above. Subsoil hydraulic conductivity results are presented and discussed in chapter 6, section 6.1.1.3.

5.2.2. Hydraulic Properties of the Groundwater

The nature of a groundwater body and the directions of groundwater flow can be determined by observation of hydraulic heads in boreholes or piezometers (refer to water table elevation maps in chapter six, Figure 6.6, and Appendix H). However, in order to determine the properties of the media, such as the ability of an aquifer to transmit water (Transmissivity*, T) or store it (Storativity*, S) large-scale tests are usually employed. The usual practice is to implement long-term pumping tests, lasting days to weeks. Pumping tests involve continuous abstraction, pumped from a large diameter borehole, and the observation of the response of the system in a number of smaller bore observation wells appropriately space usually in a grid format centring on the pumped abstraction well. The pump, and the associated piping system used to constantly pump water from the aquifer at a rate that will cause a water-table drawdown significant enough to be analysed, necessitates a large-diameter abstraction borehole. Analytical solutions, such as the Theis solution (1935) or the Cooper & Jacob (1946) modification to the Theis equation, can then be applied to field-test observations in order to calculate the aquifer properties. The concepts of T and S, however, apply to the analysis of well hydraulics in confined aquifers. Freeze & Cherry (1979) highlight that although the terms are well defined, they lose there meaning when considering two- or three-dimensional flow in unconfined units; they suggest use of the concepts of hydraulic conductivity K and specific storage S_s[1].

The nature of the geology beneath Curtin's farm, unstably fractured limestone, and the encountered borehole collapses, required all piezometers to be installed immediately upon completion of borehole drilling. Therefore, the project had no access to the large-diameter borehole required for running the pumping tests described above. The small bore Grundfoss pump, that allows sample collection from the project piezometers targeting groundwater flowing in karstified fractures, was not capable of effecting a drawdown for pumping test analysis. The Geological Survey of Ireland (Motherway, 1999) have completed pumping tests on the Moorepark Research Centre, of which Curtin's farm is a

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* The concepts of aquifer Transmissivity and Storativity are more complex than construed here; refer to Freeze & Cherry (1979) for more significant explanation.

[1] Specific storage is defined as the volume of water that a unit volume of aquifer releases from storage per unit decline in hydraulic head.

part, and the results have already been discussed in chapter 4, section 4.2, whilst describing known information on the study area.

5.2.2.1. Aquifer Hydraulic Conductivity - Piezometer Slug Tests

It is possible to determine aquifer hydraulic conductivity (K) values *in situ* by means of tests carried out in a single piezometer (Freeze & Cherry, 1979). A 'slug test' is the common name of the test in which water level recovery over time in a piezometer, that has had an instantaneous addition or abstraction of water, is monitored in order to provide an estimate of K. The slug test is much simpler than a conventional aquifer test and will work with relatively small-diameter wells of piezometers; the only drawback is that K values are considered less representative than those obtained in the aquifer test (Schwartz & Zhang, 2003).

Hvorslev (1951) pioneered a methodology for analysis of the slug test's observed field data, namely head and time, which has become the accepted standard for calculation of K for the field conditions in this study; a piezometer screened at the base only. Schwartz & Zhang (2003) outline the theory and evolution of slug test analysis and provide clear working outlines of two further progressions of the analyses methodologies, as follows:

- Cooper *et al.* (1967) provided a methodology suitable for screened or slotted piezometers open over the entire thickness of a confined aquifer (Freeze & Cherry, 1979). This was developed further by Papadopulos & Cooper (1967) and again by Papadopulos *et al.* (1973) to provide a more sophisticated approach to single well testing in a confined aquifer for a fully penetrating well. It is a curve-matching scheme of solution. Equations are provided for determination of the aquifer coefficients Transmissivity (T) and Storativity (S), both of which are required for this methodology for solving K. Domenico & Schwartz (1998) detail the problems in applying this methodology and state that is infrequently used.

- Bouwer & Rice (1976) developed another technique for determining K in a fully or partially penetrating well, later extended by Bouwer (1989) for confined conditions; the approach is similar to Hvorslev's but also requires using a set of curves to estimate the radius of influence (Schwartz & Zhang, 2003).

Domenico & Schwartz (1998) cite Hvorslev's as probably the most widely used methodology in field practice and Freeze & Cherry (1979) explain it to be the simplest interpretation of piezometer-recovery data, so it was applied to data sets generated in this study.

5.2.2.1.1. Hvorslev's Analysis Methodology (1951)

The theory and development of the Hvorslev equation is plainly explained by Freeze & Cherry (1979). The steps in running the test, selection of the appropriate shape factor and calculation equation, as well as notes for applicability in different test scenarios are comprehensively detailed by Schwartz & Zhang (2003). However, it is Domenico & Scharwtz (1998) who most succinctly outline the test method and its analysis straightforwardly as follows:

1. The original head in the borehole is first noted and recorded.
2. For the slug injection, a quantity (i.e. slug) of water is instantaneously added to the borehole, raising the original head above its static level, termed *ho* (the height of the slug at time zero).
3. The slug will then start to decay as water enters the formation. This change in head is noted over time, where *h* is designated the height of the slug at any given time.
4. For Hvorslevs analysis, data must be presented in terms of head ratios; *h/ho*. Thus, for time equal to zero, *h/ho* =1, and as time gets large, *h/ho* approaches zero, that is, the slug has been completely dissipated.
5. Field data are plotted on semi-logarithmic paper with *h/ho* on the log scale (y-axis) and time *t* on the arithmetic scale (x-axis).

The above steps describe setting up test field conditions, collection of observed response of the system and preparation of data. In terms of data analysis and calculation of the K values, the equation has different forms depending on the well/piezometer design. In short, Hvorslev accounted for the potential differences in intake areas for different boreholes, piezometer tips and differing aquifer penetrations by including a shape factor in the K formula. The evolution of the basic equation is well described in groundwater textbooks (Freeze & Cherry, 1979 and Domenico &

Schwartz, 1998). For the conditions in the Curtin's farm boreholes, the hydraulic conductivity equation becomes

$$K = [R^2 . \ln (L/R)]/[2.L.T_o] \qquad \text{(Equation 5.2)}$$

where:

T_o, the time intercept on the curve where $h/ho = 0.37$, is measured graphically

R is the radius of the piezometer

L is the length of the intake area (screen length)

In the field, instantaneous injection was quite successfully achieved using an inverted water drum, from the mineral water dispensing units commonly found in offices today. The nozzle fits nicely into the 50mm diameter piezometer and acts as a large funnel. The bottom must be sawed off the drum, which creates a large open area for addition of water. In addition, the problem of water-vacuum and time-delay, in water arrival in the fast-reacting piezometers, is avoided. It was found that using a graduated bucket to pour water into the drum, dissipating the energy off the inside of the drum, worked best. This configuration is shown in Figure 5.5.

Figure 5.5 Inverted adapted water drum used for slug tests at Curtin's farm.

During testing, the response of the piezometer water level over time was recorded using Van Essen 'DIVER' dataloggers. Barometric 'DIVERS' were used at the ground surface purely as a precaution, for explanation of any anomalies during the test periods. ENVIROMON software, and a laptop, provided instant access to the test results. On return to the office, data tables were exported from ENVIROMON to EXCEL for data manipulation, plotting and K determination. EXCEL spreadsheets associated with K calculation for each piezometer are shown in Appendix I. In most cases, the slug tests were replicated, two to three times, for each piezometer. Aquifer hydraulic conductivity tests are discussed in chapter 6.1.3.1.

5.3. GROUNDWATER MONITORING METHODS

5.3.1. Groundwater Levels

Groundwater levels were recorded in each piezometer using a dip-meter each week and prior to all sampling events. Water levels were also manually recorded during purging to contribute to understanding the hydrogeological influences at each location. Groundwater level data are presented in Appendix J. A ground elevation survey was carried out using a *Trimble* Global Positioning System (GPS) to determine the elevation of each piezometer's wellhead. It was then possible to convert water level depth data to water table elevations for use in construction of water table contour maps and these maps allow deduction of groundwater flow directions (refer to chapter six, section 6.3 & Figure 6.6).

Although groundwater levels were measured manually in the piezometers each week, manual measurements may miss peaks in trend behaviour. To overcome this difficulty OTT *'Orphimedes'* dataloggers were installed in three piezometers (BHC.2, BHC.7 and BHC.9) to collect a long-term continuous record of groundwater levels. The dataloggers were installed in April 2002. The accuracy of the datalogger was verified each time groundwater levels were measured manually and the datalogger record was downloaded to a 'palmtop' computer in the field. Data were transferred to a personal computer on return to the office and imported to the Microsoft EXCEL programme for manipulation and comparison with the trend of manually obtained groundwater levels. Datalogger records show groundwater table fluctuations follow similar trends in all three instrumented piezometers, shown in Appendix K.

5.3.2. Groundwater Sampling & Analysis

I was responsible for groundwater sampling and sample delivery to the analysis laboratory. Groundwater samples were collected using a 50mm diameter Grundfoss submersible pump powered by a generator (see Figure 5.6 for sampling instrumentation).

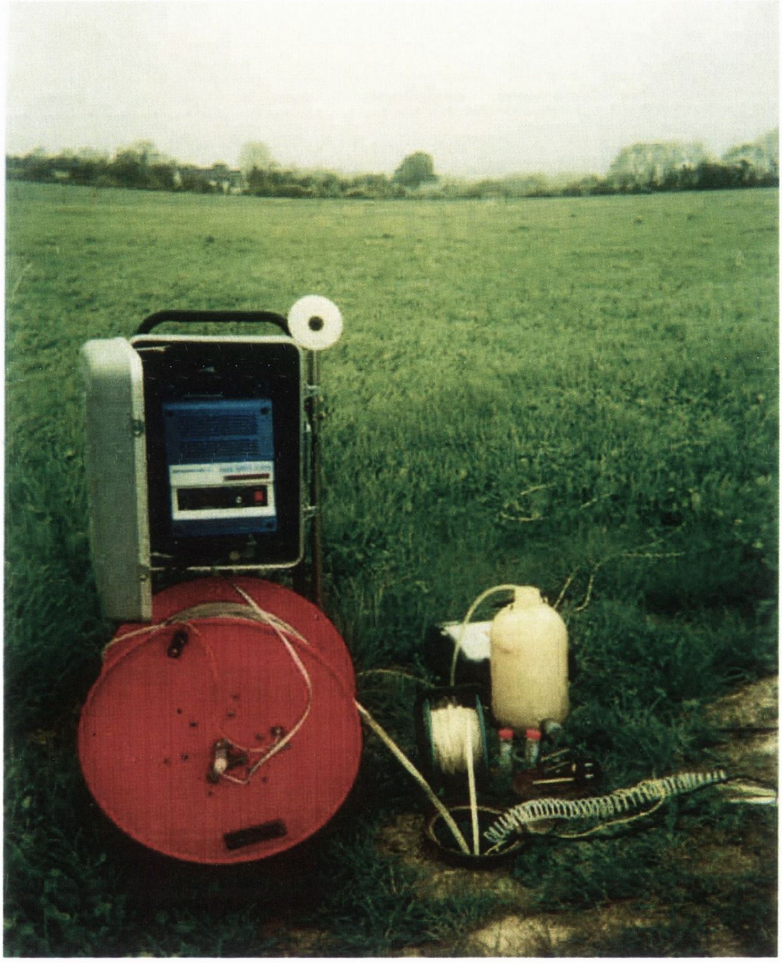

Figure 5.6 Sampling set-up at a Curtin's farm Borehole (generator not shown).

Each piezometer was purged before sampling by removing three times the casing volume (i.e. the volume of standing water in the piezometer). This is normal practice for a groundwater monitoring protocol (e.g. Szeto *et al.*, 1994; Zebarth *et al.*, 1998). Sampling frequency was twice monthly throughout the first year of the experiment but the summer sampling frequency was reduced in the second year, to once a month, following analysis of results. Groundwater temperature and electrical conductivity were measured in-situ. Duplicate samples were collected from each piezometer.

Samples were transported, under refrigeration, to the Johnstown Castle water analysis laboratory where they were analysed. Samples were not preserved in the field because they were analysed within 24 hours of collection in the Teagasc Johnstown Castle water analysis laboratory, Wexford. In addition to the suite of nutrients (Total Oxidised Nitrogen, Nitrate-Nitrogen, Nitrite-Nitrogen, Ammonium-Nitrogen and Phosphorus) a suite of ions was analysed for each sampling event: potassium; sodium; calcium; sulphate; chloride; magnesium, in order to attempt to define the hydrochemistry and the agricultural signal in the groundwater.

Nutrient analysis was carried out using the KONELAB auto analyser. Quality control procedures for the KONELAB included preparation of appropriate standards of varying known concentrations each day. Each morning, the KONELAB was initialised and known standards were tested and checked by the technician responsible for water analysis. In the laboratory, in order to ensure that samples did not enter a queue, the water analyst was given prior notification that I would be delivering groundwater samples from Curtin's farm. In that way, analysis within 24 hours of sample collection was guaranteed. I was authorized to load my samples on the appropriate auto-anlayser carousels. The water analyst and I ensured that analysers operated within the defined quality control procedures. All of this studies groundwater samples were analysed in duplicate pairs. I checked results from the KONELAB, and all other analysers in the water laboratory, immediately. If the concentration results for either the known standards or groundwater samples were questionable, new standards were prepared and a new sample run was initiated until the integrity of the results could be assured.

It should also be noted that, during this study, whenever groundwater samples were analysed for orthophosphate, the samples were analysed in their raw state and an additional filtered volume of sample was also analysed, each set in duplicate. Disposable 0.45μm filters were used. This allowed the soluble fraction to be determined. More detailed information regarding sampling protocol and laboratory analysis procedures is provided in Appendix L.

5.3.3. Assessing Groundwater Quality

The EPA has published a suggested methodology for assessing groundwater quality in Ireland (EPA, 2003a). All member states have obligations to protect, enhance and restore all bodies of groundwater under the Water Framework Directive (EC, 2000) as well as maintaining and/or attaining 'good chemical status'. This Directive requires the monitoring of oxygen content, pH value, conductivity, nitrate and ammonium as part of the surveillance monitoring. The aim of the EPA (2003a) published methodology is to establish consistent framework for the characterisation of groundwaters in Ireland in the context of a new Groundwater Directive to be published soon which will require the definition of groundwaters 'reference condition' and 'typologies'.

The EPA has therefore proposed a list of interim guideline values (IGV's) for groundwater (EPA, 2003a). The newly proposed IGV's were not newly invented but extracted from the following existing data sources and regulations: existing national Environmental Quality Standards for groundwater; proposed common indicators from the new Groundwater Directive; Ireland's Drinking Water Standards; existing/proposed Environmental Quality Standards for the aquatic environment and GSI Trigger Values[#].

When assigning an IGV for any quality parameter, the EPA used GSI Trigger Value where it applied, and where it did not apply the most stringent value of the Drinking Water Standard or the EQS for the Aquatic Environment/ Dangerous Substances, where appropriate. The EPA has also proposed a characterisation list to provide a consistent suite of parameters termed the 'Core Group' or 'Natural Substances' that allows standardised characterisation of groundwater (Appendix M contains the list and associated IGVs). In addition, a list of 'Site Specific' parameters has been developed for user selection dependent on the purpose of the monitoring and following site assessment. This 'Site Specific' list mostly concerns synthetic substances, which is not relevant to this agricultural contamination study.

In addition to setting IGVs and providing a list of parameters that should be analysed, the EPA also proposed a model/methodology to comprehensively assess groundwater quality in a standardised way. The model follows a decision framework structure in which, firstly, each analysed parameter value must be compared with the IGV: if all parameters are below the IGV then direct action is not required. However, if one or more parameter exceeds the IGV then further assessment is required. The further assessment includes assessment of the natural hydrochemistry of the groundwater. If the sites' groundwater is not in keeping with the natural hydrochemistry then remedial action 'may be required'. The strategy (EPA, 2003a) suggests, "The objective of the remedial action must be to reduce the parameter concentrations below the IGV, unless it is naturally occurring, and to ensure continued improvement of the quality of the groundwater". The model/methodology for assessing

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[#] The GSI employ six parameters to serve as groundwater quality indicators (nitrate, potassium, chloride, ammonia, K/Na ratio, and faecal coliform). The Trigger Values act as a warning that appreciable impact on groundwater quality may be occurring (GSI, 1999).

groundwater presented by the EPA will be employed in this analysis of field data collected during the course of this research.

Most, but not all, parameters from the EPA proposed characterisation list were analysed in the course of this research study (the list was circulated at the end of the monitoring period). Of the five-physiochemical parameters suggested, this project analysed for three (electrical conductivity, temperature and pH). Of the seventeen inorganic parameters presented in the list, the following were routinely determined: ammonium; nitrate; nitrite; orthophosphate; potassium; sodium; chloride; sulphate; and calcium (nine of the seventeen suggested parameters).

5.3.4. Assessing Groundwater Vulnerability

Vulnerability is term used to represent the intrinsic geological and hydrogeological characteristics that determine the ease with which groundwater may be contaminated by human activities (Fitzsimons *et al.*, 2003). In the Irish situation, vulnerability is mainly a function of the quaternary deposits, *i.e.* thickness and permeability of the subsoils (Misstear *et al.*, 1998).

Quaternary deposits are a natural feature with a huge influence on groundwater vulnerability and pollution prevention. The hydrogeological significance of Quaternary sediments is variable and is largely a function of their permeability, thickness and extent. Low permeability material restricts recharge, protects underlying groundwaters and where sufficiently thick confines them. High permeability material allows a high level of recharge, provides additional storage and where sufficiently thick can be an aquifer in their own right (Tietzsch-Tyler & Sleeman, 1994).

The Geological Survey of Ireland (GSI) has developed a comprehensive set of guidelines (Fitzsimons *et al.*, 2003) for assessment of groundwater vulnerability in an Irish context. The GSI methodology forms a basis of the preparation of Groundwater Protection Schemes and adopts a risk-based matrix approach to vulnerability mapping dependent on subsoil depth and permeability (DELG et. al, 1999). The hazard-pathway-target model forms the basis of the GSI vulnerability assessment methodology: the approach relies on the characterisation of ‘pathway’ as the basis for delineating vulnerable zones.

Essentially the vulnerability concept is based largely on the question ‘can water and contaminants move/get down to groundwater easily?’ (Fitzsimons *et al.*, 2003). Vulnerability is not an absolute property, but a relative indication of where contamination is likely to occur (NRC, 1993). Within the GSI framework the definition of subsoils' permeability is qualitative in that a ranking system assigns vulnerability ratings as either extreme, high, moderate or low.

Ideally, regional vulnerability assessments should be tested against field observations of vulnerability to lead to improved methods and a better understanding of the factors affecting aquifer vulnerability to contamination (NRC, 1993). The GSI methodology will be applied, in this study, to assess groundwater vulnerability at Curtin's farm. The significance of the approach was further demonstrated by assessment of groundwater vulnerability at Johnstown Castle, which is a contrasting hydrogeological environment. Groundwater vulnerability analyses are contained in chapter six, section 6.1.1.5.

CEC (1991) outlines the nitrate$^-$ flux into the groundwater as a result of complex processes in the soil. These processes are influenced by:

*__Climate__: amount of rainfall and variation in time, evaporation and temperature,

*__Soil__: topography, relief, type, thickness and permeability,

*__Land use__: plant type, depth of the root zone, season of plant growing and changes in land use,

*__N input__: type of fertiliser, amount, frequency and time of fertilisation.

In essence, the GSI approach relies on the 'soil type' as the basis for delineating vulnerable zones. The investigation strategy of this work is to define the response of the groundwater system to those other factors influencing nitrate$^-$ flux to groundwater; 'climate' and 'management practices', which affect loadings to the system ('Land use' and 'Nitrogen input', listed by CEC (1991) above, can conceptually be considered together as 'Management practices').

5.4. INVESTIGATING MECHANISMS OF SOLUTE LEACHING – TRACING STUDY

5.4.1. Introduction

A bromide-tracing experiment was conducted to investigate the rate of movement of surface applied water and solutes through the unsaturated zone to groundwater, in the dirty water treatment area, on Curtin's farm (central farm area, spatial zone "C" as indicated in Figure 5.1). This area of the farm was chosen, as the onus was on this research effort to definitively explain the monitored rapid-reaction of the groundwater table to recharge events.

In order to interpret the collected groundwater monitoring data, the hydrologic mechanisms that determine the fate and distribution of the chemicals in the hydrogeologic profile required definition. Nitrate concentrations in the groundwater beneath the farm were highest in the tracing area. The tracing experiment was used to validate the constructed groundwater-table elevation maps, the direction of groundwater flow and hence the source of the nitrate contamination problem.

5.4.2. Rationale: Use of bromide as a Tracer

The bromide ion has been widely used as a tracer to investigate water and contaminant transport in agricultural research (Smith & Davis, 1974; Jabro *et al.*, 1994; Kessavalou *et al.*, 1996; Schuh *et al.*, 1997; Kelly & Pomes, 1998; Richards 1999). Bromide is an ideal tracer because it is highly water-soluble and is negatively charged, making it behave almost identically to infiltrating water and leaching nitrate in the subsoil (Flury & Papritz, 1993; Schuh *et al.*, 1997). Simultaneous tracing experiments on irrigated plots have shown nitrate and bromide travel times and peak amplitudes to be identical (Everts *et al.*, 1989; Schuh *et al.*, 1997). Although chloride (Cl) behaves similarly as a tracer, bromide has the advantage of naturally low [0.01 – 0.3 mg/l Br] background concentrations in groundwater (Flury & Papritz, 1993), whereas chloride is abundant in the natural environment. The toxicity of bromide and the inherent risks associated with its use in field studies has been extensively investigated to show that there should be no toxic effects (Gilley *et al.*, 1990; Flury & Papritz, 1993; Bowman *et al.*, 1997). Richards (1999) conducted a successful bromide-tracing experiment on another Moorepark dairy farm, Ballyderown, following the same detail as described here with no ill effects to vegetation or animals on the farm. Although research shows that it is possible for bromide to be taken up by plants (Gilley *et al.*, 1990), this should not be the case for the conditions of this experiment. Chloride and bromide are both described as having minimal precipitation and adsorption tendencies under normal field conditions (Schuh *et al.*, 1997). The fast draining subsoils of Curtin's farm and typically high rainfalls experienced in the season of tracer application were believed to mitigate any possible retention in the topsoil or herbage system. The experiment was conducted during the winter-housing period. No animals grazed the area before at least eight weeks after bromide application. If a tracer experiment is successful, it should assist in determining the likely cause of elevated groundwater nitrate concentrations. Fank (2001) credits the results of his tracing experiment as having:

- Proved the field measuring and sampling devices on their ability to detect transient transport phenomena of water and solutes;
- Illustrated the differences between hydraulic reaction of water content on infiltration events and the velocity of solute movement in the unsaturated zone;
- Allowed estimation of hydraulic parameters of soil horizons;
- Enabled calibration of solute transport models in the unsaturated zone to quantify different flow components using advection-dispersion transport modelling;
- Allowed quantification of different flow components using advection-dispersion transport modelling;
- Facilitated correction of measured flow data of field lysimeters.

Bateman *et al.* (2001) successfully employed a tracing experiment to improve understanding of the vulnerability to contamination of two public supply wells in a sand and gravel aquifer near the east coast of England. The results of their experiment clearly demonstrate a connection between surface risks and contamination of groundwater abstraction wells. Under the conditions of their tracer test, breakthrough of fluorescein at the well (20m bgl) began 6-7 days after tracer injection.

Skinner (1985) cites tracer testing as an essential component of groundwater regime description; to bring realism into the otherwise conservative estimates of flux, which are likely to result from estimates based on rock permeability measurements. However, he does stress that it is essential, in all tracer tests, that estimates are based on positive breakthrough, and not inferred from negative evidence.

5.4.3. Environmental Occurrence of Bromide

Background soil bromide concentrations are generally found to be low, ~1.0 mg/kg (Flury and Papritz, 1993). Higher concentrations are found in coastal areas and a range of 0.3 to 852 mg/kg has been reported (Maw & Kempton, 1982). As mentioned, bromide has the advantage of naturally low [<0.01 – 0.3mg/l] background concentrations in groundwater (Flury & Papritz, 1993). Monitoring reports from two distinctly different climatic regions concur that typical bromide concentrations in groundwater are naturally <0.1 mg/l (in the UK: Loung *et al.*, 1980; and in Sweden: Lundstrom and Olin, 1986). However, in the southeast of England groundwater bromide concentrations Houghton (1946) reported an observed range of 0.026 to 2.26 mg/l with higher concentrations again attributed to proximity to the sea. Yuita (1983) proves the influence of the sea, showing bromide concentrations in both soil and groundwater to decrease with increasing distance from the sea.

5.4.4. Study Site Instrumentation and Layout

One field on the farm, housing one groundwater-piezometer (BHC.7) and eight subsoil-pore-water ceramic cups, was selected for ground-surface irrigation with a potassium bromide solution (see Figure 5.7 for tracing experiment location on the farm). Applying the bromide at only one location ensured that if bromide were found in groundwater samples collected from any other piezometers on the farm, groundwater flow directions could be defined. Applying the bromide$^-$ at two locations could lead to uncertainties regarding its origin if it appeared in any borehole.

The targeted groundwater-piezometer (BHC.7) had a total depth of 35m, a screened interval at 29-32m bgl and a top-water level at the time of the experiment of 19.84m bgl. The depth of subsoil cover at BHC.7 is 2m to the top surface of the bedrock, which is soft and weathered for the upper 1m (epikarst). Particle size analysis describes the subsoil to be a gravely, silty SAND at 1m bgl, as it is at most locations on the farm, and at 2m is described as a brown silty very gravely SAND (BS 1377, 1990). The Waulsortian limestone bedrock is solid until 30m bgl where a 0.5m deep cavity was encountered during drilling. Further drilling returned damp chips until 34m when a mud filled cavity yielded a significant enough water-strike to cease drilling and install the piezometer casing (Appendix B contains borehole log details).

The subsoil-pore-water ceramic cup instrumentation was instrumentation that had been installed by another work team in the group research project (EPA, 'Eutrophication from Agricultural Sources', project reference: M1-LS-2.3), which was introduced in section 1.5. Dr. Michael Ryan's team facilitated use of their ceramic cups for the bromide investigation. This subsoil instrumentation, in one plot, was used for the subsoil-monitoring component of the tracer experiment conducted by myself. Each of the eight subsoil-pore-water ceramic cups in the plot had been installed at 1m bgl. All of the field instrumentation had been in place since 2001 and two winters nitrate leaching/monitoring data had been collected. Refer to Figure 5.8 for relative location of instrumentation within the experimental plot, 12BLUE (see Figure 5.14 for farm plot delineation and identification). More specific details on the ceramic cups are provided in Appendix N.

In the month prior to the experiment samples were collected and analysed to determine the background bromide concentrations in both the subsoil pore-water and groundwater. The subsoil is never saturated; there is no perched water table within the subsoil. The water table is in the bedrock and has an annual range of ~20-28m bgl. However, there was a soil moisture deficit of zero, indicative that the subsoil moisture was at field capacity, all through January 2003 on the day of application of the bromide solution (28th January 2003). In terms of natural recharge, ~10% (66mm) of the annual effective recharge had fallen in the previous month and 5mm of rain fell on the initial day of the experiment.

The plot under investigation, 12BLUE, is part of the 7ha of the farm devoted to the treatment of dirty-water generated from yard and milking parlour washings (refer to Figure 5.1 for agronomic management zones). Therefore, in addition to natural recharge the plot receives an additional artificial recharge. A mechanised irrigator travels slowly and linearly through the plot, irrigating each and any point on the ground surface once and once only on a three to four-month rotation. The irrigator was moved into the plot two days after the bromide solution was applied. The movement of the irrigator in the plot was recorded (Figure 5.8) and the depth of irrigation was determined from daily volumes spread, as recorded in the irrigators' pump-house, and spatial area covered. Generally, the irrigator travels a distance of ~20m/d therefore taking four days to traverse the length of the field. The daily-irrigated area is ~520m^2 and the depth of dirty water irrigation is 16mm. It took twenty-six days for the irrigator to pass through the entire plot, 12BLUE, which covers an area of 0.86ha (8600m^2).

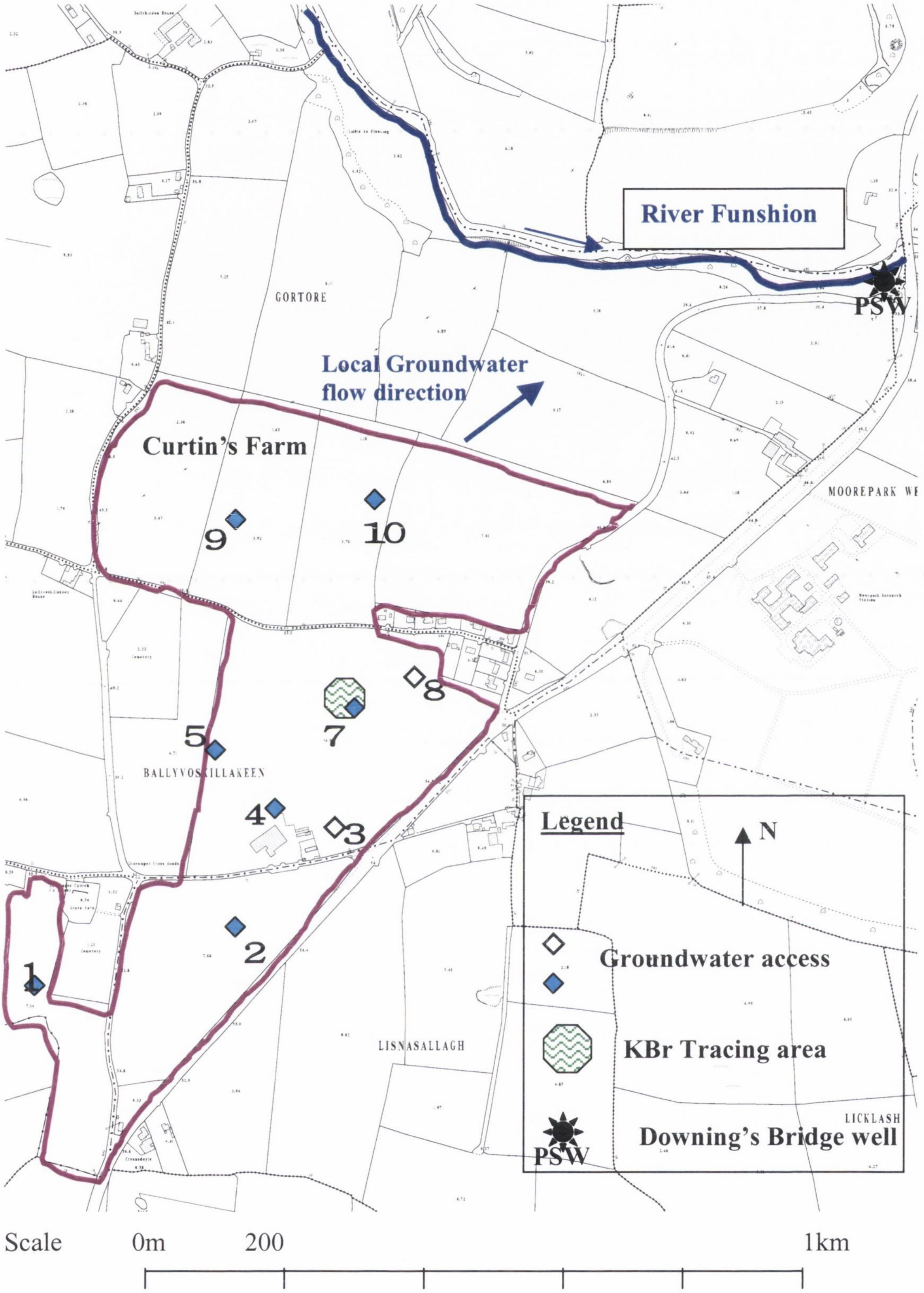

Figure 5.7 Curtin's farm and the experimental tracing area.

5.4.5. Methodology

The bromide solution was applied on the 28th January 2003 at a rate of 732kg/ha Br in the chemical stock form of potassium bromide (KBr). The detailed calculations for determination of the equivalent mass of bromide in the KBr stock chemical are provided in Appendix O. A total of nine grids were marked out each one centring on a single monitoring instrument (eight ceramic cups and one piezometer). It was financially prohibitive and deemed environmentally wasteful to dose the entire 0.86ha plot.

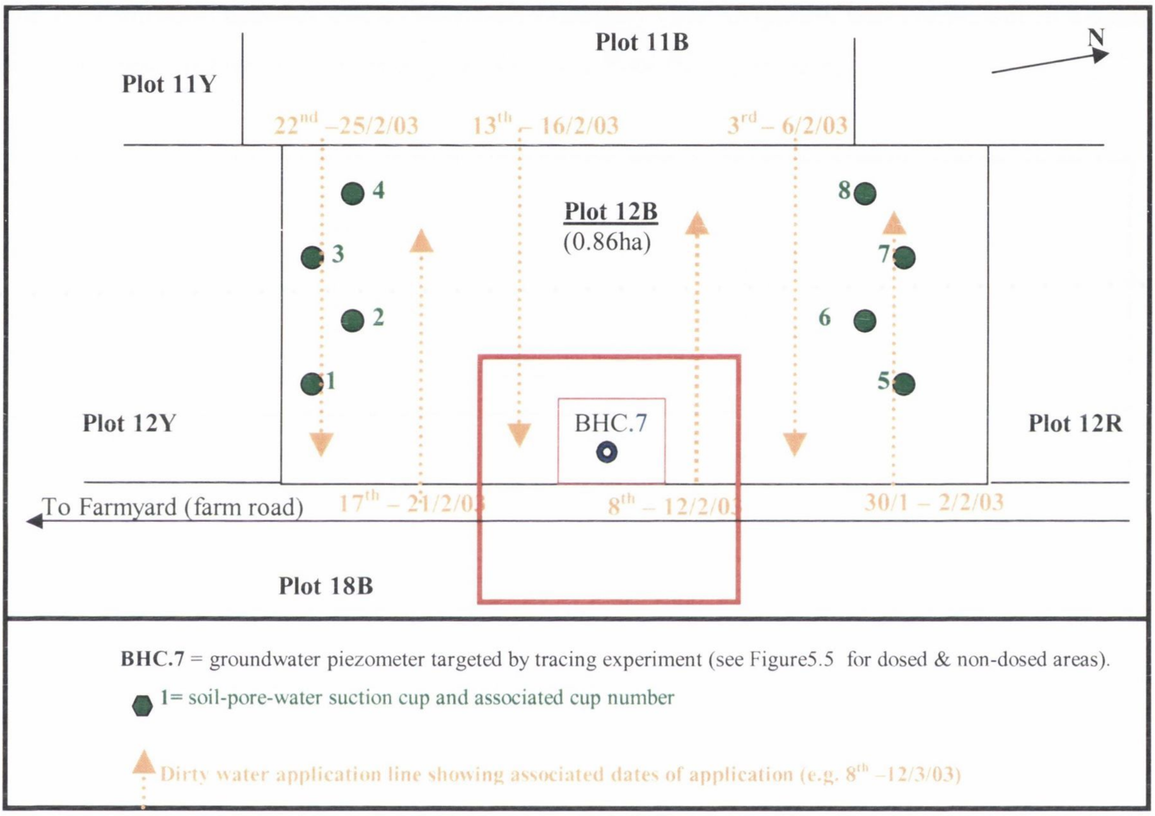

Figure 5.8 Schematic representation of targeted instrumentation in the tracing-experiment's plot and recorded movement of the dirty water irrigator (not to scale).

The total area dosed with the bromide solution was 0.024ha (240m^2). The 732kg bromide$^-$ ha^{-1} application rate was double that applied in a previous study on another local farm (Richards, 1999) because of fears of 'losing' the tracer in the Curtin's farm site conditions that had double the thickness of subsoil cover and faster groundwater flow domain than in Richards study. No detrimental effect was observed in the vegetation or grazing animals, but there was no grazing in the experimental plot for two-months after application of the tracer.

The dosing grid around the groundwater piezometer had overall external dimensions of 10m by 15m, with a total dosed area of 110m^2 (40m^2 around the piezometer was not dosed in part to ensure no preferential movement of Bromide in the immediate vicinity of the piezometer and also because of a farm road, 3m wide, adjacent to the piezometer, as shown in Figure 5.9). The dosed area was divided into 12 equal area blocks and each block was irrigated by hand using a 10-litre watering can. The discharge pipe of the watering can was fitted with a 0.5m-long, 0.25 diameter, uniformly perforated T-bar attachment to ensure even irrigation of the bromide solution. For each of the twelve-area blocks, 1kg of KBr$^-$ was dissolved in 10 litres of water and the area was evenly irrigated. The concentration applied was 67,000 mg/l bromide$^-$. The irrigation was equivalent to a recharge depth of 1mm. It took approximately two-hours to dose the entire area.

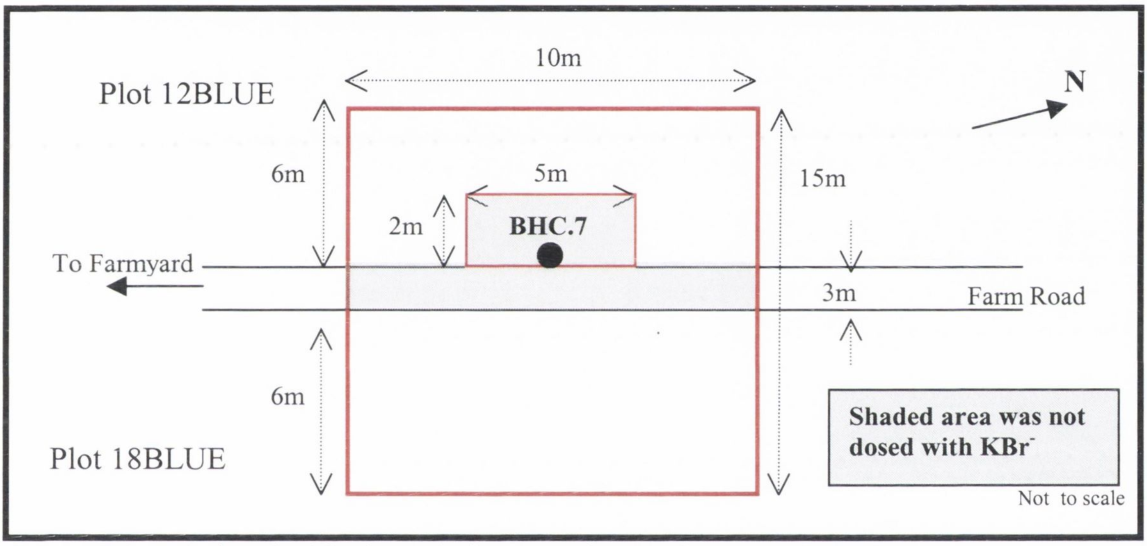

Figure 5.9 KBr dosed grid schematic for groundwater piezometer BHC.7

In the case of each of the ceramic cups a 3 x 3m square, with the cup as centre, was marked out on the ground surface. For each of the eight cups, 1kg of KBr$^-$ was dissolved in 10 litres of water and the area was evenly irrigated using the same method with the watering can and attached T-bar. The irrigation concentration and recharge depth was the same as applied to the grid around BHC.7. The area directly above the cup, which had been disturbed by installation drilling, was shielded from irrigation by an inverted bucket. The cups are staggered, as shown in Figure 5.8, at either six or eight metres from the electric fence. Tubing connects the cup at one metre depth to a Buckner vacuum flask protected by temporary fencing under the electric fence.

5.4.5.1. Monitoring

Disposable bailers, of one-litre volume, were used for groundwater sample collection. Dedicated bailers were assigned to each piezometer to avoid cross-contamination. The piezometer at the centre of the dosed area, BHC.7, and those in its immediate vicinity were bail-sampled every second day until sample analysis confirmed that Br^- persisted in the groundwater beneath the experimental field and once weekly until the pulse of bromide passed. The other piezometers on the farm were bail-sampled twice weekly. Duplicate samples were collected from the screened-interval depth. The groundwater-table elevation in all piezometers was monitored every second day. As part of the nitrate leaching experiment all piezometers on the farm were purged and sampled at two-week intervals using a 50mm diameter portable "Grundfoss" submersible pump (see section 5.3.2). The normal two-week sampling programme continued as usual throughout the tracing-experiment monitoring. The day after the bromide was applied, 29th January, the regular purge and sample routine was followed. The only change in the overall sampling procedure was that bailed samples were always collected prior to the submersible pump being installed. On the "Grundfoss" sampling days additional samples were retained during purging to examine the persistence of the bromide in the groundwater.

The ceramic cups were sampled once every week by a field technician. Extra samples were retained for this tracing experiment for use in analysis to establish the travel time of the bromide tracer, and hence solutes, to the 1m depth in the subsoil. Each week after sample collection a negative pressure of 50kpa was applied to the Buchner flask that was attached to the ceramic cup. A clamp sustained the suction until the sample was retrieved one week later.

All samples were analysed, in batches, within one-month of collection. Groundwater samples were selected for analysis after consideration of effective rainfall calculations and observed top-water levels in the piezometers. All collected subsoil samples were sent for analysis: gaps in the subsoil data indicate that the sampler yielded no sample.

5.4.5.2. Laboratory Analysis

The Centre for the Environment, University of Dublin, Trinity College, determined the bromide concentration using a DIONEX ion chromatograph. The method is extremely accurate and the limit of detection is 0.25mg/l bromide$^-$. All background samples sent for analysis had bromide concentrations below the limit of detection. The bromide tracing results are presented and discussed in section 6.5.

5.4.6. Agricultural Activity in the Experimental Farm Plot

Nitrogen fertiliser is applied incrementally on the farm. For this, and the other dirty water plots, fertiliser is usually applied a couple of days before the irrigator enters the field.

The plot (12BLUE) received the dirty water irrigator on three occasions during the tracing experiment:

1. Firstly, from the 30th January (two days after the application of 1mm of bromide) to the 25th February, irrigating for perhaps two-three hours per day at an average total depth of 16mm of dirty water (positioning and timing of irrigation is indicated on Figure 5.8);
2. For one week from 16th to 23rd May, irrigating at top speed and depositing 4mm depth of dirty water (cups 5-8 dosed on the 16th and cups 1-4 dosed on the 23rd); and
3. For six days, 14th to 19th June, irrigating 3mm of dirty water (cups 5-8 dosed on the 14th and cups 1-4 dosed on the 19th).

The dirty water irrigator is set to move at greater speeds through the fields in spring and summer and so less dirty water is applied, because the grazing activity is more intensive for the grazing fields when 45% of the farm is closed off for silage.

In terms of grazing, 39 cows graze the plot at any one time but the full field is not opened to grazing all at once. Generally, one third of any plot is grazed for one day, and on successive grazing days other portions of the field are opened. This has implications for the intensity of nitrogen load deposition and consequent risk of nitrate leaching, but this is discussed further in the section detailing agronomic load determination, it is mentioned here because the probability that urine deposition hits on a sampler must be increased in a smaller grazing area (see section 5.5.2.1.2 for more detailed loadings discussions). The plot (12BLUE) was grazed four times during the experiment for an average of two consecutive grazing days on each occasion as follows:

1. On the 31st March the plot was grazed for one full day only;

2. From the 29th to the 31st April the plot was grazed for a total of 2.5 grazing days;
3. From the 29th to the 31st May for a total of 2.5 grazing days; and
4. From the 25th-29th June for a further 2.5 grazing days.

Although the average stocking rate over the whole farm is ~2.5 cows/ha, the stocking density in the actual sectioned off plots at the time of grazing is equivalent to 130 cows/ha/day for a two-three day period.

5.5. LOADING DETERMINATIONS

Definition of groundwater- nitrate responses on the farm was the fundamental aim of this experiment. Project objectives were to quantify loadings and measure the response of the groundwater system at the farm-scale. Towards these objectives, meteorological modelling allowed determination of recharge (effective rainfall loading) and daily nitrogen applications and grazing activity data were collected and used to determine agronomic nitrogen loadings.

The loadings data collected were used in two ways:

1. Firstly, by logging the additions to each farm field on a daily/weekly basis their effect on the temporal response of groundwater could be analysed (see chapter six, sections 6.2.2 and 6.4.6).
2. Secondly, quantification of total annual nitrogen loading rates from each nitrogen source allowed examination of Curtin's farm in the context of the Nitrate Directive (EEC, 1991a), which sets limits on the total amount of organic nitrogen that can be applied on any farm (see section 5.5.2.6).

The purpose of this section is to discuss methods and data employed for both meteorological and agronomic nitrogen loading determinations. In terms of the consequent loadings results only total values are presented in this section. Much loadings data were generated and these are presented in Appendix P (meteorological data) and Appendix Q (nitrogen loadings data).

5.5.1. Meteorological Loadings

Water drives leachates through the subsoil to the groundwater system. The two sources of driving-water on Curtin's farm are rainfall (meteorological loading) and wastewater treatment (dirty-water). The dirty-water is disposed on only 7ha of the farm, or 18% of the total area, and is considered an additional agronomic loading subject to detailed analysis in section 5.5.2. Rainfall is distributed over the entire farm and its influence is discussed in detail in this chapter.

Groundwater recharge may be defined in a general sense as the downward flow of water reaching the water table, forming an addition to the groundwater reservoir. A clear distinction should then be made, both conceptually and for any modelling purposes, between the potential amount of water available for recharge from the soil zone and the actual recharge as defined above (Rushton, 1988).

Lerner *et al.* (1990) explain that recharge can be quantified by several methods and these can be grouped as follows: (a) direct measurement; (b) water balance methods; (c) Darcian approaches; (d) tracer techniques; (e) other, mainly empirical, methods, each of which is discussed below;

a) Direct measurement - complex and expensive to construct accurately in order to ensure no influence of method on measurement. In reality only recharge from precipitation can be directly measured.

b) Water balance methods – estimates recharge as the residual of all the other fluxes based on the principle that other fluxes can be measured or estimated more easily than recharge. Examples of these methods are soil moisture budgets and water table rise. In the case of soil moisture budgets rainfall and potential evapotranspiration are inputs to a soil moisture accounting procedure, with actual evapotranspiration and recharge as the outputs. A balance approach based on water table rise works on the principle that when the volume stored beneath a rising water table is equated to recharge, after allowing for other inflows and outflows such as aquifer through flow and discharges from pumped wells. The advantages of water balance methods are that they use readily available data (rainfall, runoff, water levels), are rapid to apply and account for all water entering the system (Lerner, 1990). On the other hand, propagation of errors through the mathematical process can be high if estimations have to be made at the beginning.

c) Darcian approaches – based on Darcy's founding law for groundwater flow. In principle, knowledge of hydraulic heads, pressures, moisture contents, hydraulic conductivity, other aquifer properties and boundary fluxes will allow estimation of recharge by either field measurement or numerical modelling. For saturated flow field measurement of head and accurate measurement of conductivities at the right scale are all that are needed to apply Darcy's law [Q = k.i.A]. However, difficult laboratory measurements often bear little relation to large-scale field values. When considering unsaturated flow, the sensitivity of hydraulic conductivity values to moisture contents makes flow calculations less reliable and should be avoided (Lerner, 1990). Numerical modelling, taking account of transient flows and storage changes into account, can be applied to determine recharge based on the Darcian method but data and computing requirements are high. The need to make simplifying assumptions in order to reduce overloading the computations can negate the confidence in model outcomes.

d) Tracer techniques – either environmental (i.e. naturally occurring bacteria or chloride in rainfall) or applied (i.e. bromide or dyes) tracers can be used in recharge estimations. Two methods, namely signature or throughput can be used (Lerner, 1990; Tindall & Kunkell, 1999). Signature methods are when parcels of water are dated or labelled and throughput methods attempt a mass balance of the tracer. In the case of applied tracers a mass balance is usually not feasible because of lateral dispersion, so signature methods are employed.

e) Other methods – many empirical methods can be used in the preliminary estimates of recharge.

The methodology employed in this study falls under the soil moisture budget methodology, described in section (b) above. Rain falls and can be directly measured on the ground surface. However, not all rain that falls reaches the groundwater body. The hydrologic cycle, describing the fate of rainfall, Figure 5.10, has been well defined and explained in every hydrology book that has ever been written. It is necessary to apply an empirical model to deduce how much of the rain falling on the ground surface on Curtin's farm is actually available as draining water, termed effective rainfall. Field measurements of subsoil hydraulic conductivity were carried out in order to determine the potential rate of movement to be applied to draining water as it percolated through the subsoil profile (chapter 6, section 6.1.1.3, presents these results). Within hydrogeology it is usual to consider things on a 'hydrologic year' basis, which typically starts on the 1st October with winter recharge rains and extends to 30th September in northern temperate climates.

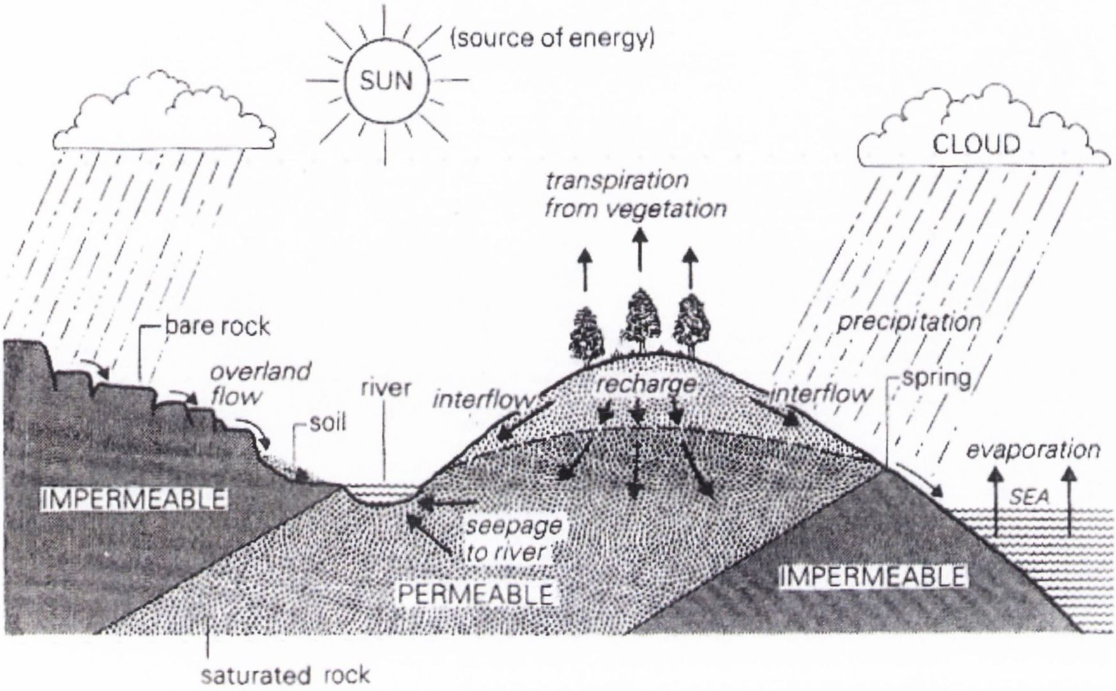

Figure 5.10 Diagramatic representation of hydrologic cycle (Price, 1996).

5.5.1.1. Source of Meteorological Data

There is a Met Eireann climatological station (station number 158, grid reference R824 012) at the Moorepark research station. Daily measurements of rain, evaporation, sunshine hours, grass growth and temperature and wind characteristics are recorded at the Moorepark station and returned to Met Eireann. The weather station is approximately 600m from Curtin's farm and so these data were deemed relevant for analysis and meteorological modelling for water balance calculations. Observed monthly rainfall patterns for the study area are shown, in Figure 5.11, to often vary greatly in successive years especially in the winter recharge months November, December, and January. The challenge is to apportion the amount of this rainfall available to drain through the soil at any time, termed effective rainfall.

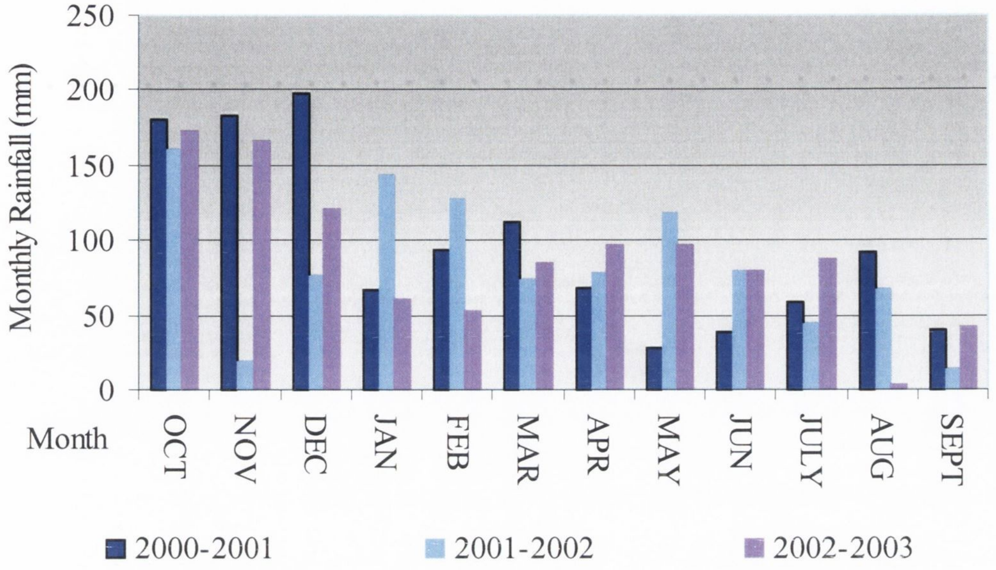

Figure 5.11 Actual monthly rainfall recorded at the Moorepark weather station.

The actual daily recorded rainfall values at the Moorepark climatological station form part of the dataset presented in Appendix P. The maximum rainfall recorded in any one day was an unusually high 63.9mm in November 2000, at the very beginning of the study. The average daily rainfall was 3mm but on at least three occasions in any year daily rainfall exceeded 20mm and sometimes 30mm.

5.5.1.2. Water Balance Theory

While the hydrologic cycle, previously shown in Figure 5.10, is a qualitative description of the fate and transport of water in the aquatic system, both fresh and saline, it is also possible to define the system quantitatively. A water balance or water budget is a method of accounting for water for any study location, catchment, region or even the whole earth. The only input to the system is precipitation, either as rainfall, snow or sleet (only rainfall is relevant to this study). Precipitation can be distributed as surface runoff, evaporation, infiltration to the unsaturated zone, which changes its storage capacity, and deep percolation to the saturated zones (Kiely, 1997). The general hydrologic equation describing the water balance of the unsaturated zone, from the soil surface to below the root zone, was originally presented by Thornthwaite & Mather (1955; 1957) and is presented by Tindall & Kunkell (1999) as:

$$P - Q \pm \Delta S_w - E \pm \Delta S_s - D = 0 \qquad \text{(Equation 5.3)}$$

where:

P	is precipitation,
Q	is runoff,
ΔS_w	is change in storage of water ponded on the surface,
E	is evapotranspiration (evaporation and transpiration),
ΔS_s	is change in soil-moisture storage, and
D	is deep percolation unrecoverable by vegetation.

All terms in the above equation are positive except for the two 'change in storage' components, which could either be positive or negative. However, when working on an annual basis it is valid to assume little change in storage in any part of the system (Kiely, 1997). Therefore, the basic method for determining the amount of water available as drainage (leachate) from the ground-surface is to apply a simple balance equation:

$$\text{Effective Rainfall} = \text{Rainfall} - \text{Evapotranspiration} - \text{Runoff} \qquad \text{(Equation 5.4)}$$

Daily rainfall measurements were provided by the weather station. Runoff on the farm is deemed negligible because the farm sits on a topographic plateau over a karst system. Any local runoff, from farm roads for example, is observed to run towards local field depressions, surface expressions of the underlying karstified bedrock, and eventually into the subsurface zone. Evapotranspiration (evaporation and transpiration) must be modelled using data from the weather station.

5.5.1.3. Evapotranspiration

Evapotranspiration (ET) cannot be measured directly. It is a significant subtraction from the rainwater supplied to the hydrologic system and so must be considered in water balance accounting. There are four components of ET: (1) evaporation from wet soil near the vegetation; (2) transpiration of water by the vegetation; (3) evaporation from the moist membrane surfaces of the vegetation; and (4) use of water by the vegetation to build up new plant tissue (Blaney & Hanson, 1965 cited in Tindall & Kunkell, 1999).

Methods for estimating evapotranspiration have been grouped as follows (Jensen, *et al.*, 1990): (1) temperature methods, (2) radiation methods and (3) combination of temperature and radiation methods. Combination methods have been shown to provide the best models for estimating ET (Tindall & Kunkell, 1999). All estimation methods predict potential evapotranspiration (PET) for a reference crop, usually short grass. For any other vegetative cover or crop PET is estimated by multiplying the reference PET by an appropriate, given crop coefficient (FAO, 1998).

Several factors affect the evapotranspiration process, among them air temperature, wind speed, solar radiation, and available soil moisture (FAO, 1998). Tindall & Kunkell (1999) provide an excellent review of all factors affecting ET and their consequent influences: the driving force for evaporation as well as ET is cited as the vapour-pressure gradient, which is highly dependent upon air temperature. The vapour-pressure gradient and resulting ET are observed to increase with increasing air temperature. Wind speed affects ET by removing water vapour immediately above wet soil and plant membranes; therefore, increased wind speed results in increased ET. The primary source of ET energy is solar radiation; increased solar radiation results in increased ET. Even though the above climatological factors can act to increase ET, vegetation can only transpire if sufficient soil moisture is available otherwise the vegetation will wilt and die with no further potential for ET. Therefore, soil-water content is a limiting factor for ET.

In this study ET is determined using the modified Penman-Monteith equation. The modified Penman-Monteith equation is recommended by the United Nations Food and Agriculture Organisation (FAO, 1998) and by the World Meteorological Organisation (WMO) as the most accurate of the empirical methods for determination of ET, specifically for short time-step calculations. The method is universally accepted for daily and hourly estimation of evapotranspiration from a reference grass surface (Tindall & Kunkell, 1999) and is widely used in field-practice, when determining irrigation requirements for example, and research studies (Alexandris & Kerkides, 2003).

5.5.1.4. Meteorological Model - The FAO Penman-Monteith method (FAO, 1998)

An FAO guide (FAO, 1998) provides a step-by-step methodology for determining daily evapotranspiration from a reference grass surface, which the FAO term ET_o (equivalent to PET in traditional literature). From the original Penman-Monteith equation and the equations of aerodynamic and surface resistance, the FAO Penman-Monteith method to estimate ET_o is derived as:

$$ET_o = \frac{0.408\,\Delta\,(R_n - G) + \gamma\,[900/(T+273)]\,u_2\,(e_s - e_a)}{\Delta + \gamma\,(1 + 0.34\,u_2)} \qquad \text{(Equation 5.5)}$$

where ET_o = reference evapotranspiration [mm day^{-1}],

Δ = slope vapour pressure curve [kPa °C^{-1}],

R_n = net radiation at the crop surface [MJ m^{-2} day^{-1}],

G = soil heat flux density [MJ m^{-2} day^{-1}],

γ = psychrometric constant [kPa °C^{-1}],

T = mean daily air temperature at 2m height [°C],

u_2 = wind speed at 2m height [m s^{-1}],

e_s = saturation vapour pressure [kPa],

e_a = actual vapour pressure [kPa].

The FAO (1998) methodology requires the altitude above sea level and latitude of the site to be defined. These data are required to adjust some weather parameters for the local average value of atmospheric pressure (a function of site elevation above mean sea level) and to compute extraterrestrial radiation (R_a) and, in some cases, daylight hours (N). In the calculation procedures for R_a and N, the latitude is expressed in radian form (*i.e.*, decimal degrees times $\pi/180$). In terms of meteorological data the FAO methodology requires air temperature, humidity, radiation and wind speed data. Soil heat flux (G) is assumed to be zero for daily time-step calculations (FAO, 1998). The vapour pressure deficit can be calculated by two methods; one, when dewpoint temperature is available; otherwise the mean temp and max daily relative humidity (in % form) are used (Tindall & Kunkell, 1999). The guide (FAO, 1998) details all the computations of the required data.

5.5.1.5. Necessary Modifications to Calculated Evapotranspiration

Because soil water content is a limiting factor for ET the water balance calculations must define soil moisture status in some way. Soil moisture deficit (SMD) is a concept used to define the shortfall of soil moisture below required field capacity. A soil is said to be at field capacity when it is holding all the water that it can hold against gravity (Price, 1996). SMD is a readily quantifiable parameter that is correlated to rainfall magnitude, degree of moisture in the soil and ET (Kiely, 1997). When a soil is at field capacity the SMD is zero. The methodology employed for SMD determination is:

1) SMD is assumed to be zero after significant rainfall in the middle of the winter months, *e.g.* December or January is a good starting point for the calculation:

$$SMD_{(day1)} = 0$$

2) For each day thereafter:

$$SMD_{(day\ 1+1)} = Rainfall_{(day\ 1+1)} - ET_{o(day1+1)} - SMD_{(day\ 1)} \qquad \text{(Equation 5.6)}$$

where a positive result indicates a surplus of soil moisture, therefore the SMD is recorded as a zero value. However, a negative result is indicative of a SMD, the value of which is the magnitude of the negative result obtained.

3) And so on for each consecutive day, the calculation is continuous.

In late spring and summer months, as rainfall decreases and increased solar radiation drives ET rates to increase, SMD can act to restrict both moisture available to plant growth and consequent loss through ET. Therefore, calculated ET_o values must be modified to account for the reality that a vegetated system loses water at rates less than those predicted by the theoretical equations during periods of significant SMD (Kiely, 1997). Aslyng (1965) proposed that when SMD exceeds 30mm there is a significant impact on grass growth and hence ET is restricted, and this has been accepted in agronomy. Aslyng (1965) derived a relationship (eq.4) that facilitates modification of a day's calculated ET_o, to give 'actual' ET, based on the previous day's SMD. The relationship proceeds from 30mm to 120mm (SMD value for grass wilting point) with ET decreasing linearly for that range:

To determine actual ET determination for any day, lets say $ET_{(day1)}$:

if $SMD_{(day\ 1\text{-}1)} \leq 30$mm, then $ET_{o\ (day1)}$ is unmodified and deemed actual ET

however,

if $SMD_{(day\ 1\text{-}1)} > 30$mm, then $ET_{(day1)} = ET_{o\ (day1)} \cdot [(120 - SMD_{(day1)})/90]$

(Equation 5.7)

5.5.1.6. Water Balance Determination for Curtin's Farm

A full daily-meteorological water balance for the study farm was completed, using the EXCEL spreadsheet programme, in order to determine daily effective rainfall. Firstly, daily evapotranspiration (ET_o) was determined employing the FAO Penman-Monteith method (FAO, 1998). Computations for daily ET_o are provided in Appendix P. Usefully, the FAO (1998) guide also provides instruction for determining ET_o where some weather data are missing. For example, the daily net radiation required by the method was missing from the data set recorded at Moorepark. However, the FAO guide (1998) provides a model to derive this missing radiation data from daily actual duration of bright sunshine (hours per day) measured with a (Campbell-Stokes) sunshine recorder, which is operational at the Moorepark weather station. Also, utilising the humidity data provided by the Moorepark weather station resulted in unrealistically large estimations of ET_o, when compared with expected ranges of evapotranspiration. Again, the FAO guide (1998) provided an alternative method for this step of the calculation based on minimum recorded daily air temperature, which provided seemingly realistic ET_o estimations.

The daily ET_o results obtained in this study were verified by comparing with another research groups work (Kuczynska, pers. comm., 2002), which had used the same FAO methodology (1998). Kuczynska's work had determined daily ET_o with no missing or modelled data for a site in county Kildare, which contains a fully instrumented and automated weather station. Dr. Rogier Schulte, Teagasc, Johnstown Castle, also checked the methodology with a dataset from the Johnstown Castle weather station in order to compare evapotranspiration values yielded by the FAO methodology presented in this work and those obtained by the Johnstown Castle model. The FAO methodology was again verified and therefore accepted.

Observed daily rainfall, from the Moorepark weather station, and calculated evapotranspiration, ET_o, details were then used to determine daily soil moisture deficit values (daily computed SMD values for each hydrologic year can be found in Appendix P). The daily SMD information was used to modify potentially overestimated evapotranspiration data using the Asylng scale (Aslyng, 1965). The results of this modification can be seen, in Appendix P, by comparing ET_o with ET on any day when the SMD value is above 30mm. Daily effective rainfall (recharge) was the balance of the rainfall addition to the system and SMD and ET losses from the system. Refer to Appendix P for formulaic computations of the completed meteorologic water balance.

5.5.1.7. Effective Rainfall Results for Curtin's farm

Daily effective rainfall data are presented in Appendix P. Daily data has been used to create annual totals presented in Table 5.3. Runoff was judged to be negligible on this study farm because the nature of the karst landscape encouraged rainfall towards surface depressions and drainage to groundwater.

Table 5.3 Meteorological Water Budget Curtin's Farm – Hydrological Years.

Water Budget Terms	**2000 – 2001 (mm)**	**2001-2002 (mm)**	**2002-2003 (mm)**
Actual rainfall [RF]	1163	995	1055
Calculated Actual Evapotranspiration [E_t]	484	532	521
Actual Effective Recharge [RF - E_t]	679mm	464mm	537mm

Groundwater sampling actually began in November 2001 but 2000-2001 data were shown in Table 5.3 to illustrate the significant differences that could occur each year. While perhaps annual totals may be similar from one year to the next, the season in which the recharge occurs is of critical importance with respect to nitrate leaching. Monthly effective rainfall totals are presented graphically, in Figure 5.12, to demonstrate the wide variation.

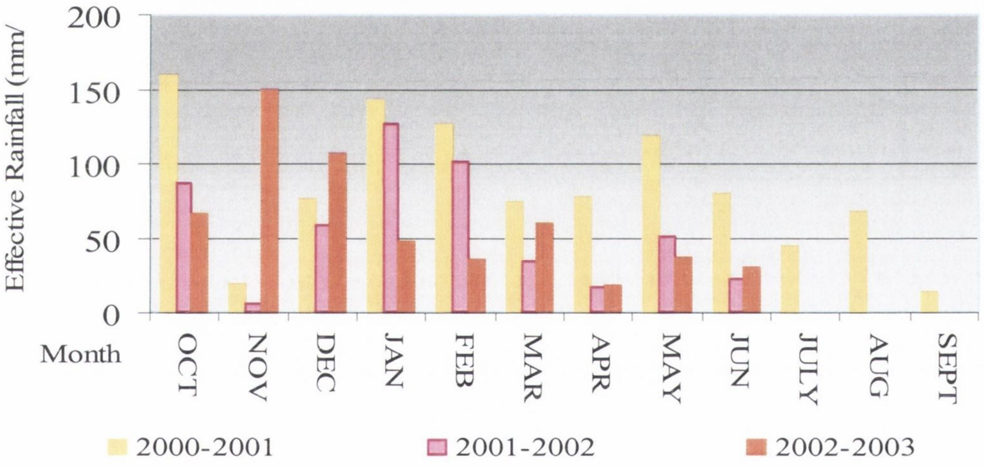

Figure 5.12 Monthly distribution of effective rainfall at Curtin's farm.

Taking Figure 5.12 a step further, it is interesting to observe the differences in seasonal totals for effective rainfall for the duration of the experiment. Seasonal totals are presented in Table 5.4, which shows that there can be a substantial difference between the amounts of winter recharge in each year. These data are presented because the leachate risk is reliant not only on the load of nitrate in the subsoil at the end of the growing season but also on the volume of effective recharge entering the system in the recharge season (autumn and winter).

Table 5.4 Seasonal Effective Rainfall at Curtin's Farm.

SEASON	2000 – 2001	2001-2002	2002-2003
Autumn (August – November)	134	87	66
Winter (November – February)	406	191	303
Spring (February - May)	167	152	112
Summer (June – August)	0	73	66

Effective rainfall calculations allowed delineation of recharge and non-recharge seasons and this information is presented in Figure 5.13. It can be noted that although the total effective rainfall might be similar in two successive hydrological years, 2001-2002 and 2002-2003, the timing of the peak monthly effective rainfall can be very different. The maximum monthly effective rainfall, approximately 150mm, fell in January 2002 in the first hydrological year. However, in the following hydrological year the maximum monthly effective rainfall, again approximately 150mm, fell in November 2002.

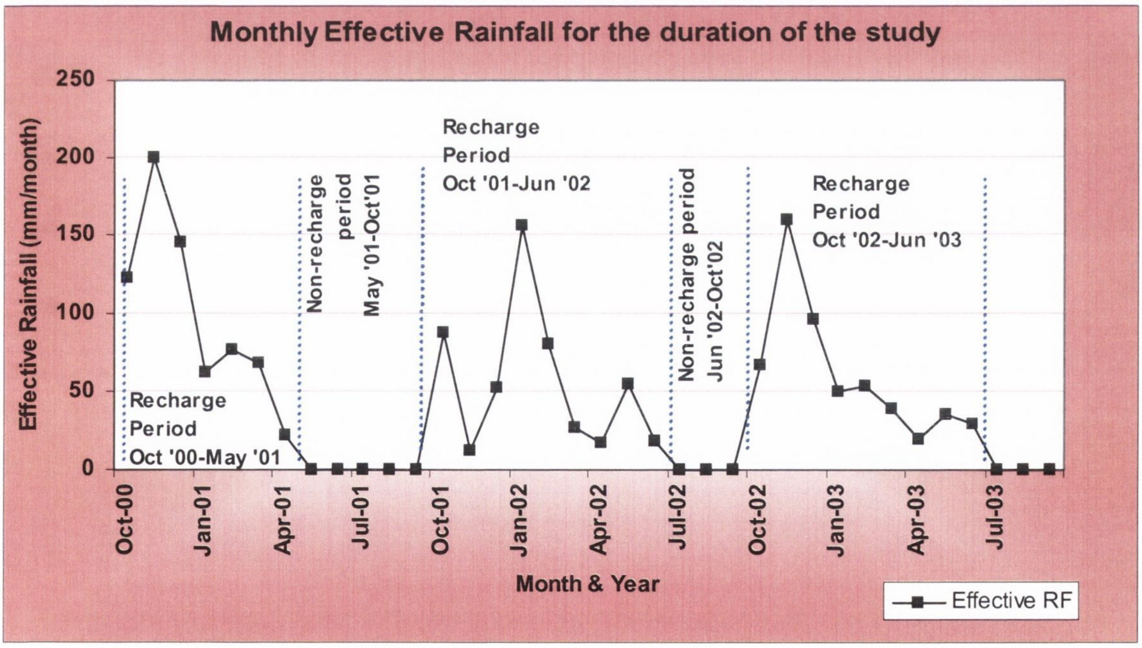

Figure 5.13 Effective rainfall distribution for the duration of the study and the consequent delineation of recharge and non-recharge periods.

The results of the effective rainfall calculations were ultimately used, at a weekly time-scale, to determine the role of recharge in the nitrate response of groundwater (see chapter six, section 6.4.6). The final step in the loading determinations was to quantify all nitrogen loadings to the system.

5.5.2. Nitrogen Loadings

5.5.2.1. Rationale for Nitrogen Loading's Detail

All agronomic loadings on the farm area were recorded. Essentially, the approach taken was to convert all nitrogen loadings (kg) to rate values (kg/ha). In that way individual nitrogen sources loading rates could be compared and also combined, where appropriate, to give a total nitrogen loading rate to each farm field or each of the four agricultural management options under investigation.

Field-scale nitrogen loading details were generated, for daily and weekly time-scales, from daily farm supplied data (see section 5.5.2.2 below). The field-scale nitrogen loadings were then used in analysis of each individual piezometers temporal groundwater nitrate response (see chapter six, section 6.4.6). In addition, the field-scale nitrogen loadings data were analysed further to generate agricultural management-scale nitrogen loading rates data sets on an annual time-scale. Collating fields according to the four managements in operation (grazing only, one or two cut silage, or dirty water and grazing) facilitated analysis of the most significant pressures in this intensive dairy farming system in the context of organic nitrogen loading rates and the Nitrate Directive (EC, 1991a), within a single farm scale.

It is usual for nitrate leaching research to present fertiliser, slurry and dirty water applications in rate format. However, relating the nitrogen loading rate deposited by grazing animals to underlying groundwater quality was not found in the literature even though the information existed to allow this level of calculation (e.g. Lantinga *et al.*, 1987; Haynes & Williams, 1992a; Whitehead, 1995; Humphreys *et al.*, 2003) and the effect of grazing animals on nitrate leaching was well documented in the literature (refer to section 2.4 and also section 6.7 for more recent research findings of significance to the findings of this research).

In the following discussions reference is made to farm management zones. These areas are outlined in Figure 5.14, which also shows farm field identifiers and piezometer locations. The 50ha farm consists of nineteen fields. Curtin's farm management divide each of the nineteen fields into three plots, which are referred to as red, yellow or blue plots. The colour coding is a component of a livestock breeding and milk yield experiment of the Moorepark centre's research programme and as such the reader should not consider the colours important. Generally, all three plots within a field received the same loadings.

5.5.2.2. Sources of Nitrogen on Curtin's Farm

5.5.2.2.1. Potential Point Sources of Agricultural Pollution on Curtin's Farm

As mentioned in section 1.1.3, farmyards, silage pits, septic tanks, underground slurry storage tanks and dairy lagoons are classified as potential point sources on a farm, given that the location of the source can be specified. Curtin's farm yard is indicated in Figure 5.14.

In common with most dairy farms, within Curtin's farm yard there is a silage pit, an underground slurry tank and septic tank. Another underground potential point source on the farm is the dirty water tank that stores the dirty water prior to its irrigation. The dirty water tank is located in the subsurface of a field between the farm yard and the field in which BHC.3 is located. Dirty water is irrigated daily on the farm so there is never a capacity issue with this tank. Of all project piezometers, BHC.3, BHC.4 and BHC.2 are closest to the farmyard area, relative to other piezometers. In the course of the results presented in chapter six, section 6.2.2.1, analysis of the groundwater regime and generation of associated water table elevation maps will clarify the significance of the farm yard on groundwater chemistry at Curtin's farm. In addition, Sapek (2000) provides a characterisation of groundwater quality, in the context of the influence of farm yard point sources of pollution, which will be employed for comparison with groundwater quality observations at Curtin's farm.

Management of silage pit effluent is a crucial component of minimising agricultural pollution. The silage pit stores cut grass for use during the winter housing period, which operates from late November to early February on Curtin's farm. The grass is cut from the silage growing areas in early June and late July. Silage pit effluent is most voluminous immediately after grass harvesting (June/July). Silage effluent management on Curtin's farm improved during this investigation and in the most part the effluent was routed for collection in the underground dirty water tank. However, on some occasions there was surface runoff in the direction of BHC.4, sited 50m, approximately, from the pit.

The slurry tank is located beneath the housing sheds in the farmyard. Analysis of the potential leakage of stored slurry is presented in section 5.5.2.5.2.

The only septic tank in proximity to the piezometers in this study is that at the farm yard, which serves a population of approximately five people during working hours only. The nature of the local vicinity's plateau topography, in association with the very low population density in the area upgradient of the farm, indicate that septic tanks are not a potentially significant source of nitrogen to the system under investigation.

5.5.2.2.2. Diffuse Sources of Nitrogen on Curtin's Farm

Nitrogen is added to dairy farming systems, and the Curtin's farm system, from the following sources:

1. Inorganic fertiliser nitrogen
2. Organic nitrogen, generated by the herd's excretions, and redistributed to the land either by:
    a. Grazing animals; or
    b. Waste application in daily land spreading of dirty water or bi-annual land spreading of slurry.

Data for each of the above sources was collected, on a daily basis, by farm technical staff. I then collated these data to create weekly loading rate diaries for each farm field. A separate diary was created for each of the nineteen farm fields and each is presented in Appendix Q.

An additional source of nitrogen is that deposited in rainfall. Atmospheric nitrogen depositions were monitored by analysing rainfall samples collected on site. An annual rate of 9kg N/ha was recorded in each study year (Ryan, pers. comm., 2003), which is an amount that is dwarfed by the magnitude of the agronomic nitrogen loading rates. The pertinent issues regarding each nitrogen source on Curtin's farm and the methods employed for quantifying nitrogen loadings and rates are presented in the following sections.

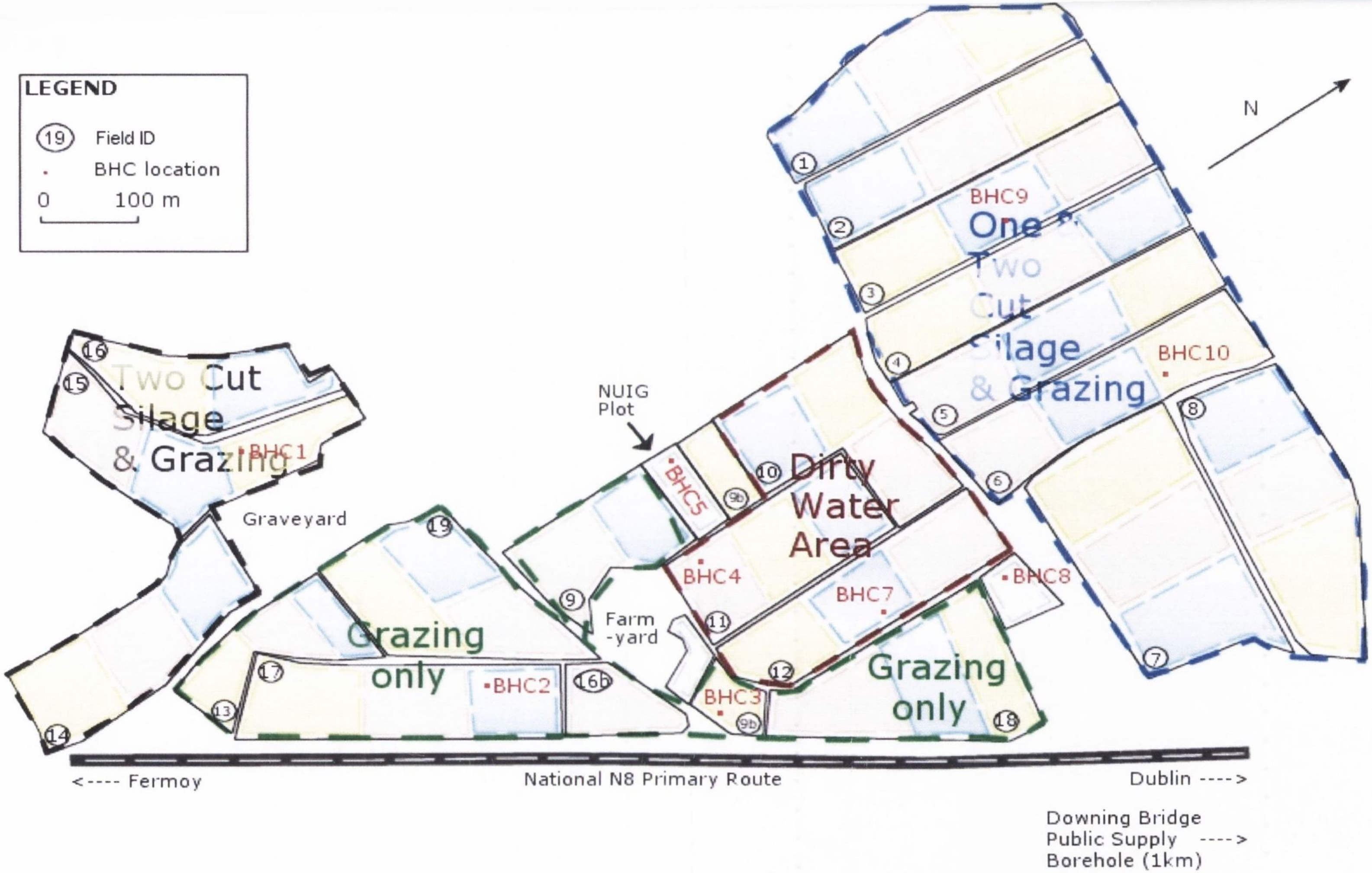

Figure 5.14 Curtins farm agronomic management areas, field layout and identifiers, and piezometer locations..

5.5.2.3. Inorganic Nitrogen Fertiliser Application on Curtin's Farm

Each of the nineteen fields on Curtin's farm receives inorganic nitrogen from bagged fertiliser. Data regarding nitrogen fertiliser applications were supplied by Curtin's farm to this study in the rate format. Inorganic fertiliser was applied incrementally from the middle of January to the end of September each year. A field technician collected the information on a field-by-field basis for each incremental application. The rates of application were usually 50kg N/ha in the six to seven applications each year. The only deviation from the 50kg N/ha rate was on the silage plots, which usually receive a 100kg N/ha rate in the same week as slurry is applied, and in the last application of the season when only 33 kg N/ha was applied in the fertiliser dressing. Each application of nitrogen fertiliser is documented in the nitrogen loading diaries presented for each farm field in Appendix Q. The average inorganic fertiliser nitrogen application rates of the four management zones are presented in Table 5.5. Section 5.5.3 will collate all loadings and discuss them in more detail.

Table 5.5 Average fertiliser application rates (kg/ha/yr) on Curtin's farm in the context of agricultural management zone, for each hydrological year of the study.

Agricultural Management Zone	**Inorganic Nitrogen Fertiliser (kg/ha/yr)**	
	(2001 – 2002)	**(2002 – 2003)**
Grazing Only	295	290
Dirty Water & Grazing	290	248
One-Cut Silage & Grazing	285	298
Two-Cut Silage & Grazing	340	310
Area Weighted Application Rate[2]	**306**	**290**

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[2] The area weighted application rate is derived based on the total load applied to each management area. The total farm load is then normalised over the entire farm area. For example, in the first year the grazing only area has a footprint of 22ha, therefore the total load to the grazing area is 295 kg N/ha/yr * 22 ha = 6490 kg N/yr. Similarly, the two-cut silage & grazing area receives 340 kg N/ha/yr over 12.7ha to yield a total load of 4318 kg N/yr, and so on for each zone. The total farm load is then calculated to be 14, 976 kg N/yr, which is equivalent to a rate of 306 kg N/yr applied over a working farm area of 49 ha. (Management zone areas are tabulated in Table 5.5).

Inorganic nitrogen application rates ranged from 290 to 340 kg N/ha/year in the first year (2001-2002). In ascending order, inorganic nitrogen fertiliser rates in each zone were as follows: one cut silage & grazing<dirty water & grazing<grazing only<two cut silage and grazing. Inorganic nitrogen application rates were slightly lower on average, in the second year, ranging from 248 to 310 kg N/ha/year. However, the variance in each year was similar, being 50 kg N/ha/year in the first year and 60 kg N/ha/year in the second. The farm area weighted inorganic fertiliser application rate was 305 kg N/ha/yr in the first monitoring year (2001-2002) and 290 kg N/ha/yr in the second year. However, individual fields received between 250 to 350 kg N/ha/yr depending on the grass-growth requirements or agricultural management of individual fields (individual field's nitrogen loading details can be found in Appendix Q).

The form of nitrogen applied changed throughout the year. The first application of fertiliser, in January of each year, was nitrogen as 'Sulpha CAN'. Spring and early summer applications were as urea and summer applications were CAN (calcium ammonium nitrate). There are agronomic reasons for changing the form of nitrogen applied to fields as season's progress but considering this is a loading-response study I confined my calculations and discussions to the rates, rather than forms, of nitrogen applied. The potential differences in groundwater response with respect to applied inorganic nitrogen fertiliser type are discussed in section 6.4.6, where the response of each individual piezometer is discussed.

5.5.2.4. Organic Nitrogen on Curtin's Farm

As previously mentioned, in section 5.5.2.1, organic nitrogen that was generated by Curtin's farm's dairy herd was quantified on a daily, weekly and annual time-scale. The daily and weekly time-scale data are relevant only to the analysis of each piezometers response (see section 6.4.6). Calculation of total loads and spatial allocation is the function of the current analysis.

5.5.2.4.1. Total Organic Nitrogen Generated by Animals

Curtin's farm manages a herd of 117 cows, on a 50 ha farm at a stocking rate of 2.34 LU/ha. At present, a dairy cow in Ireland is classified as contributing an organic nitrogen loading of 85 kg/cow/year (Humphreys *et al.*, 2003), that is the excretion load in the form of dung and urine. Therefore, the total organic nitrogen load excreted by animals on Curtin's farm is calculated as follows:

- 117 cows *85 kg/cow/year = 9945 kg N/year;

The total farm area is 50 ha. Therefore, using the methodology to be operated by the Nitrate Directive Action Plan DEHLG & DAF (2004) this load is distributed evenly over the entire farm area. The organic nitrogen loading rate becomes as follows:

- 9945 kg N/year over 50ha = 199 kg N/ha/yr.

This organic nitrogen loading rate clearly exceeds the 170 kg N/h/yr limit set by the Nitrate Directive (EEC, 1991a).

In reality, the organic nitrogen loading rate is not distributed evenly over the entire farm area. The organic nitrogen load generated by the animals is redistributed in a non-uniform, patch-wise fashion, directly by grazing animals or spread uniformly as dirty water and slurry in dedicated areas of the farm (see Figure 5.14). Closer examination of the spatial and temporal distribution of the organic nitrogen load is important to this study. The simplified approach of the Nitrate Directive (EEC, 1991a) is necessarily political. In my work, however, quantification of temporal loads is crucial to the response relationships (chapter six, section 6.4.6). In addition, the spatial allocation of the organic nitrogen load is crucial to investigations of how each of the four agricultural managements affect local nitrogen loadings on a typical intensive dairy farm. Spatially, these data were organised for both field- and agricultural management zone-scale analysis. Data relating to both spatial scales are presented in the following sections.

5.5.2.4.2. Field Scale Grazing Day Data

The number of days for which the entire herd grazed each field in each year of the study was recorded and these data are represented in Figure 5.15, which also shows piezometer locations and outlines agricultural management zones.

5.5.2.4.3. Organic Nitrogen Load Deposited in the Field by Grazing Animals

For each day of this research project the grazing activity of the herd was recorded. A field technician logged the herd's grazing location and grazing duration. I added this information to each field's nitrogen loading diary in both full grazing day's number format and then calculated an organic nitrogen loading rate (Appendix Q for loading diaries).

The daily organic nitrogen loading rate from grazing animals on Curtin's farm was calculated, again working with the organic nitrogen loading of 85 kg/cow/year (Humphreys *et al.*, 2003), as follows:

- 85 kg N/cow/year ÷ 365 days = 0.23 kg N/cow/day;
- 0.23 kg N/cow/day * 117 cows = 27 kg N/day.

Calculated daily organic nitrogen grazing loading rates were summed to provide first weekly, then annual, rates for each field. In turn, combining fields by agricultural management resulted in quantification of annual organic nitrogen loading rates deposited directly by grazing animals in each of the four management zones. These data are presented in Table 5.6. Information is also presented for the average number of days that a field within each management zone was grazed.

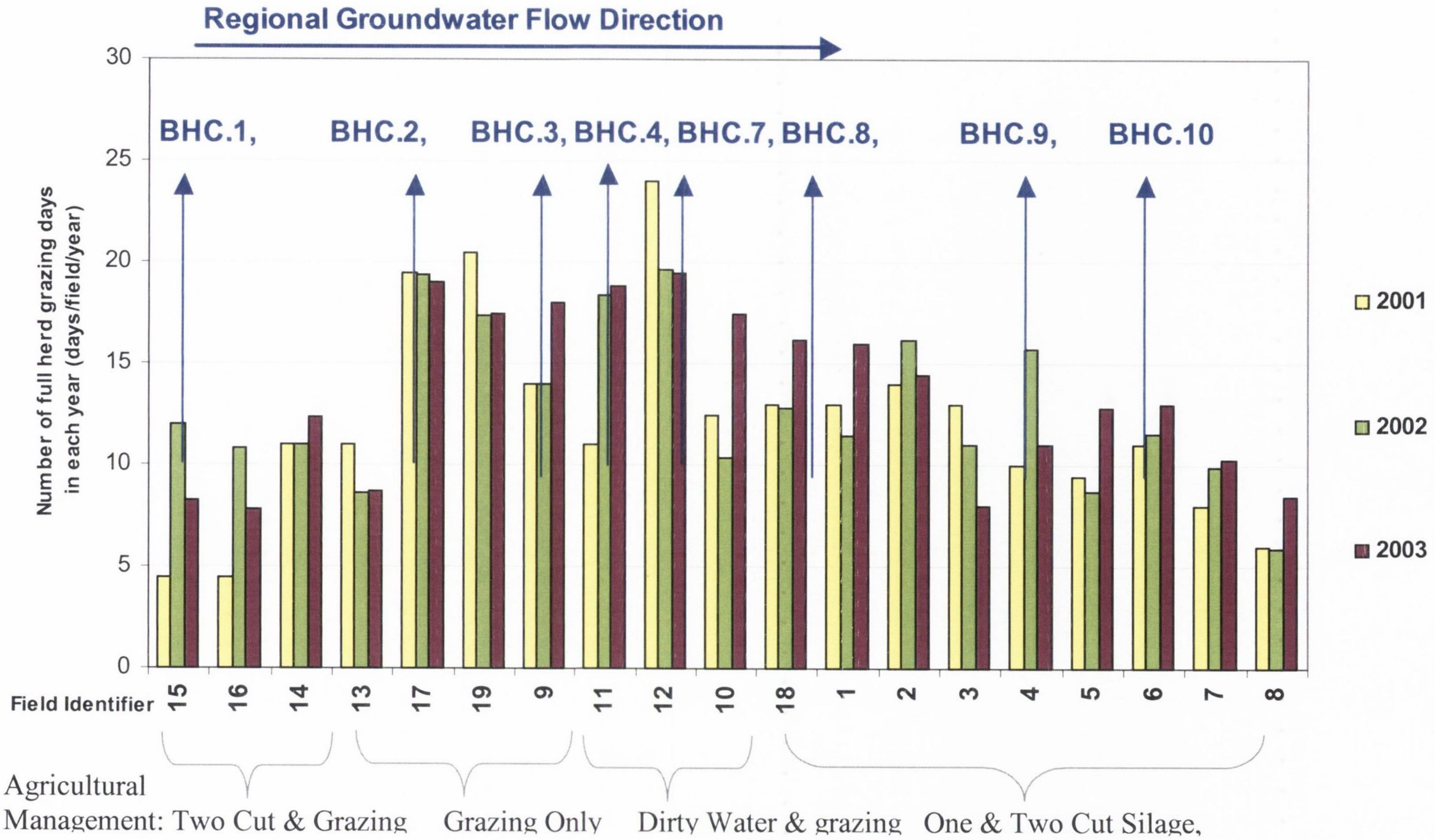

Figure 5.15 Full herd grazing days for each field on Curtins farm, for each year 2001-2003. The relative positioning of groundwater piezometers and farm management zones are also shown. The relative location of fields and field identifiers were shown in Figure 5.14.

Table 5.6 Calculated average organic nitrogen loading rates (kg/ha/yr) deposited directly by grazing animals on Curtin's farm in the context of agricultural management area, for each hydrological year of the study.

Agricultural Management Zone	**Grazing Animal's Organic Nitrogen (kg/ha/yr)**		**Number of Grazing Days (days/field/yr)**	
	(2001–2002)	**(2002–2003)**	**(2001–2002)**	**(2002–2003)**
Grazing Only	179	165	16	15
Dirty Water & Grazing	198	211	17	19
One-Cut Silage & Grazing	138	121	13	11
Two-Cut Silage & Grazing	98	76	11	8
Area Weighted Animal Organic N Application Rate	**152**	**142**	**14**	**14**

The obvious differences in organic loading rates deposited directly by grazing animals in each agronomic management zone is indicative of the purpose of each zone; for example, the grazing loading rate deposited in the two-cut silage and grazing area is approximately half that which was deposited in the grazing only area because the two-cut silage area was shut off, from grazing animals, for silage production from April to August each year, approximately.

5.5.2.4.4. Proportion of Excreted Nitrogen Load Not Deposited By Grazing Animals

The grazing season at Curtin's farm operates as follows:

- Mid February: 25% of the herd are out grazing day-time only;
- End February: 75% of the herd are out grazing day-time only;
- Mid March: herd that is out is out full-time, day and night;
- Early April: 100% of the herd are out full-time grazing;
- Mid November: herd stays in at night;
- End November: herd is taken in for winter housing;
- Herd remains in until mid February: two and a half months.

Analysis of this grazing season information collected at Curtin's farm and collation of all grazing day data suggested that the full herd spent approximately 250 days (day and night) in the field in each year. Therefore, only a fraction of the total excreted load is deposited directly in the field by the animals, calculated as follows:

- (250 grazing days ÷ 365 days/year) * 100 = 68%;
- The total annual excreted organic nitrogen load = 9945 kg (see section 5.5.2.4.1);
- Therefore, 68% of 9945 kg = 6811 kg N/year deposited directly by grazing animals;
- On balance, the organic nitrogen load for slurry and dirty water should equal:
  - 9945 – 6811 = 3134 kg N/yr

(Note: I acknowledge that the concentration of nitrogen in excretions varies seasonally but simplifications are necessary for this annual approach).

All nitrogen contributions from dirty water and slurry were quantified by analysis of samples at the Teagasc Johnstown Castle laboratory; therefore the above balance calculation was verified (see section 5.5.2.5).

5.5.2.5. Organic Nitrogen Contributed by Stored Agronomic Waste

5.5.2.5.1. Dirty Water Irrigation

Quantifying the organic nitrogen loading rate from dirty water irrigation is relevant to only one of the agronomic managements, that is the 7ha that is dedicated to dirty water treatment and managed in rotation with grazing (see Figure 5.14).

The dirty water irrigator is controlled from a pump house and a technician records the daily volumes spread. Chemical analysis of dirty water samples, as spread on the plots, facilitated recorded volumes to be converted to nitrogen loading rates that could easily be compared to fertiliser additions (these data were collected by Dr. Michael Ryan's team as part of their farm-scale subsoil investigation introduced in section 1.5).

The spatial movement of the dirty water irrigator as it moved to, and through, each plot was recorded and these data were used in the analyses of temporal nitrogen loading and piezometer responses, section 6.4.6.

Dirty water irrigation depths ranged from 1-29mm over the entire study period, however it should be noted that irrigation at the lower end of the scale occurred only in summer months. The average depth of dirty water irrigation was 11mm at any point, for each residence of the irrigator in any plot dedicated to dirty water treatment, for the study duration. Each of the nine dirty water plots housed the dirty water irrigator approximately four times in each year, though some plots were irrigated only once and some 5-6 times. This variation is a reality on farms and was beyond the control of this experiment.

The range of nitrogen deposited by the irrigator, on each stay in a plot, was 1-26kg N/ha in 2002 and 10-100 kg N/ha in 2003. The average concentration of Total Nitrogen in the dirty water was much higher in 2003 (~340mg/l Total Nitrogen) than in 2002 (~170mg/l Total Nitrogen). This suggests that less water was irrigated in the second year, as the herd number and load generated was most probably similar.

The dirty water irrigator has four gears that control the speed of movement through the field while it is irrigating. The irrigator is positioned to travel field lengths and the speed is set manually according to the season. In the summer the irrigator is set to move at its quickest speed and its velocity is 40m/ hr, approximately. In the winter the irrigator is set to move at the slowest speed: resulting in a velocity of 13m/hr, approximately. At higher rates of movement lower depths of dirty water are deposited. The average depths of dirty water irrigation in the summer and winter are 6mm and 15mm, respectively. Whilst irrigating, dirty water is distributed over a circular area having an approximate diameter of 20m. In winter, at a velocity of 13m/hr it takes approximately 1.5 hours for the irrigator to travel over any point in the field. The Code of Good Agricultural Practice (DELG & DAFF, 1996) recommends that the appropriate rates of application of soiled water by irrigation in sensitive and other areas should not exceed 2.5 mm/hr and 5.0 mm/hr, respectively. The reason for setting the irrigator at different speeds in summer and winter is purely for animal grazing considerations. In summer time, the irrigator moves quickest because the rotation of grazing animals needs to be more dynamic: due to the fact that a large proportion of the farm is closed off for silage production. But it is during summer that infiltration capacities are highest and higher irrigation rates would be accepted by soils, which have a natural soil moisture deficit. In the winter, during the leaching season, the current practice makes little sense: to have high rates of irrigation at a time when natural rainfall is high, thereby adding to the leaching potential of the soil. Because Curtin's soil is very permeable there is never visible ponding of dirty water on the ground surface and so there is little impetus on the farm staff to move the irrigator.

How do the rates of dirty water irrigation compare with naturally occurring rainfall? The Met Eireann website reports that "hourly rainfall of 10mm is not uncommon and totals of 15-20mm/hr may be experienced 1 in 5 years". Data in the Flood Studies report (NERC, 1975) also suggests that 10mm/hr has a 1 in 5 year return period. Hourly rainfall is recorded at all Met Eireann synoptic weather stations and the Munster region stations are Cork Airport; Shannon; Kilkenny and Birr (located 43km, 100km, 115km and 136km from Fermoy, respectively). Analysis of eight years recent records at each of these stations reveal that hourly rainfalls greater than 10mm occurred approximately nine times at each site. Therefore, the actual return period for hourly rainfall of 10mm, or greater, is once each year, on average, at the four weather stations in the region. Hourly rainfall of 15mm, or greater, is returned 1 in 2 years at both Birr and Cork. Analysis of actual measured hourly rainfall data, recorded between 1996-1998, at the Johnstown Castle weather station (distances) revealed that rainfall of 10mm/hr has a return period of 1 in 3 years. Long term data presented by Rohan (1986) shows that maximum rainfalls of 24mm, 32mm and 38mm have been in recorded in 15minute, 30 minute and one hour time intervals respectively in the synoptic weather stations in the Munster region, mentioned above. The intensity of natural rainfall is likely to increase as a consequence of climate change and these changes in rainfall intensities and duration of recharge are likely to create a new challenge in the area of nitrate leaching investigations (Robins, 1998).

The additional annual nitrogen loading rates added to the system by dirty water irrigation alone were calculated to be as follows:

- 180 kg N/ha in the first year (2001-2002);
- 260 kg N/ha in the second monitoring year (2002-2003).

Readers are reminded that this rate was applied over only 7ha of the farm. Therefore, the approximate load of organic nitrogen redistributed by dirty water irrigation was 1260 kg and 1820 kg in the first year and second years, respectively. The rates of nitrogen added by each dirty water irrigation is presented for each relevant field in the loading diaries of Appendix Q.

The contribution of this source to groundwater nitrate response is discussed in sections 6.4.6.5 & 6.4.6.7.

5.5.2.5.2. Slurry Application

Volumes of slurry collected in the slurry tanks beneath the animal's winter housing, and subsequently spread on the silage areas of the farm, were recorded at the time of land application by field technicians. The nutrient concentration of slurry samples was determined in the Johnstown Castle laboratories by technical staff. Combining the nitrogen concentration of the slurry with the volume spread on each plot resulted in the equivalent loading rate per hectare. Recorded slurry composition and rates at which slurry was spread on Curtin's farm is contained within Appendix Q. Readers are reminded that the one-cut silage area covers a total area of 20.2ha and of this 20.2ha; 12.7ha is retained for the second cut of silage.

In terms of total loading rates, the silage grounds received approximately 95 kg N/ha/yr in the 2001-2002 hydrological year. In that year farm records report that slurry was spread once in late March/early April 2002 only, at the same rate to both silage-cutting areas. The loading difference then, between the one-cut and two-cut silage management options is the duration of animal grazing on the lands, being longer in the one-cut system. However, it may be that some slurry was exported in the first year because the total load generated and spread (95kg N/ha*20.2ha = 1919 kg N) does not concur with the amount that would be generated during the winter housing period (approximately 115 winter housing days * 27 kg N excreted/herd/day = 3100 kg N, see sections 5.5.2.4.3 and 5.5.2.4.4 for source data). Enquiries were made, as to whether a slurry export took place, but no further information was available.

For the second monitoring year, slurry applications alone contributed 135 kg N/ha/yr the one-cut silage area and 187 kg N/ha/yr in the two-cut area. The load of nitrogen in the slurry was calculated to be 3000 kg N/year, approximately, based on the number of days the animals were housed. Chemical analysis of samples and records of volumes spread determined the actual load of slurry, as spread on fields of Curtin's farm, to be 3400 kg N/year in 2002-2003. These figures suggest that there is no loss of slurry from the underground slurry storage tanks.

Repeated applications of slurry, on the same area, have a cumulative effect. Whitehead (1995) reports research by Smith & Peterson (1982) regarding the 'decay series' applicable to the rates of nitrogen mineralised in successive years after slurry application and strongly suggests that the rates of slurry be decreased from year to year to take previous years applications into account. Alternatively slurry application areas should be rotated. Typical Irish dairy farming practice, however, is to maintain the same spatial allocation of slurry application lands each year. The effect of this practice on groundwater nitrate concentrations will be examined in section 6.4.6 where individual piezometer response to loading is presented.

5.5.2.6. Collated Nitrogen Loading Data

This section collates average nitrogen loading data for each agricultural management zone under investigation and discusses their potential significance. Tables 5.7 and 5.8 collate annual average nitrogen loading rates that were calculated in sections 5.5.2.3-6, above. All loadings data presented in this section are available at the weekly time-scale for each in Appendix Q for each of Curtin's farm field.

Table 5.7 Calculated average annual total nitrogen loading rates (kg/ha/yr) for each nitrogen source for each management zone for the 2001-2002 hydrological year.

Agricultural Management Zone	**Zone Area (ha)**	**Total Inorganic N Fertiliser (kg/ha/yr)**	**Recycled Organic N (kg/ha/yr)**			
			Total Organic N	**Contributors to Total Organic N load**		
				Grazing Animals	**Dirty Water**	**Slurry**
Grazing Only	22	**295**	**179**	179	None	None
Dirty Water & Grazing	7	**290**	**378**	198	180	None
One-Cut Silage & Grazing	7.5	**285**	**230**	138	None	92
Two-Cut Silage & Grazing	12.7	**340**	**194**	98	None	96
Area Weighted Application Rate		306	216	152	26	38

Table 5.8 Calculated average annual total nitrogen loading rates (kg/ha/yr) for each nitrogen source for each management zone for the 2002-2003 hydrological year.

Agricultural Management Zone	**Zone Area (ha)**	**Total Inorganic N Fertiliser (kg/ha/yr)**	**Recycled Organic N (kg/ha/yr)**			
			Total Organic N	**Contributors to Total Organic N load**		
				Grazing Animals	**Dirty Water**	**Slurry**
Grazing Only	22	**290**	**165**	165	None	None
Dirty Water & Grazing	7	**248**	**471**	211	260	None
One-Cut Silage & Grazing	7.5	**298**	**256**	121	None	135
Two-Cut Silage & Grazing	12.7	**310**	**263**	76	None	187
Area Weighted Application Rate		290	248	142	38	69

It is clear from Tables 5.7 & 5.8 that average inorganic nitrogen loading rates vary only by 50 and 60 kg N/ha/yr in different agronomic management zones in successive years of the study. This difference represents only one incremental application of inorganic fertiliser (see section 5.5.2.3). Therefore, I conclude that inorganic fertiliser rates do not vary greatly in each of the four different management zones. Differences thus observed in groundwater nitrate concentrations in different management zones will therefore not be related to inorganic fertiliser application rates.

It is also clear from Tables 5.7 & 5.8 that it is the total organic nitrogen loading rates that vary dramatically in each management zone. In each year, the average total organic nitrogen loading rate is highest in the area dedicated to dirty water treatment relative to the other three zones.

The average organic nitrogen load contributed by grazing animals was calculated to be 179 kg N/ha/yr and 198 kg N/ha/yr in the grazing only and dirty water treatment zones, respectively, in the first year (2001 – 2002). However, the additional organic nitrogen load contributed by dirty water irrigation results in almost doubling the total organic nitrogen load to 378 kg N/ha/yr in the dirty water treatment zone. The other areas of the farm are silage zones, which are also grazed but to a lesser degree. These silage areas receive approximately half their organic nitrogen loading from slurry application and half from grazing animal's depositions. In the first year the average total organic nitrogen loadings were 230 kg N/ha/yr and 194 kg N/ha/yr to the one-cut and two-cut silage areas, respectively (see section 5.5.2.5.2 for slurry application details). These data again reinforce the significantly higher organic nitrogen loading rate over the 7ha devoted to dirty water irrigation.

In the second monitoring year (2002-2003) the total organic nitrogen loading rate trend is similar: the dirty water zone received the highest rate (471 kg N/ha/yr) and the grazing zone received the lowest (165 kg N/ha/yr). The one- and two-cut zones received organic nitrogen at a rate of 256 kg N/ha/yr and 263 kg N/ha/yr, respectively. These values for the two different silage management zones are similar when totals are compared, but it is the nature of the components that is important. The two-cut silage zone received 71% of its total organic nitrogen loading as slurry, which is applied to the land following good farming practice guidelines (DAF, 2001). Therefore the load is evenly distributed and applied with regard to good weather conditions in order to minimise risk to the environment. In the one-cut silage zone 50%, approximately, of the organic nitrogen load was applied as slurry and the remainder was deposited by grazing animals. The special significance of grazing animals is discussed in section 5.5.2.7.

Area weighted average organic nitrogen application rates suggest values of 216 kg N/ha/yr and 248 kg N/ha/y in the first and second years, respectively. These areas weighted values mask the impact of the dirty water zone organic loading rates because the dirty water area represents only 14% of the total farm area.

In the context of the Nitrate Directive's (EEC, 1991a) organic nitrogen loading rate limit of 170 kg N/ha/yr the dirty water area is a big pressure point. I acknowledge that the limit in said Directive concerns a farm averaged loading rate. However, the environmental significance of a small area of the farm receiving double the organic nitrogen than other areas should not be ignored. The implications of these loadings calculations will be discussed in section 6.4.6 when the response of each individual piezometer is analysed. However, I will make a further observation here concerning the problematic way in which the dirty water area is managed. As previously mentioned, nitrogen fertiliser is applied incrementally on the farm. In the dirty water plots, fertiliser is usually applied a couple of days before the irrigator enters the field. The loading pattern, then, is to allow animals to intensively graze a plot, subsequently apply fertiliser at a rate of ~50kg/ha and then irrigate with dirty water, all within the same week. This loading pattern must create an enhanced leaching environment.

5.5.2.7. Special Significance of Grazing Depositions

All previous nitrogen loadings discussions have presented excreted loadings as equivalent loading rates over field or management zone scales. However, my conversions of organic nitrogen contributed from grazing animals to areal loading rates are a simplification of reality. Before I leave this section I must raise awareness of the significance of each single excretion.

Grazing animals are likely to cause large leaching losses because of the highly concentrated excretions deposited on the soil. Uneven deposition of excretal nitrogen by grazing livestock can lead to spot application rates equivalent to 400 to 2000 kg N/ha (Jarvis *et al.*, 1997). Others report urine patches in swards grazed by cattle to often receive nitrogen at rates equivalent to more than 500kg N/ha in a single addition (Whitehead, 1995). Urinations are applied under significant hydraulic loading, which aids the vertical migration of the nitrogen in the urine, even in the summer under SMD conditions. Dung patches hardly affect nitrate leaching, because 65 to 80% of the nitrogen excreted is contained in urine, the area covered by dung patches is relatively small and furthermore the organic nitrogen in dung patches only slowly degrades and so it is usual for dung not to be considered in leaching studies (Hack-ten Broeke *et al.*, 1996).

The hydraulic load that accompanies urinations is relevant because hydraulic loading is one driver on the leaching process. In terms of hydraulic loading, each cow urinates approximately 10 times per day in the field (Lantinga *et al.*, 1987) at a rate of ~3l/urination (Whitehead, 1995) over an area covering 0.2-0.5m^2/urination (Haynes & Williams, 1993, cited in Whitehead, 1995) or 0.68m^2 (Lantinga *et al.*, 1987). So, taking a volume of 0.003m^3 deposited over an area of 0.5m^2 results in an instantaneous recharge rate of 6mm/urination.

On an annual basis, calculations reveal that 12.6ha of the 50ha total farm area are directly affected by grazing animal depositions per year, which means an instantaneous, hydraulically charged, nitrogen load of more than 500 kg/ha on 25% of the farm. These calculations are supported by the literature: Whitehead (1995) calculates 24% of farm area to be affected by grazing animals' urinations. The concentration of nitrate that develops in the soil of a urine patch greatly exceeds the uptake capacity of the grass (Whitehead, 1995). Excess nitrate, derived from urine and surplus fertiliser nitrogen, accumulates until the autumn and is susceptible to leaching (Sherwood & Fanning, 1989). There were over one thousand urinations per day, on a daily grazing area of less than 1ha, approximately. The significance of the grazing animal excretions in the field is therefore stressed.

5.5.2.8. Farm Gate Nitrogen Balance

It is possible to approximate the efficiency of nitrogen use in any farming system by comparing all imports of Nitrogen to all exports across the farm gate. The nitrogen balance approach is often used and is well documented in the literature (see Whitehead, 1995). Richards (1999) describes two different types of nutrient balances: the farm gate balance and the surface balance. A farm gate balance involves quantification of all nitrogen imported and exported across the farm gate. In a surface balance approach the soil surface is regarded as the boundary of the system. Whitehead (1995) lists potential inputs and outputs for a surface balance as follows:

Potential nitrogen Inputs

1. Wet & dry deposition from the atmosphere;
2. Symbiotic biological fixation of atmospheric N_2;
3. Non-symbiotic biological fixation of atmospheric N_2;
4. Application of fertiliser;
5. Application of organic manures or slurries (including grazing animal depositions).

Potential nitrogen Outputs

1. Removal in cut grass herbage or animal liveweight gain, milk or wool;
2. Leaching, mainly of nitrate;
3. Volatilisation of ammonia;
4. Volatilisation of N_2, N_2O and NO through denitrification/nitrification.

Richards (1999) reports that many soil-nitrogen balance approaches assume a constant soil nitrogen content. However, Whitehead (1995) stresses that soil nitrogen content should not be assumed to remain constant, especially in grazed grassland situations.

A farm gate balance is presented, in Table.5.9 below, for both hydrological years monitored in this study, 2001-2002 and 2002-2003. The method follows the agronomic methodology suggested for Irish dairy farms (Humphreys, 2003). Raw data used to generate the presented farm gate balance were supplied by Curtin's farm-manager. These data were supplied as volumes of milk sold to the co-operative each month and the measured the protein content of that milk, and recorded animal liveweight gains. The nitrogen concentration was determined using information published by Kemp *et al.* (1979). I then calculated the balance. The balance suggests a 25% efficiency rate of imported nitrogen on Curtin's farm. This efficiency rate concurs with balances determined by others (Sherwood & Tunney, 1991; Watson *et al.*, 1992; Jarvis 1993; Richards, 1999; Humphreys, 2003).

Table 5.9 Farm gate nitrogen balance for Curtin's farm (source data: Curtin's farm manager routinely collects the nitrogen export data).

	2001-2002	2002-2003
N imported onto the farm (kg/ha/yr)		
Inorganic Fertiliser N	298	296
Concentrate N	27	26
Atmospheric N Deposition (REF)	9	9
N exported from the farm (kg/ha/yr)		
N content of Milk produced	72	76
N in calves and exported livestock	6	6
Animal liveweight gain	2	2
Surplus N (kg/ha/yr)	254	247
Imported N-use Efficiency	**24%**	**25%**

Given that only 25% of the nitrogen added to the system is removed in product, there is a large proportion of nitrogen available for loss to the environment. Much of the nitrogen lost from grassland and ruminant livestock production systems through leaching, ammonia volatilisation and denitrification, is derived from animal excreta and reflects and inefficient use of dietary nitrogen (Whitehead, 1995).

5.5.3. Combining Meteorological & Nitrogen Loading Calculations

For nitrate leaching to occur it is necessary to have a supply of nitrogen in the soil. However, a hydrological element is also required. Thus far, in this loadings section I have calculated the potential effective rainfall available to the leaching process (detailed in section 5.5.1 and summarised in Table 5.3). In addition, the amounts of nitrogen applied to the land, in both inorganic and organic forms, were calculated.

Inorganic nitrogen is applied for grass growth. Animals consume grass and retain a proportion of its nitrogen content but they excrete the majority of the nitrogen (see section 2.4). As previously mentioned in section 3.6.2, nitrogen use efficiency in Irish dairy cattle is only 16% of inputs, namely inorganic nitrogen and wet and dry atmospheric deposition (Sherwood & Tunney, 1991). Therefore, the excreted nitrogen load is great. Judging the correct component of the nitrogen sources that should be considered for the purposes of defining response relationships and modelling nitrate loss to the groundwater body in this thesis was a great challenge. Given that organic nitrogen is derived from the inorganic nitrogen source, to sum both to give a total nitrogen input would amount to double accounting because dirty water, slurry and grazing animal loads are all recycled nitrogen that was originally sourced in the fertiliser applied to the grass. The grazing animals are merely processing plants that excrete a large proportion of the nitrogen they consume (see section 2.4). If only one nitrogen source was to be considered I decided that, for this work, the animal deposition loads were of greater importance than the fertiliser applications. The rationale is based on the following facts:

- The literature (e.g. Addiscott *et al.*, 1991; Jarvis & Dampney, 1993; Whitehead, 1995) suggests that nitrogen fertiliser that is applied at low rates, as it is on Curtin's farm, matches grass growth requirements well and therefore is not available to direct loss as leachate.
- The special significance of grazing loads, in terms of nitrogen load available directly under a urine patch and the hydraulic load that accompanies urinations, has been stressed in the literature (see sections 2.4 and 5.5.2.7, and also discussion of recently published research findings in section 6.7).
- Others have used organic nitrogen loading as a key component of nitrogen available for loss (e.g. Dunn *et al.*, 2003a).
- The whole tenet of the Nitrate Directive (EEC, 1991a) is the organic nitrogen loading rate.

Therefore, considering calculated effective rainfall amounts (Table 5.3) and area weighted average organic nitrogen application rates (Tables 5.7 & 5.8) it is possible to provide a first step estimation of an indicative recharge nitrogen concentration to groundwater at Curtin's farm, on an annual basis. The mechanics of the calculation are as follows:

For the 2001-2002 hydrological year,

- Annual effective rainfall = 464 mm = 0.464m;
- Total farm area = 50ha = 500,000 m^2;
- Therefore, the volume of recharge = 500,000*0.0464 = 232,000m^3 or 2.32*10^8 litres;
- Area weighted average annual organic nitrogen loading rate = 216 kg N/ha, over a total farmed area of 49ha, results in a total load of 10,548 kg N, which is equivalent to 1.06*10^{10} mg N;
- Therefore, an indicative annual recharge concentration is as follows:
    - ((1.06*10^{10} mg N)/(2.32*10^8 litres)) = **45.6 mg N/l.**

Using the same methodology for the second year's data: for the 2002-2003 hydrological year effective rainfall was calculated to be 537mm (Table 5.3) and the area weighted organic N loading rate was determined to be 248 kg N/ha (Table 5.8), which provides an indicative recharge concentration of **52 mg/l N** the second year.

However, the total organic N load is not necessarily available for leaching as nitrate. The various processes in the nitrogen cycle will reduce the recharge concentration. These calculations presented do not consider volatilisation, dentitrification or immobilisation. While denitrification is unlikely to reduce the nitrogen content of recharge in the soils of Curtin's farm, volatilisation losses of 9% of N have been measured from grazing animals (Hutchings *et al.*, 1996). Organic nitrogen applied as slurry and irrigated as dirty water will also occur volatilisation losses. NCYCLE (Scholefield *et al.*, 1991) model simulations are presented in chapter six, section 6.6. Those simulations facilitate closer examination of the potential recharge concentrations. However, these data presented above highlight the significance of potential N loading from intensive dairy farms. The difference, then, between Curtin's farm and farms in other parts of the country will be the degree of vulnerability the subsoil and groundwater exhibit.

CHAPTER SIX ANALYSIS & INTERPRETATION OF FIELD RESEARCH

This project installed nine groundwater piezometers at farm scale, 50ha area, on an intensive dairy farm. The variation in the magnitude of water level and nitrate response in each individual piezometer distracts from clear characterisation of groundwater response. Therefore, the system will initially be characterised broadly in order to try to obtain a general response picture. Farm-averaged groundwater levels (section 6.2.2.4) and nitrate concentrations (section 6.4.1) are presented in order that an overall picture is obtained. Then, once the behaviour of the total system is understood, the response of individual piezometers to loadings in their vicinity will be examined (section 6.4.6).

6.1. Subsurface Characterisation

6.1.1. Subsoils

6.1.1.1. Subsoil Overview

Curtin's farm's subsoils comprise a mixture of coarse and fine-grained materials and are directly influenced by the underlying bedrock, which is limestone. Limestone fragments tend to dominate the subsoil, which varies from silty sand with frequent/abundant gravels to angular sandy gravels with clay (Kelly & Motherway, 2000). Laboratory analyses of subsoil samples returned during borehole drilling in the course of this study (see section 6.1.1.2) concur with the GSI soils classification.

Generally, over the entire farm the overburden stratigraphy is as follows:

- 0.3-0.4m of rich brown topsoil in the upper layer that contains many rounded pebbles; then
- 0.4m of a very gravely silty/sandy layer;
- Followed by a thick sandy layer and a subsoil containing almost equal measures of silt, sand and gravel to the top of bedrock.

A typical subsoil profile is shown in Figure 6.1. This profile was exposed by excavation with a JCB. The hole was dug in the NUIG experimental plot in the central farm area, north of the farm yard (see Figure 5.14). This scale of excavation is required for testing subsoil hydraulic conductivity according to the method advocated by Mulqueen & Rodgers (2001).

Figure 6.1 Typical soil profile at Curtin's farm.

The epikarst, top of weathered limestone bedrock, is approximately 2.5m below ground level, on average, but undulates in depth from 0-4.5m, consistent with the karst terrain. Bedrock outcrops abound in the general area and rock is visible at the surface at four locations, at least, on Curtin's farm. The depth to bedrock map is shown in Figure 6.2.

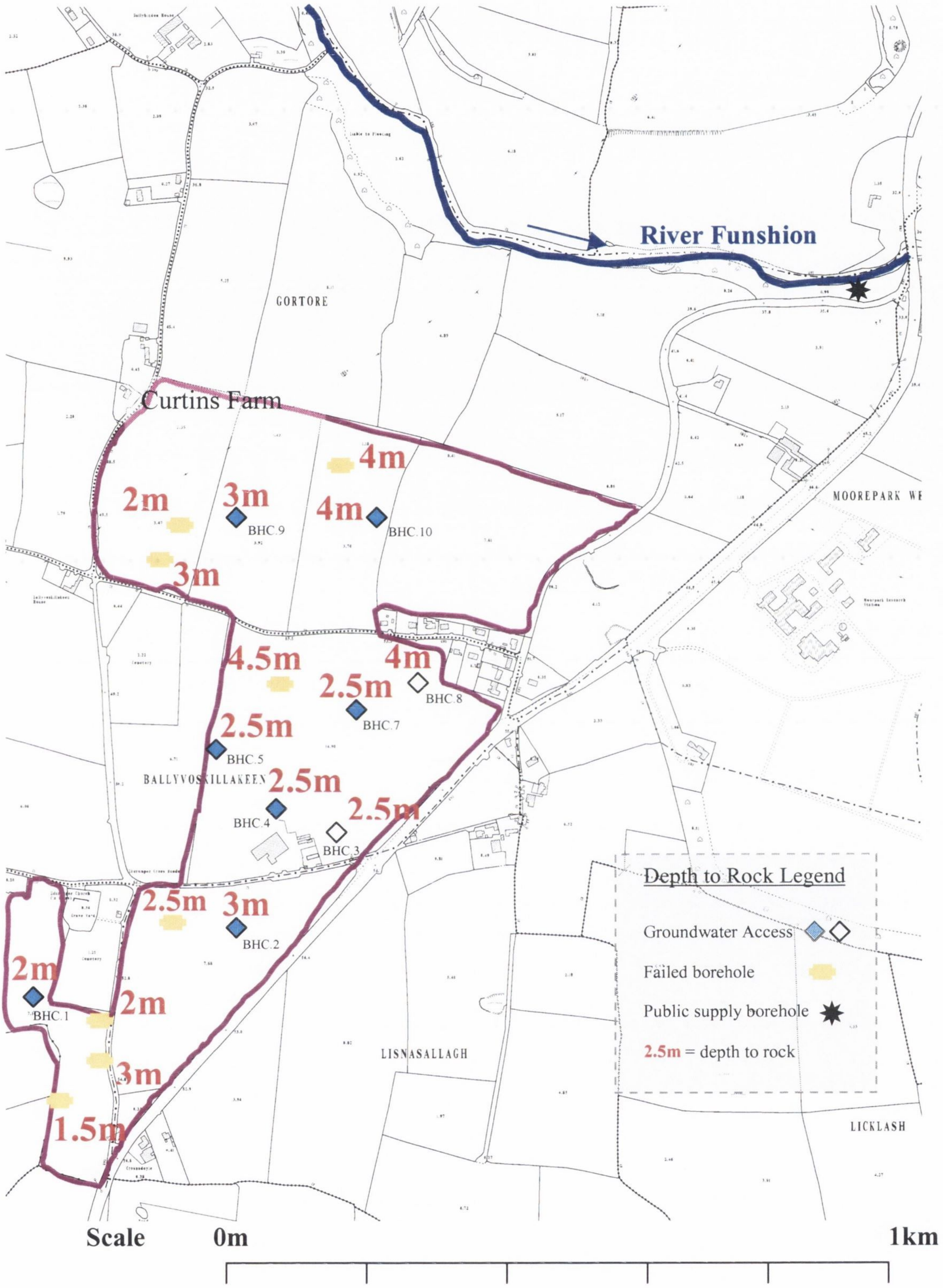

Figure 6.2 Measured depth to bedrock on Curtin's farm.

6.1.1.2. Subsoil Classification - British Standard 1377 (1990)

In general, when applying the British Standard (BS 1377, 1990) for classification throughout all the subsoil profiles investigated, SAND is the dominant end term. The percentage textural classification is 35% sand, 30% gravel, 26% silt and 10% clay, on average considering all the samples analysed. The subsoil is therefore very free draining which is borne out by the excellent traffic-ability of the land on this farm, which makes it great dairy grazing pasture. On textural basis high sand content of subsoils suggests high permeability. However, sandy soils can be quite compacted in the upper layers (Diamond, pers. comm., 2003). Soil grading curves and particle size distribution analyses results are provided in Appendix F. Table 6.1 presents a subset of the textural analysis results, all hydraulic conductivity values and the depth of soil cover measured by this author at Curtin's farm.

6.1.1.3. Subsoil Hydraulic Conductivity Results

Field-testing of hydraulic conductivity allows *in-situ* examination of potential rates of water movement through the subsoil. Table 6.1 presents saturated hydraulic conductivity (K_{sat}) at 0.5m intervals in the subsoil profile at five locations on Curtin's farm (see Figure 5.2 for locations). Saturated hydraulic conductivity was calculated using the appropriate Hvorslev equation and the methodology that was outlined in section 5.2.2.1. Appendix G contains all the graphs, calculations and the head values used for determination of K_{sat} in each case. When considered as a whole, there appears to be wide variation over the site, indicative of soil anisotropy. However, some separation of the data is required. Bouwer (1978) discusses the complex situation reflected by raw K_{sat} data, which he suggests must be simplified to obtain a manageable system amenable to analysis. Therefore, in this work the data are presented in two ways. Firstly, Figure 6.3 shows all measured potassium values using a separate graph for each 0.5m depth interval in the subsoil. Secondly, the spatial variation in measured subsoil hydraulic conductivity is presented for the 0.5m depth in Figure 6.4.

Table 6.1 Soil Textural Classifications (BS 1377, 1990) & Saturated Hydraulic Conductivity (K_{sat}) results [Inverse Auger method].

Depth (m bgl)	**BHC.1**	**BHC.2**	**BHC.5**	**BHC.7**	**BHC.9**
0.5	Gravelly SAND K_{sat} = 0.013 m/day	Gravelly silty SAND K_{sat} = 0.034 m/day	K_{sat} = 0.034 m/day	Silty gravelly SAND K_{sat} = 0.57 m/day	Sandy GRAVEL K_{sat} = 0.042 m/day
1.0	Silty SAND K_{sat} = 0.009 m/day	Gravelly silty SAND K_{sat} = 0.085 m/day	Very silty SAND K_{sat} = 0.08 m/day	Gravelly silty SAND K_{sat} = 0.166 m/day	K_{sat} = 0.015 m/day
1.5	Gravelly SAND K_{sat} = 0.319 m/day	Gravelly silty SAND K_{sat} = 0.013 m/day	K_{sat} = 0.069 m/day	K_{sat} = 0.044 m/day	K_{sat} = 0.51 m/day
2.0	Sandy GRAVEL K_{sat} = 1.05 m/day	Gravelly silty SAND K_{sat} = 0.038 m/day	Silty gravelly SAND K_{sat} = 0.68 m/day	Silty gravelly SAND K_{sat} = 2.2 m/day	Sandy GRAVEL K_{sat} = 11.24 m/day
Depth to Epikarst **(Depth to Rock)**	2m (3.5m)	3m (4m)	2.5m (3m)	2m (3m)	2.5m (3.6m)
Farm Plot ID	**15BLUE**	**17BLUE**	**NUIG PLOT**	**12BLUE**	**3BLUE**

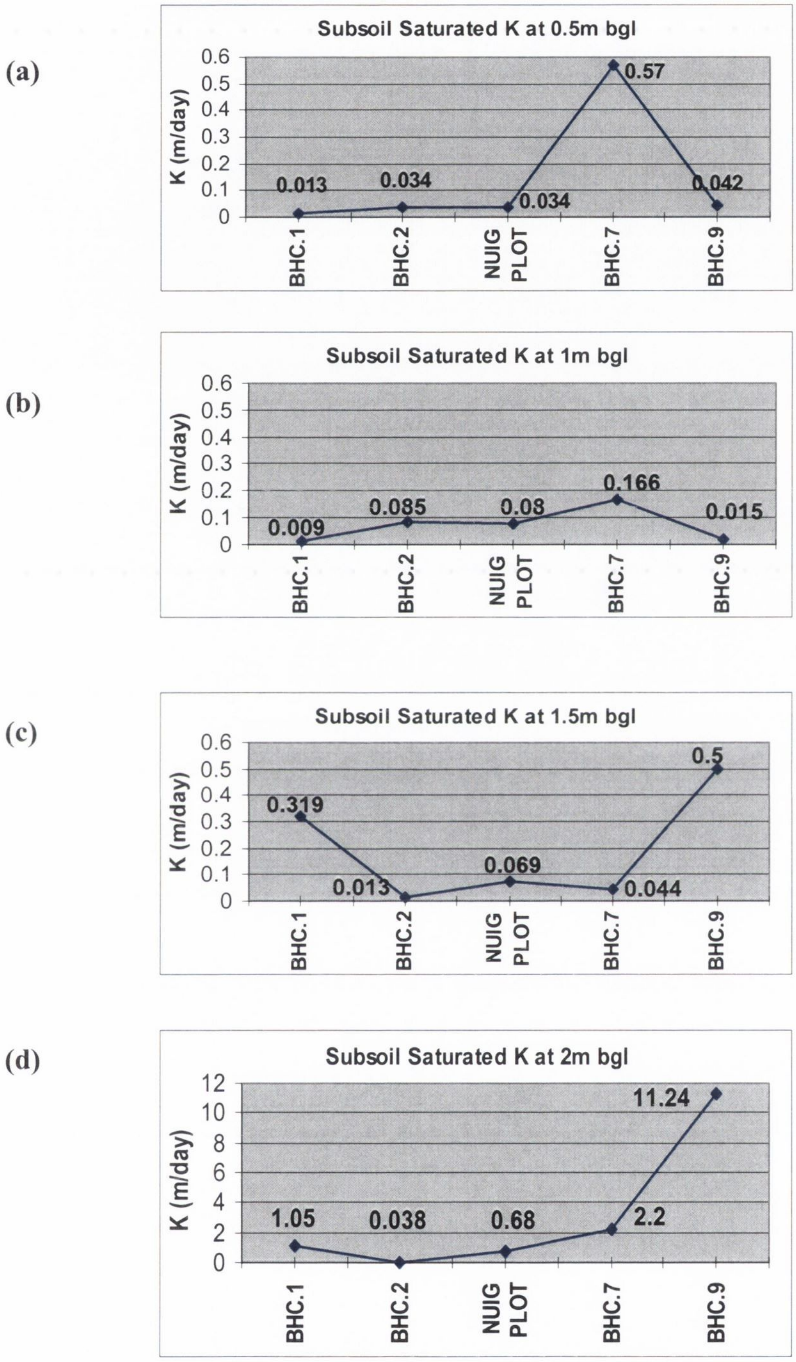

Figure 6.3 Measured saturated hydraulic conductivity (K_{sat}) at each 0.5m depth intervals investigated on the five farm plots, which are identified by the piezometers located within: (a) being 0.5m bgl; (b) at 1m bgl; (c) at 1.5m bgl and (d) 2m bgl.

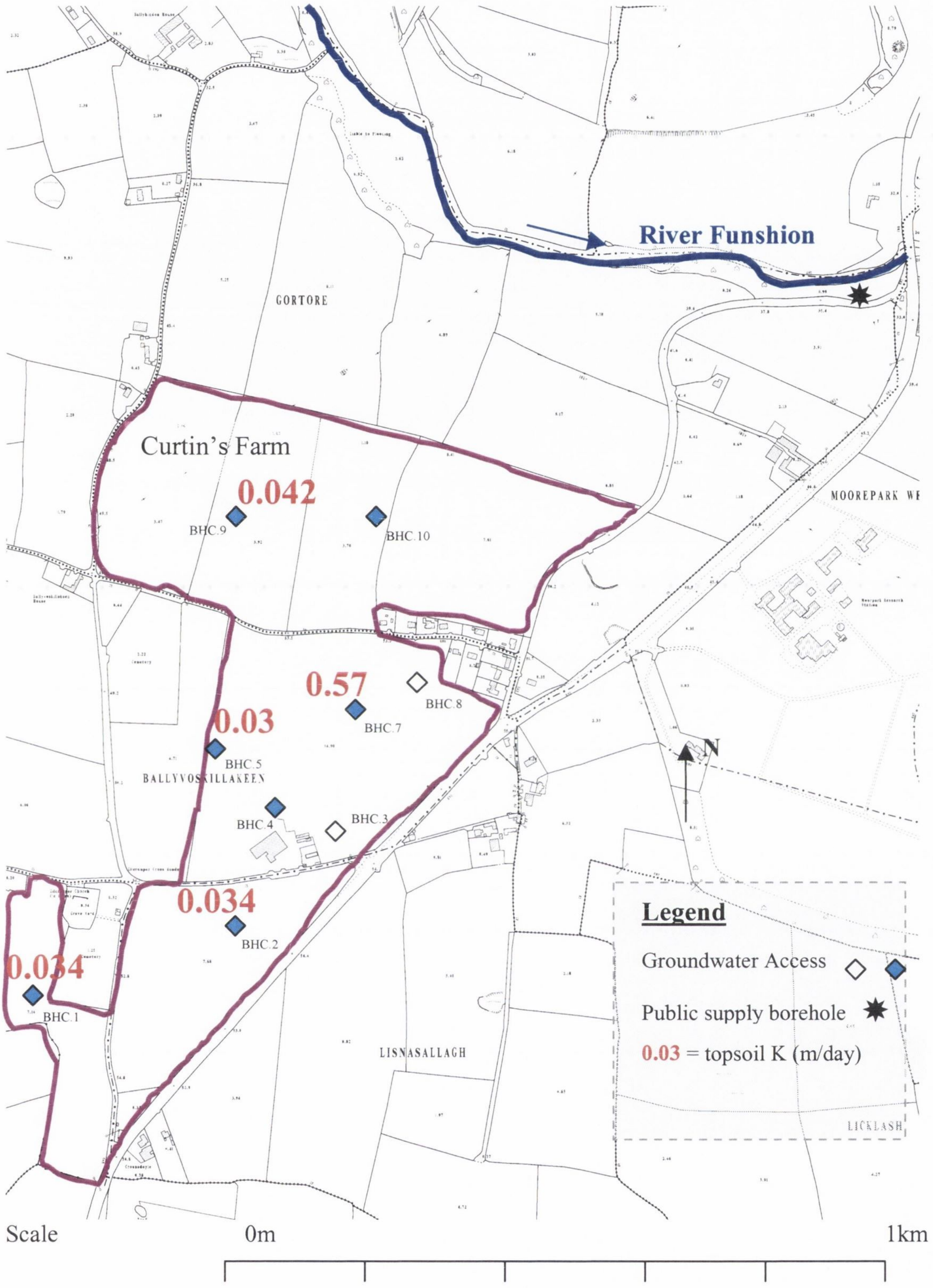

Figure 6.4 Measured saturated hydraulic conductivity (K_{sat} m/day) at 0.5m depth in the subsoil of Curtin's farm.

6.1.1.4. Significance of Subsoil Investigation Results

Free draining conditions prevail at Curtin's farm. The topsoil, subsoil and bedrock hydraulic conductivities were determined in-situ. In this investigation the auger hole method (Bouwer, 1978; Ritzema, 1994) was used to investigate K_{sat} at five different farm plot locations (full methodologies were explained in chapter five, section 5.2.2.1). My investigations reveal relatively compacted topsoil layers in all but one plot, a plot in which dirty water is irrigated: plot 12BLUE where BHC.7 is sited demonstrates K_{sat} = 0.57m/day, which is an order of magnitude greater than values in the four other plots investigated. This plot has elevated K_{sat} at 1m-depth also, relative to other sites investigated (K_{sat}=0.166 m/day, see Figure 6.3 (b)). These results would seem to substantiate the suggestion by Bohlke (2002) that the potential indirect effects of infiltration of agriculturally contaminated water, with a high ionic strength or acidity, include increasing weathering rates and solubilities of minerals and higher release rates of sorbed or included trace elements in soils. The higher hydraulic conductivities in the plots dedicated to dirty water irrigation may indicate that physical and biological changes have occurred in this soil and were caused by increased acidity and ionic strengths of the dirty water recharge. Bohlke (2002) further suggests that this type of scenario will enhance leaching rates. Soil phosphorus and potassium tests in the dirty water area are higher than at any other location and are double those observed in the grazing area (see chapter four, Figures 4.2 & 4.3), which also demonstrates the significant impact caused by the dirty water treatment.

Results from another investigation (Gibbons *et al.* 2003) provided additional hydraulic conductivity information at the field scale. In an alternative methodology to that presented in this work Gibbons *et al.* (2003) determined K_{sat} from data collected during field-testing that employed the square-hole method at the base of pits excavated at 0.5m depth intervals (after Mulqueen & Rodgers, 2001). This methodology yielded 'fully saturated' hydraulic conductivity values of 0.395, 0.186 and 1.125 m/day in the topsoil, at 1.5m and at 2m-depth respectively. These values are much higher than those measured using the auger-hole methodology.

Further implications of the subsoil investigation results will be discussed in the context of their role in nitrate leaching at each individual piezometer location.

6.1.1.5. Groundwater Vulnerability Assessments

6.1.1.5.1. Assessment of Groundwater Vulnerability at Curtin's Farm

Using the GSI vulnerability assessment methodology (Fitzsimons *et al.*, 2003), it is the nature of the subsoil materials overlying groundwater that determines intrinsic vulnerability. Based on the information presented in Table 6.1:

- the subsoil is thin (0-4m thickness over the entire farm, but at least 2m at each groundwater monitoring station);
- the subsoil is classified either as a SAND or SANDY GRAVEL (BS 1377, 1990); and
- the subsoil hydraulic conductivities are relatively high;
- therefore, the groundwater vulnerability rating is 'extreme'.

6.1.1.5.2. Assessment of Groundwater Vulnerability at Johnstown Castle

The glacial deposits overlying groundwater at Johnstown Castle have a relatively low permeability. The land under the conventional dairy farm would not have been artificially drained unless necessary. However, the varying thickness of deposits, occurrence of preferential flow and the occasional sand lenses that exist may allow areas where significant recharge can occur. In the areas where till is overlain by sand it is probable that a shallow groundwater system is present in the sand which is separated from the bedrock by the till (Daly & Hudson, *pers. comm.*, 1995).

Because there is over 10m of soil cover at all instrumented locations and the subsoil is of low permeability, the groundwater at this site is classified as having a 'low vulnerability' rating.

6.1.2. Bedrock Geology

6.1.2.1. Geology Overview

The farm lies on the top of a gently sloping ridge of Waulsortian reef limestone having a ground-surface elevation of approximately 50m AOD and some 25m above the adjacent River Funshion. The Waulsortian Limestone has been described as a massive unbedded lime-mudstone (Sleeman & McConnell, 1995). The ridge itself trends east to west, but is curtailed where the River Funshion flows in a south-easterly direction into the larger River Blackwater, flowing eastwards, some 2km east of the farm. Only one type of bedrock was encountered during drilling, as was expected given that Shearley (1988) suggests a thickness of 500-700m bgl for the Waulsortian Limestone. The bedrock beneath the farm was found to be variable in structure. Overall, the drill chippings and rock cores confirmed that the bedrock is a solid muddy reef limestone irregularly and often sparsely fractured. At the seventeen drilling locations bedrock was encountered between 1m and 4.5m bgl. The upper bedrock surface was usually soft weathered rock for the first 1-2m as is expected in the epikarst region.

6.1.2.2. Borehole Stratigraphy

The only discernable difference between project boreholes is the degree of fracturing (*i.e.* the secondary permeability that governs water flow in limestone aquifers). Borehole logs are presented in Appendix B. A topographic survey in conjunction with vertical sections, constructed from numerous borehole-log details across the site, show that the fractured conduits appear in far from erratic patterns with respect to elevations above datum. This finding aids the conceptualisation of the model in terms of contaminant transport. Figures 6.5 and 6.6 present two cross-section lines A-A, running south-south-west to north-north-east, and B-B, running west-north-west to east-south-east, to demonstrate local stratigraphy encountered during borehole drilling, the cross-section lines have been indicated on Figure 5.2.

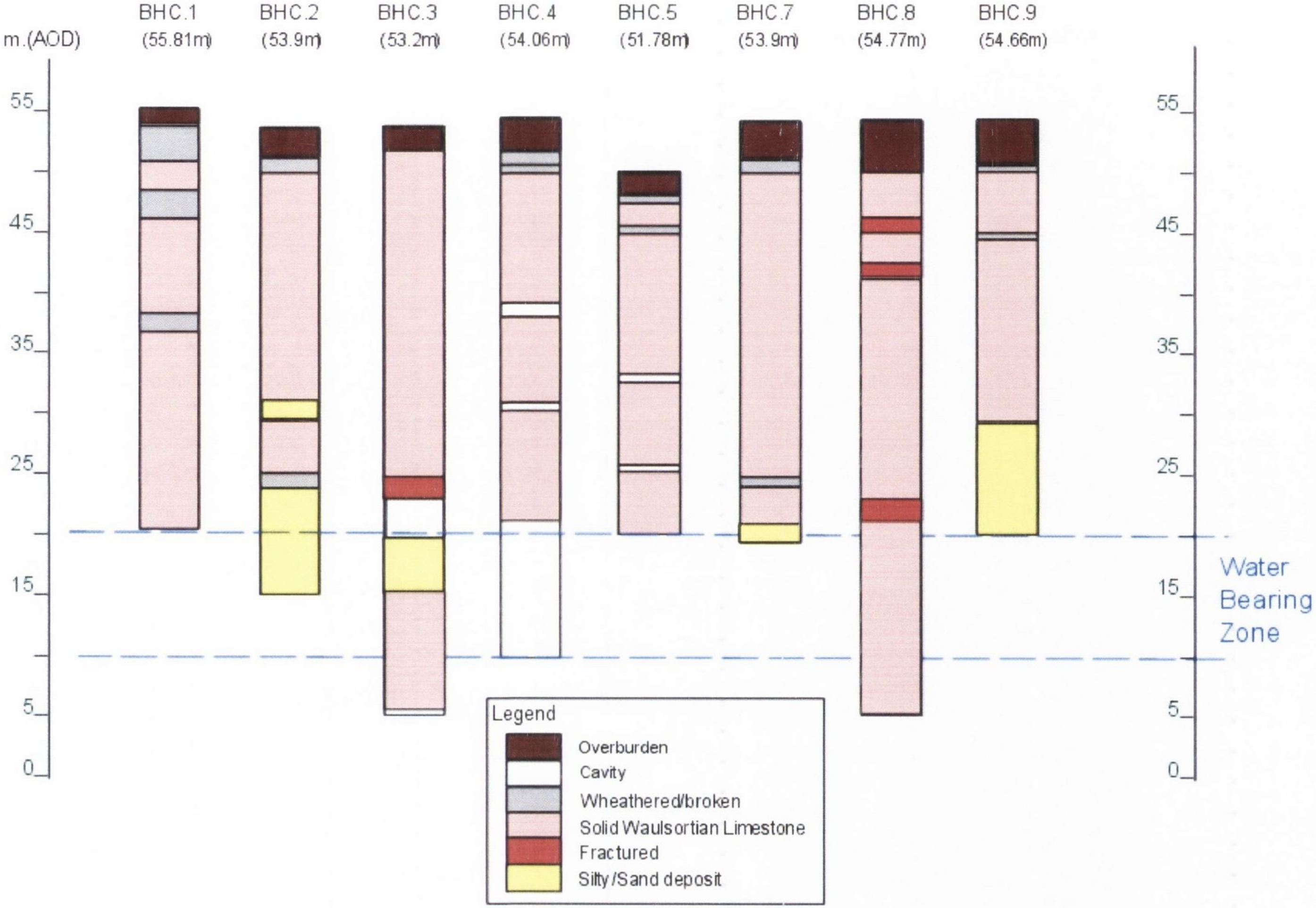

Figure 6.5 Cross-section line A-A, running south-south-west to north-north-east, showing local stratigraphy encountered during borehole drilling on Curtin's farm, the cross-section lines have been indicated on Figure 5.2.

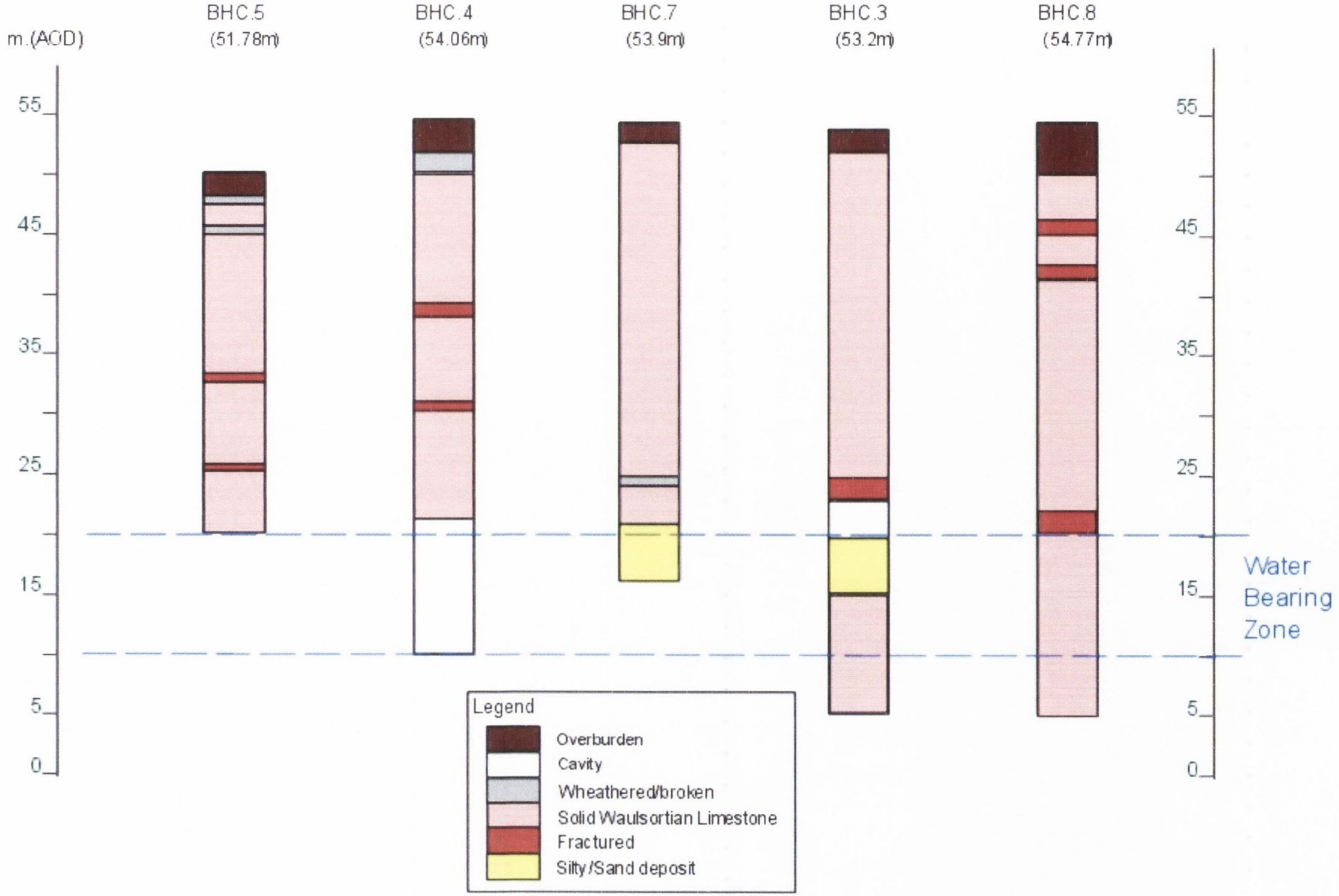

Figure 6.6 Cross-section line B-B, running west-north-west to east-south-east, showing local stratigraphy encountered during borehole drilling on Curtin's farm, the cross-section lines have been indicated on Figure 5.2.

As previously stated, bedrock core removal was not a feature of the drilling technique that created monitoring boreholes for the nitrate leaching research investigation. However, a mineral exploration company in the course of their mineral prospecting investigations in north Cork in February 2001 cored two boreholes on Curtin's farm. The two mineral exploration company's cored-boreholes formed part of the monitoring programme at Curtin's farm, labelled BHC.3 & BHC.8. Therefore, a detailed picture of the lithology does exist and the logs of the cores retrieved at these two locations are provided in Appendix B. The geologists confirm the bedrock to be Waulsortian Mudbank complex. The upper bedrock surface is described as very broken with surficial weathering and rounded weathered fragments for 2-3m into the bedrock.

The returns from bedrock drilling to the water-strike zone mostly indicated solid rock. In general, water was only encountered in mud or sand filled cavities, or in slight bedrock anomalies/cracks, all in the region 30-35m bgl. These water-bearing fractures have elevations in the range of 20-25m AOD. At many locations cavities were encountered through the drilling profile, which were not water bearing (see borehole logs, Appendix B). The weathered zones were identified by either free fall of the drilling rod or drilling returns of gravel. The success rate for striking water in a borehole was 53%, with only nine of the seventeen bores gaining access to groundwater. Land survey of the farm boreholes and the Funshion River confirmed that the groundwater beneath the farm was draining in the direction of the river (river-bed elevation being ~20m AOD at Downing's Bridge). I completed the surveying work.

6.2. Hydrogeology

There is strong evidence of karstification with the topographic depressions indicating 'collapse' structures, which act as fast drainage conduits to the groundwater table. Other areas of the ridge must be relatively impermeable below the overburden, given the low incidence of water-strike during project drilling. The groundwater table appears relatively flat, indicating high hydraulic conductivity at depth. The hypothesised conceptual model is that the reef limestone ridge with a thin soil cover perforated with deep collapse structures controls the hydrogeology. The collapsed areas may form conduits for rapid drainage to a relatively flat but deep groundwater table, at 20-30m depth, draining northwards to the River Funshion (groundwater elevations and response to recharge is presented in section 6.3). The predominant sand content of the subsoil aids rapid infiltration to bedrock (particle size analysis results are provided in Appendix F). Water then possibly follows the bedrock interface laterally until moving downward in the areas of broken rock that form vertical drainage pathways. From the evidence of water-strike incidents, it would appear that broken rock only contains flowing groundwater when that broken rock was filled with a sandy or gravel deposit. Samples of cavity fills were collected, where possible, during drilling and analysed for particle size distribution (see Appendix F). Groundwater travel velocity calculations suggest a turnover rate of 4-6 per year (see section 6.5.3.2).

6.2.1. Groundwater Hydraulic Conductivity Results

All the piezometers reacted differently to the slug addition of water, as can be seen from the ENVIROMON graphs in Appendix I. Most piezometers' water levels returned to their original pre-test levels in seconds but a couple took much longer. The results are presented in Table 6.2 where calculated values are presented but, along side, the data has been approximated to the normal convention for presenting groundwater potassium values; that is in orders of magnitude because one can never be overly exact about such a variable parameter measured in an underground setting. Figure 6.7 demonstrates the variation of groundwater hydraulic conductivity spatially on Curtin's farm. The range of measured hydraulic conductivities, 10^{-3} – 10^{1} m/day, falls within the range offered by Brassington (1998) for the secondary permeability of limestone bedrock; 10^{-5} – 10^{1} m/day. The significance of these results is examined during discussion of individual piezometer response to loadings. These results are also used for input parameters to the RAM model (see section 6.6).

Table 6.2 Calculated Hydraulic Conductivity for Piezometer Slug Tests.

Piezometer	Calculated Hydraulic Conductivity	potassium (m/day)
BHC.1	0.77 m/day	10^{0}
BHC.2	27 m/day	10^{1}
BHC.3	0.36 m/day	10^{-1}
BHC.4	0.13 m/day	10^{-1}
BHC.5	17.8 m/day	10^{1}
BHC.7	2.8 m/day	10^{0}
BHC.8	2.6 m/day	10^{0}
BHC.9	15.5 m/day	10^{1}
BHC.10	0.004 m/day	10^{-3}

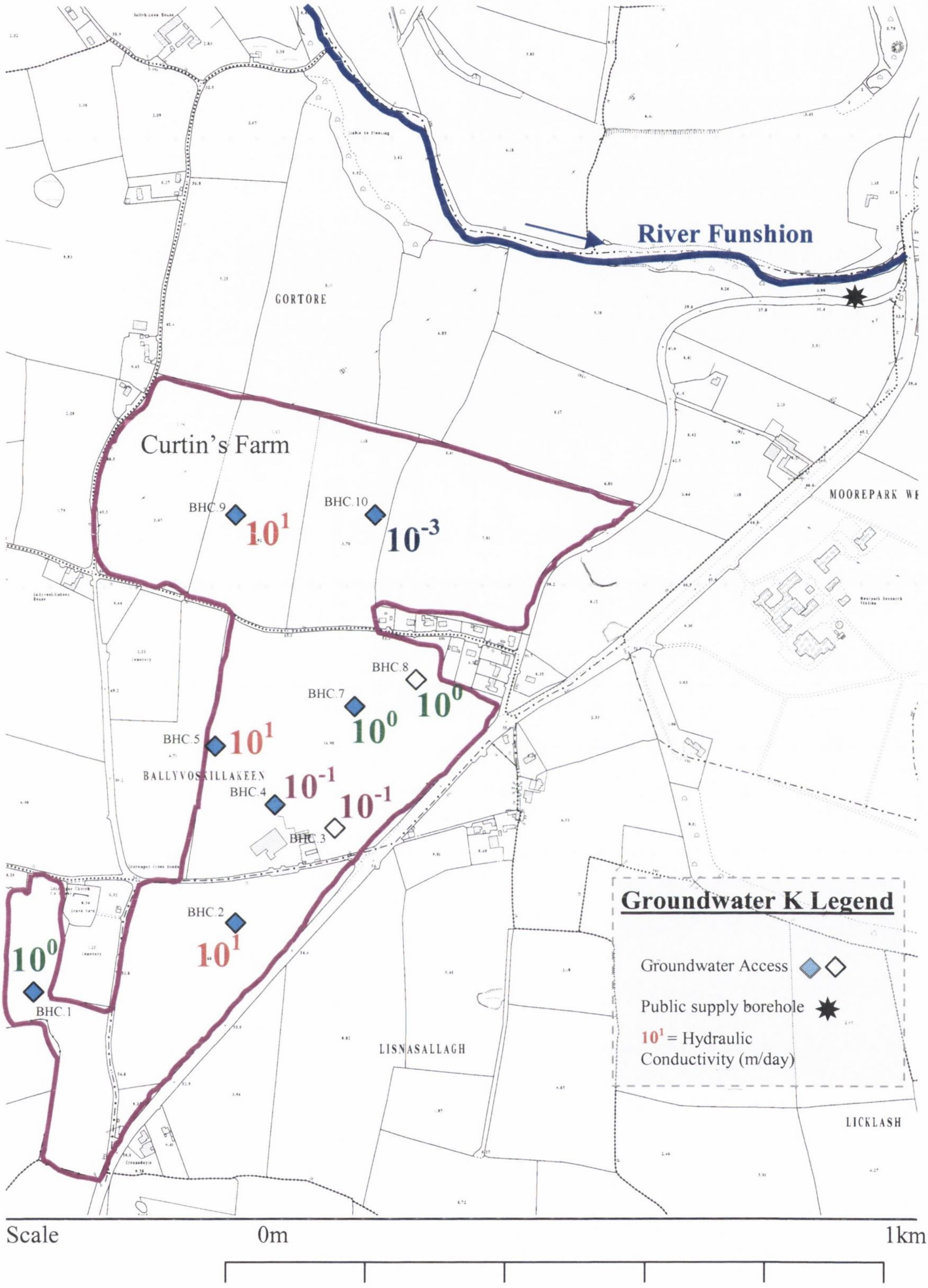

Figure 6.7 Curtin's farm measured groundwater hydraulic conductivity (m/day).

6.2.2. Observed Groundwater Responses To Recharge

6.2.2.1. Groundwater Elevations

A borehole elevation survey was conducted using the 'Trimble' Differential Global Positioning System. The survey showed that the farmyard itself sits on slightly higher ground relative to the rest of the farm area (~0.5m higher). There is a topographic-low 'muted valley' in the area devoted to dirty water spreading (~0.25m lower). Using the borehole-surface elevation data, borehole water level data and stage data from the OPW gauging station at Downing's Bridge, water table elevation maps were constructed. Raw data pertaining to field observations of water level and consequent conversion to water level elevations is contained in Appendix J, as is the magnitude of water level change between each monitoring event.

The average groundwater table elevation beneath the Curtin's' farm area throughout the two-year monitoring period was 30m AOD (25m bgl). The River Funshion, at the Downing's Bridge OPW gauging station, had a lower water-surface elevation. This suggests that the groundwater in the study area discharges to the River Funshion. The presumed groundwater gradient from the farm to the river was found to be 1:150 in the winter and 1:250 in the summer. A representative water table map is shown for December 2002 in Figure 6.8. Water table maps for different seasons are presented in Appendix H.

Generally, it can be observed that the hydraulic gradient between BHC.1 and BHC.3 is not steep; approximately 1m head difference over 500m horizontal distance therefore the groundwater gradient in this area is 1:500. This is expected because of the topography of this plateau site. The only digression from expected conditions was that which was observed in the area around BHC.7.

The hydraulic conductivity of the aquifer tested at BHC.7 was 2.8m/day. This suggests a lower transmissive capacity for groundwater at this location on the farm, which leads to the groundwater mound observed in constructed water table contour maps generated in this study. The localised groundwater mounding in the area of BHC.7 also coincides with the dirty water area. Originally, I believed that the dirty water irrigator was the cause of higher recharge and groundwater mounding. However, results for the hydraulic conductivity of the aquifer indicate that the mounding is a result of a combination of factors, amongst them surface loading rates and subsurface storage conditions. The water-table mound observed at BHC.7 affects local groundwater flow directions. However, the underlying groundwater flow direction is towards the River Funshion.

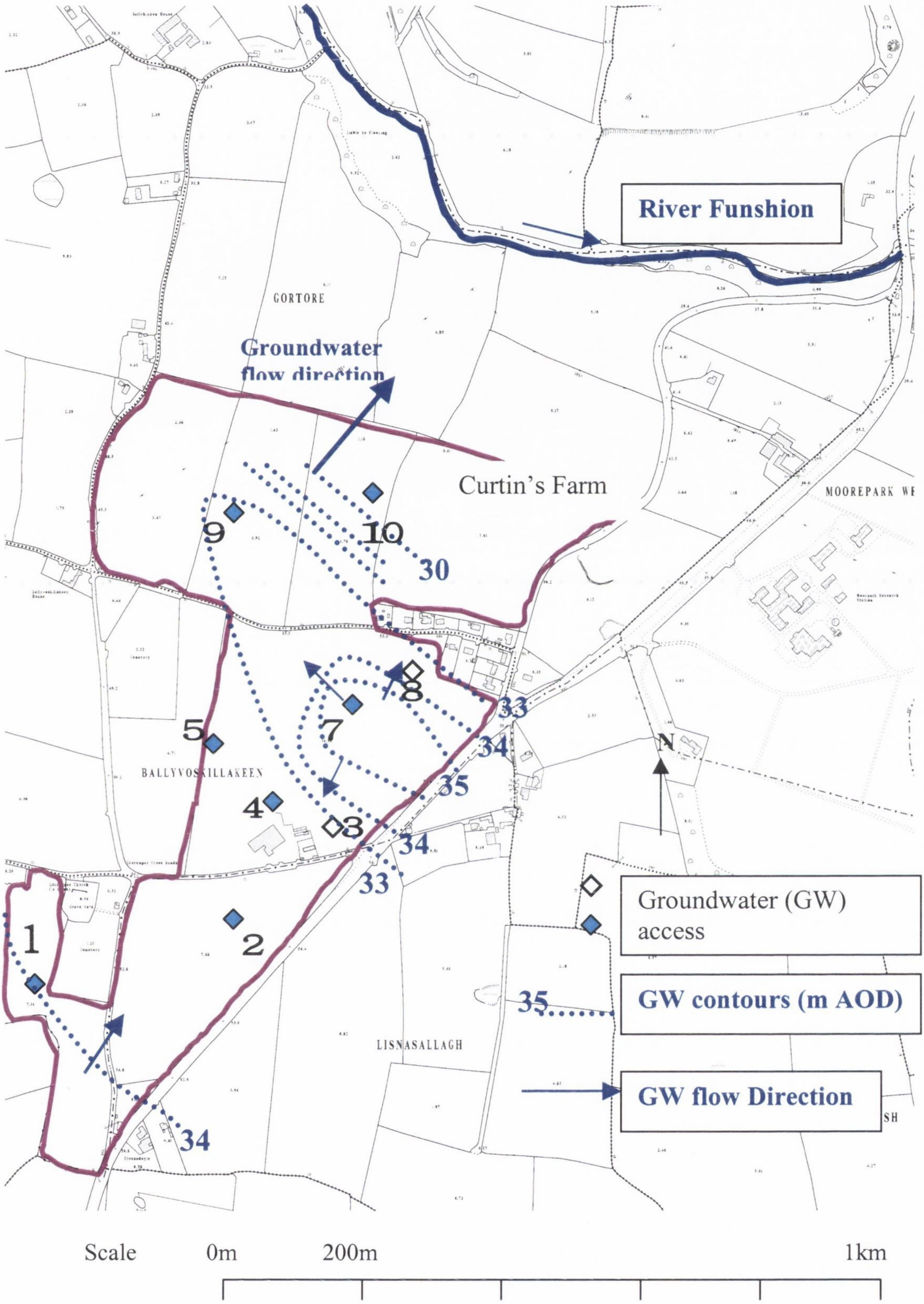

Figure 6.8 Water table elevations for December 2002 with groundwater flow directions indicated.

6.2.2.2. Recharge Pattern

Given that a fundamental aim of this work was definition of piezometer response to loadings, the most significant influence on leachate is rainfall. The methods and model employed for effective rainfall determination have previously been outlined in section 5.5.1. Cumulative recharge on Curtin's farm is represented in Figure 6.9. The recharge and non-recharge seasons are clearly defined by cumulatively plotting the monthly totals for effective rainfall (RF_{eff}) over the time period of the study. Recharge to the groundwater begins in October of each year and continues until May or June, generally.

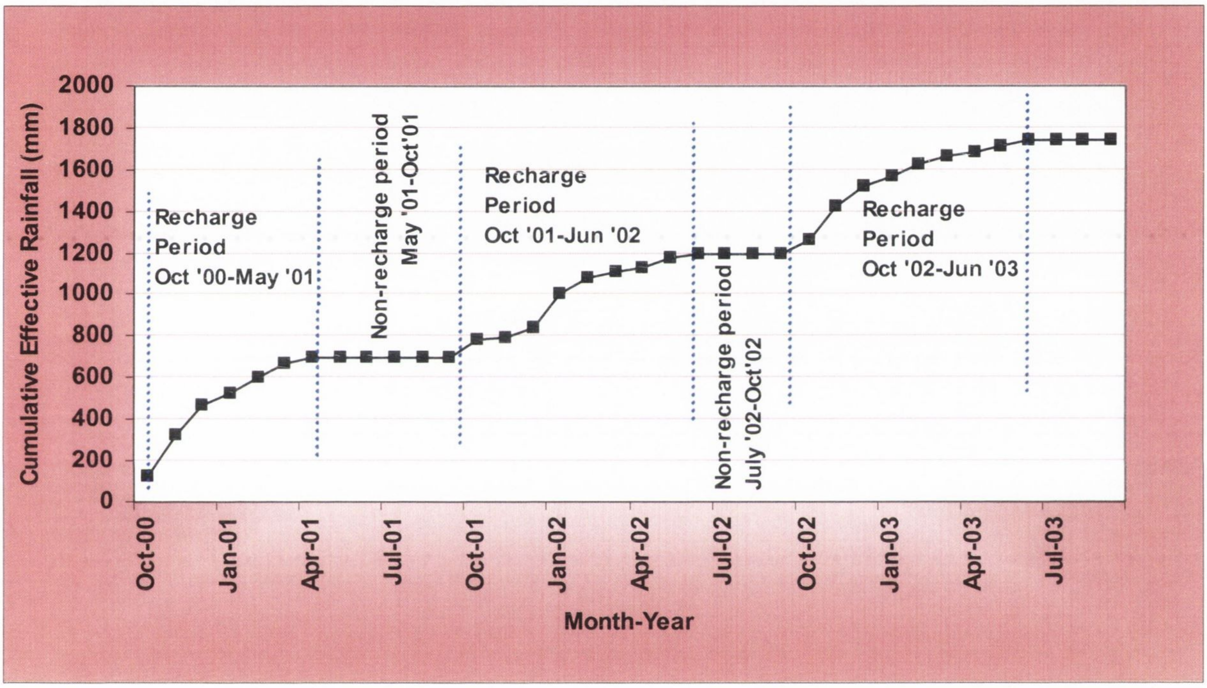

Figure 6.9 Cumulative effective rainfall (groundwater recharge) trend at Curtin's farm for the period October 2000-October 2003 clearly demonstrating recharge and non-recharge periods.

6.2.2.3. Water Table Response to Recharge

The water level trend in each individual piezometer is shown in Figure 6.10. Whilst all piezometers reacted with similar trends the magnitude of the response was quite different in some piezometers, as is to be expected for non-homogeneous field conditions. Similarly rapid water table responses to recharge are reported for another Waulsortian unit in Cork (Fitzsimons *et al.*, 2003).

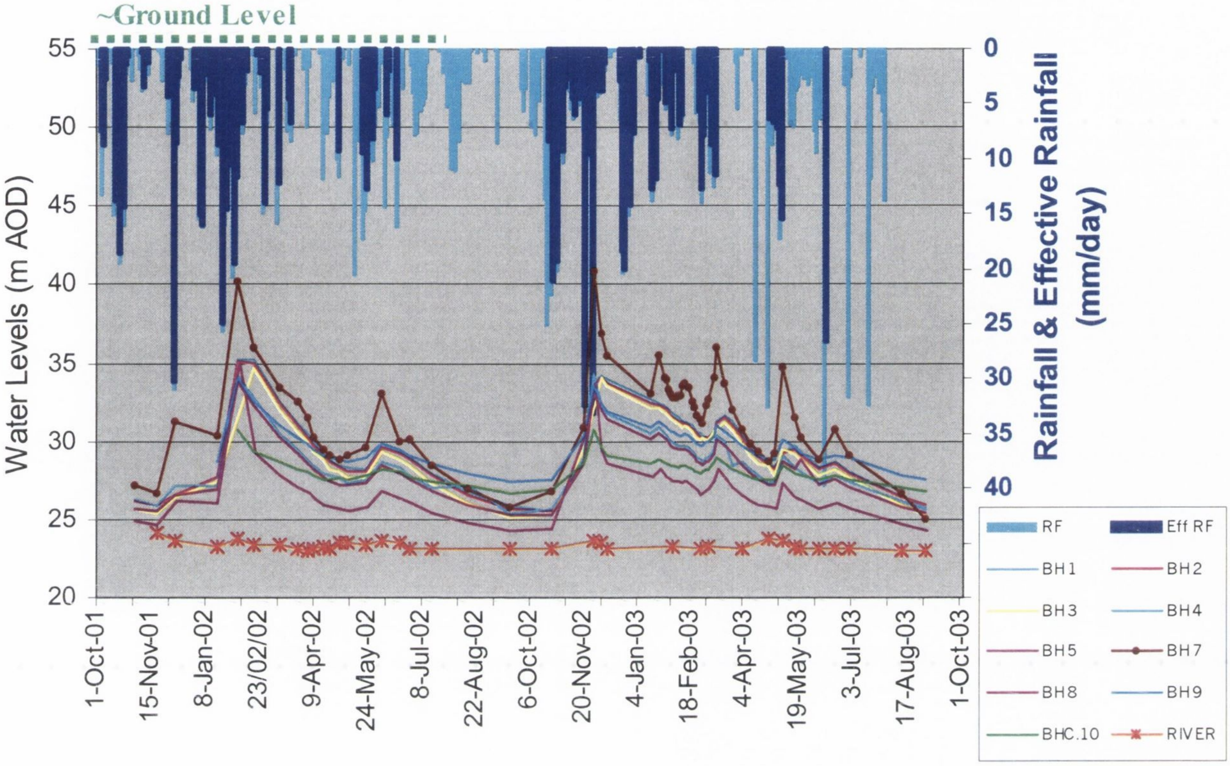

Figure 6.10 Groundwater level trend in each individual piezometer and River Funshion water level trend measured at the OPW gauging station at Downing's Bridge.

6.2.2.4. Quantifying the Effect of Recharge on Groundwater Levels

The RF_{eff} methodology (used to generate Figure 6.9) suggests that there is no summer recharge to the groundwater system. Average groundwater level response in all nine piezometers to RF_{eff} is shown in Figure 6.11 (the response of each individual piezometer was presented in the Figure 6.10). Water levels in all the piezometers were observed to decline steadily throughout the summer (non-recharge) period and so I conclude that the effective recharge calculation method is validated for determining meteorological loading to the groundwater system.

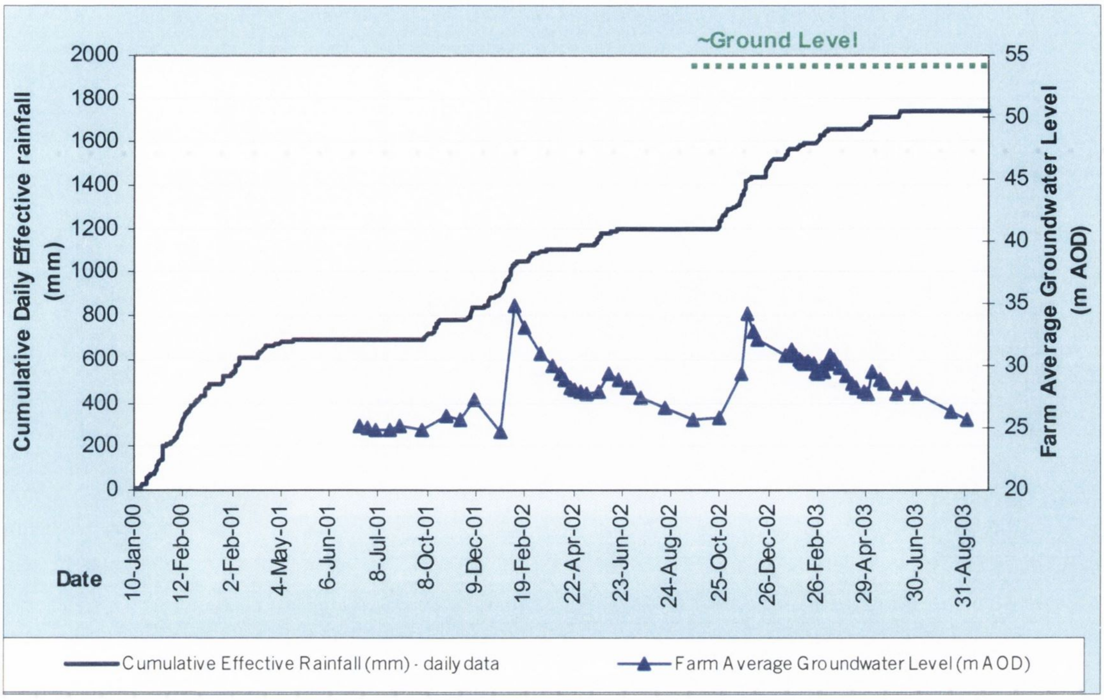

Figure 6.11 Average response of the groundwater beneath Curtin's farm to effective rainfall.

It was observed in three consecutive years following non-recharge periods that the groundwater body is at its lowest level by the end of September each year (Figure 6.11). When at its lowest level, the upper piezometric level is 28.5m below ground surface, on average, which translates to an elevation of 25.5m above Ordnance Datum (AOD).

The response of the groundwater to meteorologic loadings is most clearly observed with the onset of recharge each winter. The reaction of the groundwater to the first recharge of a hydrological year, in October/November was observed for two recharge seasons, winter 2001 and 2002. In each hydrological year, piezometer water levels demonstrated a significant response to RF_{eff} within one month of the onset of recharge. At the end of October 2001, after the first month of recharge in the new hydrological year, groundwater levels rose by approximately 1m as a consequence of the first 80mm RF_{eff}. In that first year of the study the following rains were neither intense nor numerous and so did not significantly impact groundwater levels until the end of January 2002. In that month nearly five consecutive weeks of heavy rainfall, totalling 205mm of RF_{eff}, effected an average rise of 7.5m in groundwater piezometers: observed in early February. In the following hydrological year recharge began in the last week of October 2002. Rainfall was intense straight away and a total of 200mm RF_{eff} fell in the first month of recharge, with two individual storm events bringing more than 33mm each day in one week. This initial intense recharge activity caused an average rise of 8m in groundwater levels in one month. The magnitude of the rise was different in each piezometer but this will be discussed later (see section 6.4.6). Overall in both years investigated, approximately 200mm RF_{eff} fell in the wettest month of each year and the different effect of this maximum monthly rainfall on each of the piezometers water levels is shown in Table 6.3.

Table 6.3 Maximum groundwater level increase in response to the wettest month in each year, in which 200mm RF_{eff} was contributed to the system.

Piezometer	Maximum Groundwater Level Increase (m)
BHC.1	8
BHC.2	8.7
BHC.3	8.2
BHC.4	8.6
BHC.5	4
BHC.7	15
BHC.8	9
BHC.9	6
BHC.10	See section 6.4.6.10

So, the initial stages of the winter recharge season have been shown to cause substantial rise in groundwater levels. What effect does further recharge have on the groundwater body? In both monitoring years, groundwater levels steadily decline from their winter maximum after the first onslaught of recharge. It is difficult to discern the effects of additional recharge because the magnitude of the initial surge on the system would suggest that relenting of intense pressure on the system would prevail over the influence of any further relatively small recharge additions in Spring or Summer. In the first monitoring year, 2001-2002, there was only one other recorded rise in groundwater levels, in early June (summer). Groundwater levels rose by 1.5m, on average over all piezometers, in a two-week monitoring interval between the 28-May-02 and 4-Jun-02. The rise is attributable to 50mm of RF_{eff}, which fell in ten days, from the 19th to the 29-May-02, in the two weeks directly preceding the observed peak. Natural weather patterns aid our interpretation of the response of the groundwater system because there was no significant RF_{eff} in either March, April or early May (full daily values for each component of the daily water balance have been presented in Appendix P). Low levels of Spring-rainfall in combination with constant evapotranspiration demands had created a soil moisture deficit (SMD) that twice approached 30mm[*] in April and early May. Any rainfall that had fallen in this dry spell was consumed to restore soil moisture conditions and to fulfil grass growth requirements. Therefore it can be confidently asserted that the June-2002 groundwater level peak, observed in all piezometers, was caused by 54mm of RFeff in the previous two weeks.

In the second hydrological year 2002-2003 apart from the massive winter peak, only on three occasions can a distinct rise in groundwater levels be observed: a rise of approximately 0.5m in late January in response to 125mm of RF_{eff} in the previous month; a 1.3m rise in mid March following 82mm RF_{eff} in the previous month and an observed 0.5m Summer rise in groundwater water levels (on the 6-May-03) in response to four significant rainfall events that created 50mm in the previous two weeks. Significantly, it is the intensity of recharge that affects a groundwater level change. If more than 50mm RF_{eff} falls within a two week period there is repeated evidence that groundwater levels will rise by at least 0.5m.

6.2.2.5. Conclusions- Groundwater Response to Recharge

Effective rainfall effects groundwater levels, at 25-28m bgl, within a short period on Curtin's farm. Within one month of the heavy block of winter recharge, observed to be 200mm in the wettest winter month in both years, groundwater levels rise by up to 8m. After the massive winter peak in groundwater levels the influence of further recharge is difficult to discern unless >50mm RF_{eff} falls within a two-week period, then a 0.5-1.5m rise in water levels is observed. The issue now is whether the delivery of recharge to the groundwater impacts negatively on groundwater quality at Curtin's farm. The primary focus of this thesis is groundwater nitrate concentrations. Firstly however, general groundwater quality will be discussed.

6.3. Groundwater Quality At Curtin's Farm

The EPA guideline document regarding assessment of groundwater quality (EPA, 2003a) has been discussed in section 5.3.3. The strategy suggests that each analysed parameter value must be compared with the IGV: if all parameters are below the IGV then direct action is not required.

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[*] 30mm is the value proposed by Aslyng (1965) to restrict grass growth and actual evapotranspiration. Refer to chapter 5, section 5.5.1.5, for more details.

However, if one or more parameter exceeds the IGV then further assessment is required. The further assessment includes assessment of the natural hydrochemistry of the groundwater. If the sites' groundwater is not in keeping with the natural hydrochemistry then remedial action 'may be required'. This strategy has been applied in this work. Hydrochemical results for each piezometer for the monitoring period are presented in Appendix R and hydrochemical parameters are more fully discussed when reviewing the impact of agricultural loadings on each individual piezometer. The discussion in this section is intended to give a general overview of the groundwater status and the potential agricultural signature in the groundwater beneath Curtin's Farm.

6.3.1. Physiochemical Characteristics

6.3.1.1. Temperature

In-situ measurement of groundwater temperature ('down-the-hole') revealed that the temperature measured in all piezometers on any given sampling day was approximately the same: the daily range being approximately +/-0.5°C. Minimum groundwater temperatures were approximately 11°C and were recorded in February and March each year, during the recharge season. Maximum observed groundwater temperatures were approximately 13°C, which occurred in summer and autumn each year, during the non-recharge period. At no location on the farm, at any time, did the groundwater exhibit unexpected variations in temperature. The EPA IGV for groundwater temperature, 25°C, was neither breached nor even approached during the monitoring period.

6.3.1.2. Electrical Conductivity (EC)

In-situ groundwater EC varied greatly throughout the monitoring period in each piezometer. Variation in EC is directly related to variation in ion concentration: the greater the number of ions the higher the EC (Dojlido & Best, 1993). Generally, maximum EC values were observed in the winter-recharge season. The range of concentrations observed in any one piezometer over the entire two-year monitoring period could be as great as 380μS/cm: Table 6.4 details summary groundwater and River Funshion recorded EC values. Most piezometers yielded EC values between 800 and 900μS/cm, which are within the IGV standards. However, one piezometer, BHC.4 sited in the dirty water irrigation area, consistently breached the EPA IGV for groundwater EC, 1000μS/cm, during the monitoring period (see section 6.4.6.5 for more discussion about this piezometer). The variation in groundwater EC for each piezometer throughout the monitoring period is presented in Appendix R, along with all other hydrochemical results. The EC of the water in the River Funshion was also monitored throughout the study to reveal a range of 354-630μS/cm.

Table 6.4 Summary electrical conductivity details (μS/cm) at Curtin's farm piezometers and the River Funshion (2001- 2003).

	BHC1	BHC2	BHC3	BHC4	BHC5	BHC7	BHC8	BHC9	BHC10	RIVER
AVERAGE	804	852	940	1170	797	897	881	789	764	455
MAX	1070	910	1087	1378	885	950	927	817	881	630
MIN	706	700	880	1021	744	860	850	770	505	354
RANGE	364	210	207	357	141	90	77	47	376	276

The EC trends for nearly all piezometers displayed similar trends, which fluctuate between approximately 800 and 900μS/cm. Two piezometers stand out: in BHC.4 EC values are consistently high and BHC.10 EC values are lower than the rest.

6.3.1.3. Groundwater pH

The pH of the groundwater did not vary appreciably and values of 6.9-7.2 were always returned. Therefore the EPA IGV range, 6.5-9.5, for pH was always conformed to.

6.3.2. Hydrochemical Quality at Curtin's Farm

The general hydrochemistry of the groundwater was assessed using the following parameters – potassium, sodium, and chloride in addition to the ratio of K:Na. Other parameters analysed were calcium and sulphate.

6.3.2.1. Groundwater Potassium (K) Concentrations

Generally the groundwater beneath the farm conforms to the Drinking Water Standards limit of 12 mg/l potassium and the IGV value of 5 mg/l potassium. However, BHC.3 and BHC.4 consistently breach the higher 12mg/l potassium concentration. A GSI survey of principal springs in Ireland found mean potassium concentrations 2.9mg/l K (Daly, *et al.*, 1989). The overall median value observed in the groundwater was 4.7mg/l K, which is close to the IGV. However, groundwater potassium concentrations ranged from 1-215 mg/l K depending on location and agricultural management in the vicinity of the monitoring location. Highest values were observed in August 2002 and September of both monitoring years. These autumn values are extremely high and alert grave concern. Table 6.5 details summary groundwater and River Funshion recorded potassium concentrations.

Table 6.5 Summary potassium concentrations (K mg/l) at Curtin's farm piezometers and the River Funshion (2001- 2003).

	BHC1	BHC2	BHC3	BHC4	BHC5	BHC7	BHC8	BHC9	BHC10	RIVER
Average	1.3	5.5	23.2	36.3	1.3	13.2	7.6	4.2	5.5	12.8
Max	4.4	62.0	72.3	197.3	6.0	215.0	30.4	16.5	11.2	58.2
MIN	0.3	1.0	11.3	1.0	0.5	1.3	3.3	2.4	2.2	2.1
Range	4.1	61.0	61.0	196.4	5.6	213.7	27.1	14.1	9.1	56.1
MEDIAN	0.7	1.5	15.5	30.3	0.9	4.4	5.3	2.9	4.7	6.4

6.3.2.2. Groundwater Sodium (Na) Concentrations

A typical Irish Carboniferous limestone aquifer might have sodium concentrations of approximately 9mg/l (EPA, 2003a). Sodium is always present in natural waters (Flanagan, 1992) it is not a harmful constituent but is used as an indicator that appreciable impact on groundwater quality may be occurring (GSI, 1999). The Irish Drinking Water Standards set a limit of 150 mg/l Na and this is never breached on Curtin's farm. There is no GSI trigger value. Piezometers BHC.1, BHC.2, BHC.5, BHC.8 and BHC.9 returned groundwater samples with Na concentrations similar to those expected as natural hydrochemistry in a Carboniferous limestone aquifer (median values in these piezometers were below 9mg/l). Summary Na concentrations for all Curtin's farm monitoring locations are shown in Table 6.6.

Table 6.6 Summary sodium (mg/l Na) concentrations at Curtin's farm piezometers and the River Funshion (2001- 2003).

	BHC1	BHC2	BHC3	BHC4	BHC5	BHC7	BHC8	BHC9	BHC10	RIVER
Average	8.7	8.7	9.6	14.0	7.8	13.0	10.4	8.5	12.3	22.8
Max	28.5	17.9	12.0	17.6	9.5	28.7	23.4	9.6	45.8	39.1
MIN	5.0	6.7	7.4	10.8	6.5	9.8	7.3	7.7	2.0	9.6
Range	23.5	11.1	4.7	6.8	3.0	18.9	16.1	1.9	43.7	29.6
MEDIAN	**7.2**	**7.9**	**9.3**	**13.8**	**7.5**	**11.5**	**9.9**	**8.5**	**10.6**	**26.1**

Slightly elevated Na concentrations were persistently identified in the first year at BHC.3 (mean 2002 concentration 11mg/l Na) and in both years at BHC.4 and BHC.7. These latter piezometers are located in the dirty water irrigation area and the significance of the impact of management practices in this area is discussed in sections 6.4.6.5, 6.4.6.7 and 6.7.

6.3.2.3. Groundwater Chloride (Cl) Concentrations

All natural waters contain dissolved ionic constituents in varying amounts. The dominant ion in rainwater is chloride because rainwater is largely derived from seawater (Kiely, 1997). Chloride is also a constituent of organic wastes and so levels appreciably above background values have been taken to indicate contamination by organic wastes. However, chloride can also be derived from potassium fertiliser (Kiely, 1997). If rainfall were the principal source of chloride in a groundwater body then levels would be fairly consistent.

Natural chloride concentration in Carboniferous limestone aquifers would be approximately 26 mg/l (Kiely, 1997 adapted from Daly, 1994). The GSI trigger value for this constituent is 30mg/l Cl and this is also the value that has been adopted by the EPA as an interim guideline value (IGV) for assessing groundwater quality (EPA, 2003a). However, it has been suggested that for a karst aquifer of this nature chloride concentrations above 20mg/l may indicate contamination (Coxon, *pers. comm.*, 2004).

Details regarding chloride concentrations in the groundwater monitored at Curtin's farm are presented in Table 6.7. It can be noted that, on average, all monitoring locations returned groundwater samples with chloride concentrations less than the IGV and only BHC.4 and BHC.5 breach the IGV. Richards (1999) found that high chloride concentrations were associated with dirty water irrigation. The high chloride concentrations observed in BHC.5 are not supported by elevated concentrations of any other constituents in any of the groundwater samples from this source.

Table 6.7 Summary chloride (mg/l Cl) concentrations at Curtin's farm piezometers and the River Funshion (2001- 2003).

Cl (mg/l)	Average	Max	MIN	Range	Median
BHC1	16.1	23.2	5.7	17.6	16.5
BHC2	14.4	17.7	7.5	10.2	15.1
BHC3	11.8	16.6	5.5	11.1	12.6
BHC4	35.6	56.6	10.6	46.1	34.6
BHC5	39.9	52.3	6.5	45.8	40.1
BHC7	16.8	22.4	8.0	14.4	16.5
BHC8	14.8	19.8	9.3	10.5	16.6
BHC9	21.3	25.4	11.0	14.4	22.8
BHC10	26.2	34.8	7.4	27.5	26.5
RIVER	39.0	69.9	17.6	52.3	34.6

6.3.2.4. Groundwater potassium to sodium (K:Na) ratios

Daly & Daly (1982) point to the significance of a K:Na ratio greater than 0.3 as an indicator of contamination from dirty water, farmyard and other wastes derived of plant origin. The K:Na ratio of soiled water and other wastes derived from plant organic matter is considerably greater than 0.4: consequently a K:Na ratio greater than 0.4 can be used to indicate contamination by organic wastes (Kiely, 1997).

The K:Na ratio of groundwater abstracted from BHC.3 was greater than 0.4 for every sampling event. Similarly consistently high K:Na ratios were returned from BHC.4. Hydrochemical results for these two piezometers suggest that they are impacted by point source contamination from the farmyard. Other piezometers sporadically returned groundwater samples with K:Na ratios > 0.4, but mostly in the first year. BHC.7, located in the dirty water area, had a particularly bad record for K:Na ratios in the first year but all samples returned in the second year conformed to a ratio of <0.4, indicating improvement in some area of farm management. Summary details regarding K:Na ratios are provided in Table 6.8.

Table 6.8 Summary K:Na ratios at Curtin's farm piezometers and the River Funshion (2001-2003).

K:Na ratio	Average	Maximum	Minimum	Range	Median
BHC1	0.1	0.7	0.0	0.7	0.1
BHC2	0.5	3.7	0.1	3.6	0.2
BHC3	2.4	6.2	1.1	5.1	1.8
BHC4	2.6	12.2	0.1	12.1	2.2
BHC5	0.2	0.7	0.05	0.7	0.1
BHC7	0.7	8.1	0.1	8.0	0.4
BHC8	0.8	3.1	0.2	2.8	0.5
BHC9	0.5	1.9	0.3	1.7	0.3
BHC10	0.6	2.3	0.1	2.2	0.3
RIVER	0.5	1.5	0.2	1.3	0.3

6.3.2.5. Groundwater Sulphate (SO_4)

The EPA (2003a) acknowledges SO_4 as a significant indicator of groundwater contamination and labels its sources as agriculture, acid rain and urban sources. Bohlke (2002) suggests that SO_4 is a useful tracer of agriculturally impacted groundwater. The Environmental Quality Standard (EQS) for sulphate is 200mg/l and the EPA has adopted this value as the IGV for groundwater (EPA, 2003a). There were no breaches of IGV at Curtin's farm. Summarised groundwater sulphate data is contained in Table 6.9. When describing the natural groundwater chemistry of Carboniferous limestone aquifers (EPA, 2003a), sulphate concentration was not determined and so it is not possible to relate the concentrations reported here to a natural state. However, it can be observed that all piezometers returned groundwater samples with similar sulphate values and ranges.

Table 6.9 Summary sulphate data (mg/l SO_4) at Curtin's farm piezometers and the River Funshion (2001-2003).

SO4 (mg/l)	**Average**	**Max**	**MIN**	**Range**	**Median**
BHC1	12.6	24.3	3.4	20.9	13.1
BHC2	11.0	22.6	4.8	17.9	9.4
BHC3	13.0	19.3	6.8	12.5	13.6
BHC4	13.0	33.1	6.0	27.2	10.3
BHC5	13.3	16.7	10.5	6.2	13.0
BHC7	11.4	24.4	5.0	19.4	9.8
BHC8	12.7	19.3	8.0	11.3	10.5
BHC9	16.0	20.1	4.0	16.1	18.0
BHC10	13.1	19.6	7.1	12.6	13.5
RIVER	6.7	12.6	1.7	10.9	6.7

6.3.2.6. Groundwater Calcium (Ca)

Calcium concentrations did not vary significantly, spatially throughout the farm and the average concentration observed was 125 mg/l Ca, which is below the 200mg/l IGV set by the EPA (EPA, 2003a). Full hydrochemical analysis results are available in Appendix R.

6.3.3. General Groundwater Nutrient Status

Groundwater nutrient trends are presented graphically in Appendix R and the peaks and contamination incidences are more visible in that format. This section generally evaluates the status of the groundwater. Full discussion of groundwater nutrient trends is presented in section 6.4.6, where groundwater response at each piezometer is analysed.

6.3.3.1. Nitrogen Species in the Groundwater

All groundwater samples were subjected to analysis for ammonium (NH_4-N), nitrite (NO_2-N), and the nitrate ion.

6.3.3.1.1. Summary Groundwater Nitrate Concentrations

Groundwater nitrate concentrations were nearly always above the EU 11.3mg/l NO_3-N MAC (EC, 1998). Summary data for groundwater nitrate concentrations at each piezometer location, for the entire monitoring period, are shown in Table 6.10. Groundwater nitrate concentrations beneath Curtin's farm ranged from <1-31 mg/l NO_3-N. More detailed analysis follows in succeeding sections. However, with respect to assessing general groundwater status, Table 6.10 shows that average groundwater nitrate concentrations are high with respect to the Drinking Water Directive MAC (EC, 1998) of 11.3 mg/l NO_3-N.

Table 6.10 Summary details regarding groundwater nitrate (mg/l NO_3-N) concentrations at Curtin's farm (2001-2003).

NO3-N (mg/l)	Average	Maximum	Minimum	Range	Median
BHC1	7.3	12.2	4.0	8.2	7.2
BHC2	15.9	22.3	9.4	12.9	15.6
BHC3	12.8	20.6	7.6	13.0	10.6
BHC4	15.1	23.2	4.0	19.2	14.6
BHC5	13.1	17.3	7.2	10.1	13.4
BHC7	19.1	27.0	8.6	18.3	18.0
BHC8	18.7	31.0	8.6	22.3	16.2
BHC9	11.9	23.0	8.2	14.9	11.3
BHC10	4.1	15.3	0.8	14.5	3.5
RIVER	4.7	6.0	3.0	2.9	4.9

The EPA IGV (EPA, 2003a) is set at 25mg/l NO_3^- (note it is the nitrate form). For the purposes of comparison with results presented here, and in most nitrate leaching research studies, the 25mg/l NO_3^- is equivalent to 5.6mg/l as NO_3-N. Most sites, except those on the fringes of the farm (BHC.1 and BHC.10), consistently breach the IGV and so the site warrants further assessment.

6.3.3.1.2. Summary Groundwater Ammonium Concentrations

Although ammonium has a low mobility because it is usually tightly bound to soil particles the ammonium-N ion can enter water systems on occasion (Jarvis, 1999a). Because it is a transitory constituent in the nitrogen cycle (refer to section 2.3) it is not often subject to investigation. Some suggest that the presence of ammonium in water at levels much above 0.1mg/l N indicates point source contamination (e.g. Flanagan, 1992; Jarvis, 1999a). However, others acknowledge that vulnerable conditions may also be the cause of elevated ammonia in groundwater (Kiely, 1997). Summary details regarding occurrence of the ammonium ion in groundwater beneath Curtin's farm are presented in Table 6.11.

Table 6.11 Summary details regarding groundwater ammonium concentrations (mg/l NH_4-N) at Curtin's farm (2001-2003).

NH4-N (mg/l)	Average	Maximum	Minimum	Median
BHC1	0.06	0.24	0.05	0.05
BHC2	0.18	2.28	0.05	0.05
BHC3	0.05	0.09	0.05	0.05
BHC4	1.28	3.98	0.125	1.15
BHC5	0.06	0.17	0.05	0.05
BHC7	0.05	0.13	0.05	0.05
BHC8	0.05	0.10	0.05	0.05
BHC9	0.05	0.26	0.05	0.05
BHC10	0.32	1.90	0.05	0.15
RIVER	0.06	0.14	0.05	0.05

The EPA IGV (EPA, 2003a) is set at 0.15mg/l as NH_4 (note it is the ammonium form), which is the GSI trigger value. Results presented in Table 6.11 report the groundwater concentration as the ammonium-N ion (NH4-N). The IGV of 0.15mg/l as NH_4 converts to 0.12mg/l as NH_4-N. Average concentrations conform to acceptable limits in most boreholes but BHC.2 and BHC.10 show occasional problems and BHC.4 demonstrates a persistent problem. Additionally the observed maximum concentrations at most boreholes are extremely high and 77% of the monitoring locations reveal peak NH4-N concentrations that breach the IGV. These results highlight a significantly vulnerable groundwater. A concurrent leaching investigation at Curtin's farm, which targeted 1m depth in the subsoil, revealed ammonium-N concentrations at 1m that consistently breached the Drinking Water Regulations MAC of 0.23mg/l NH_4-N (DELG, 2000) during the winter monitoring period (Ryan, *pers. comm.*, 2003; to be published in EPA final report for Eutrophication from Agricultural Sources – Nitrogen research project).

6.3.3.1.3. Summary Groundwater Nitrite Concentrations

Nitrite is an intermediary in the oxidisation of ammonium to nitrate and levels in unpolluted water are normally below 0.01 mg/l as NO_2-N (Flanagan, 1992). Appreciable concentrations indicate a substantial source of ammonia. The EPA IGV (EPA, 2003a) was adopted based on the 0.1mg/l as NO_2 limit set by the Drinking Water Regulations (DELG, 2000), which is equivalent to 0.03 mg/l as NO_2-N and it is the latter format in which is reported here, in Table 6.12, for summary information regarding groundwater concentrations in both monitoring years at Curtin's farm.

With respect to the IGV of 0.03 mg/l as NO_2-N, median results suggest that on the whole there is not a persistent problem, such as a constant release of ammonia from an underground waste source. However, the sometimes-high nitrite concentrations, revealed by the maximum concentrations in Table 6.12, suggest an intermittent problem most probably a function of agricultural management at the lands surface in this intrinsically vulnerable environment.

Table 6.12 Summary groundwater nitrite concentrations (mg/l NO_2-N) for all piezometers at Curtin's farm and the River Funshion (2001-2003).

NO2-N (mg/l)	Average	Max	MIN	Range	Median
BHC1	0.017	0.180	<0.001	0.180	<0.001
BHC2	0.340	4.680	<0.001	4.680	0.0300
BHC3	0.003	0.025	<0.001	0.025	<0.001
BHC4	0.037	0.475	<0.001	0.475	0.0100
BHC5	0.005	0.010	<0.001	0.010	<0.001
BHC7	0.036	0.650	<0.001	0.650	<0.001
BHC8	0.034	0.400	<0.001	0.400	<0.001
BHC9	0.005	0.070	<0.001	0.070	<0.001
BHC10	0.014	0.030	<0.001	0.030	0.0170
RIVER	0.015	0.039	<0.001	0.038	0.0130

6.3.3.2. Phosphorus in the Groundwater

In this study all groundwater samples were analysed for phosphorus in both raw and filtered states (see chapter five, section 5.3.2). Groundwater phosphorus concentration summary statistics, for the unfiltered raw samples, are presented in Table 6.13. All phosphorus analyses results are provided in Appendix R.

Neither the Irish EPA (EPA, 2003a) nor European drinking water legislation (EC, 1998) set limits for phosphorus in groundwater. However, the trophic status of groundwater-fed surface water features is controlled by the nutrient content of the inflowing groundwater and the chief nutrient of concern is phosphorus (Coxon & Drew, 1998). Total phosphorus concentrations in excess of only 0.02 mg/l may trigger eutrophication in some lakes (Champ, 1998). Analysis of Irish river data suggests that adverse impacts become apparent once unfiltered phosphorus levels exceed 0.03 mg/l (McGarrigle, 1998). Although phosphorus was conventionally thought *not* to be a problem in groundwater because of its immobility (Kiely, 1997), further evidence now exists demonstrating its occurrence in groundwater, in this karstified environment. Kilroy *et al.* (1998) showed that phosphorus is found in some Irish groundwaters at concentrations that induce eutrophication in surface waters.

Table 6.13 Summary groundwater phosphorus concentrations (mg/l PO_4) for all piezometers at Curtin's farm and the River Funshion (2001-2003).

PO4 (mg/l)	AVERAGE	MEDIAN	MAXIMUM	MINIMUM
BHC.1	0.011	<0.005	0.100	<0.005
BHC.2	0.015	0.010	0.060	<0.005
BHC.3	0.022	0.012	0.127	<0.005
BHC.4	0.080	0.033	0.987	<0.005
BHC.5	0.019	0.010	0.094	<0.005
BHC.7	0.025	0.017	0.112	<0.005
BHC.8	0.016	<0.005	0.092	<0.005
BHC.9	0.023	0.015	0.088	<0.005
BHC.10	0.065	0.059	0.144	<0.005
RIVER	0.077	0.078	0.131	<0.005

Figure 6.12 shows the concentrations of dissolved reactive phosphorus (filtered groundwater samples) in samples abstracted from piezometers under different agronomic treatments at Curtin's farm for each monitoring year. It is noted that there is a clear response to effective rainfall and also that phosphorus peaks occur in all treatments but are highest in the dirty water and one cut silage areas.

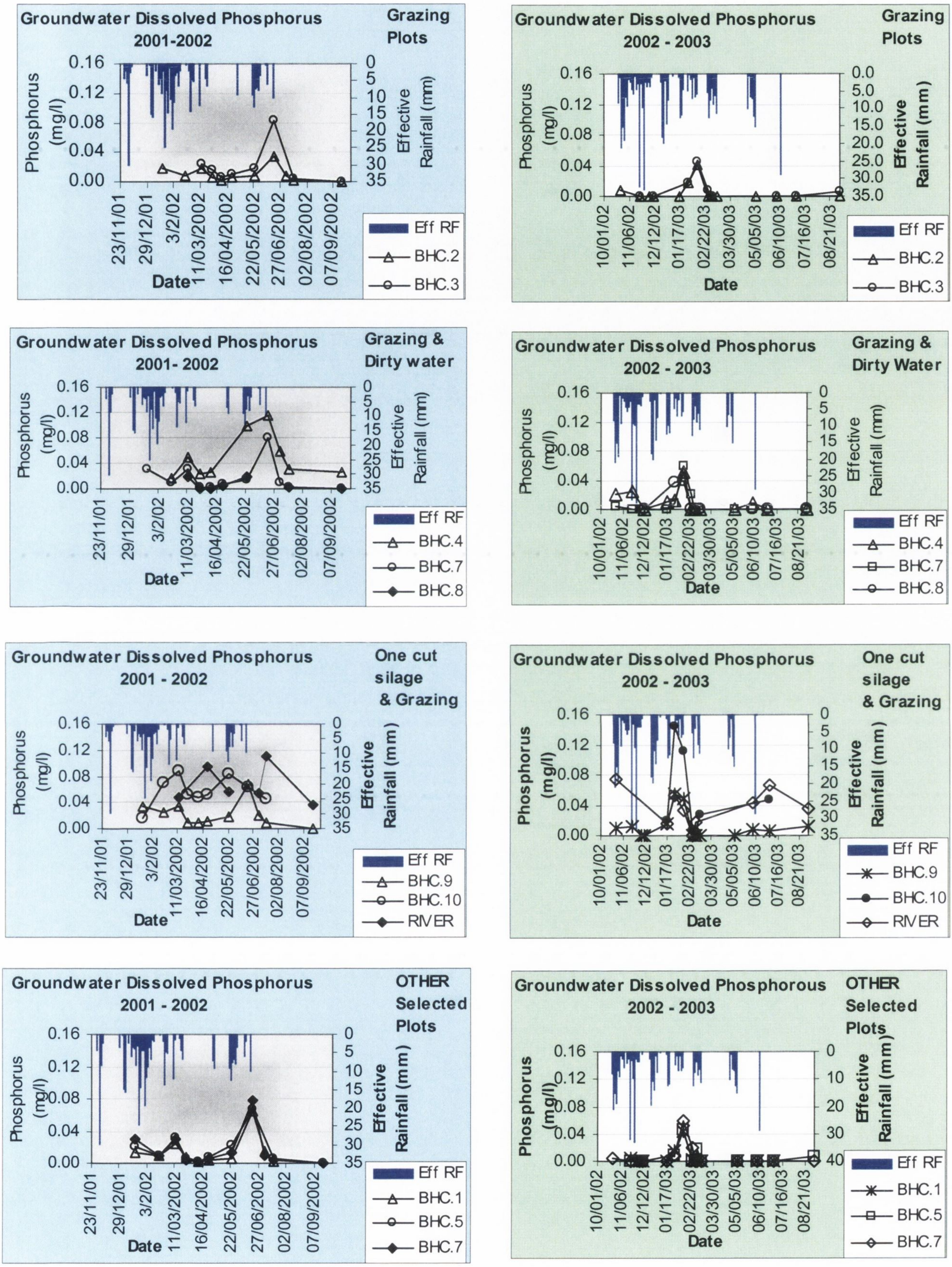


Figure 6.12 Groundwater phosphorus concentrations and effective rainfall at Curtin's farm.

6.4. Observed Groundwater Nitrate Response

Groundwater nitrate concentration is presented according to location (section 6.4.2) and also by agricultural management in the direct vicinity of each piezometer (section 6.4.3). Generally, there was a decline in groundwater nitrate concentration in the second monitoring year; this is discussed in section 6.4.4. A popular question is: how can it be ascertained that nitrate observed in the groundwater was delivered by recharge from the ground surface above? This question is addressed in section 6.4.5. Individual piezometer response to loadings, both meteorological and agronomic, is then discussed in detail in section 6.4.6. An observed groundwater response to grazing animal loadings is analysed in section 6.4.7.

6.4.1. Overview: Nitrate Response

While, as a first attempt at characterising the response of the system, it may have been suitable to show how groundwater levels responded to recharge by averaging the observed water level response in nine-piezometers for each monitoring day, this may not be so appropriate a method for characterising overall changes groundwater nitrate concentrations. However, purely for illustrative purposes, Figure 6.13 shows the average response of groundwater nitrate concentrations with respect to averaged groundwater level data.

Generally, it is observed that there is a clear groundwater nitrate response to meteorological loading. When peaks in groundwater nitrate concentrations correspond to the peaks in groundwater levels the temporal behaviour of water flow is said to explain the fluctuations in nitrate concentrations (de Vos, 2000).

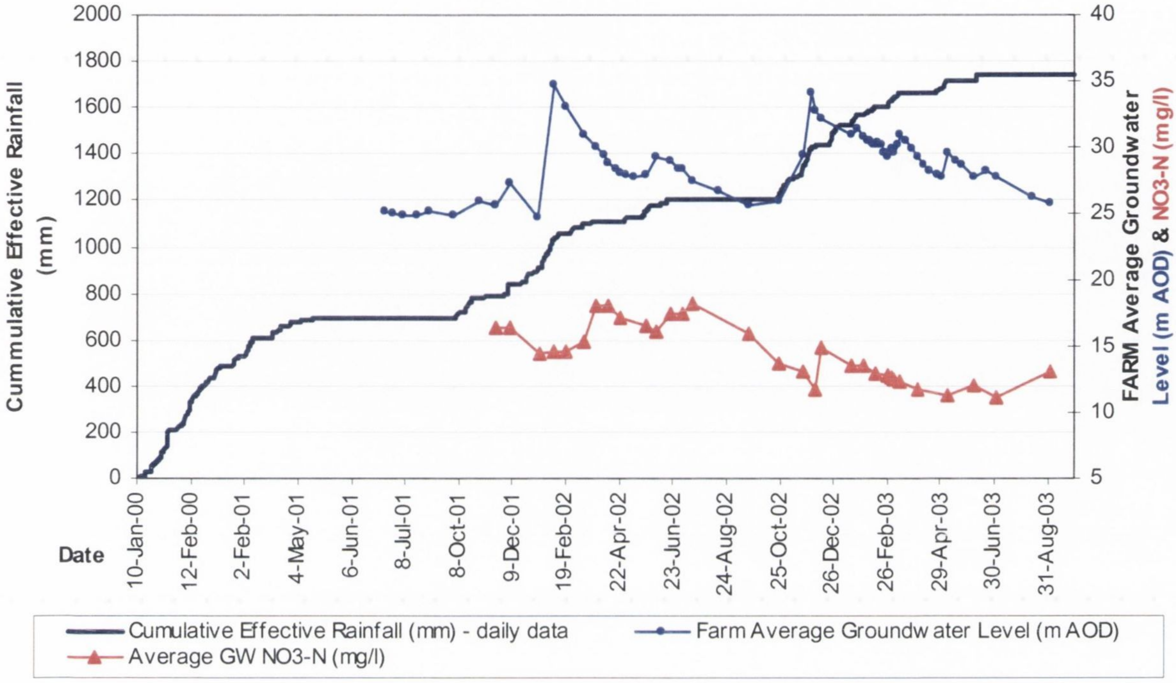


Figure 6.13 Average response of groundwater levels and groundwater nitrate concentrations to effective rainfall.

Figure 6.13 shows that the first flush of recharge initially dilutes the groundwater nitrate concentration a little, but a within a short while of peak groundwater levels being reached a nitrate peak manifests. This subsequent nitrate peak is always greater than the original nitrate concentration prior to the recharge that caused the short-duration dilution. A dilution effect, or inverse relationship, observed as stage increases is supported by previous research (e.g. Adamski & Steele, 1988; Davis *et al.*, 1995; Steele *et al.*, 1986). The initial decrease in concentration is a result of less source material being available in proportion to the amount of water that enters the system (Peterson, et al., 2002).

The summer rains of May 2002, when 54mm RF_{eff} in one week caused in a 1.5m rise in groundwater levels, correspond to a small decline in overall nitrate concentrations but within six weeks groundwater nitrate concentrations were again 18mg/l NO_3-N, on average. However, all piezometers targeted different spatial areas that received differing loads of nitrogen. Results for 30 sampling events spanning 22 months are presented in Appendix R. There was a marked difference in groundwater nitrate concentration depending on piezometer location.

6.4.2. Nitrate Concentration with respect to Location

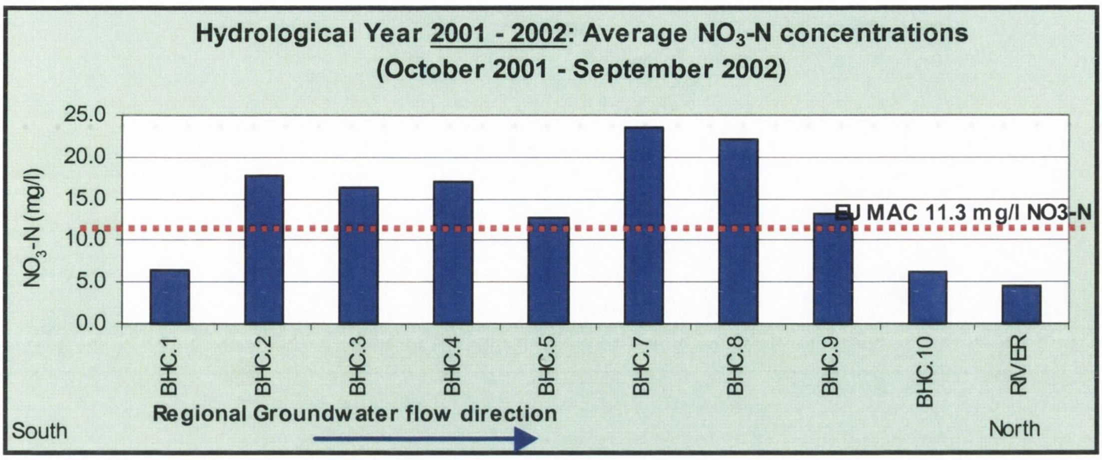
For the 2001-2002 hydrological year average concentrations in groundwater ranged from 7-25 mg/l nitrate, depending on the location of the borehole within the 50ha farm. In the second hydrological year the observed range was lower than in 2001 (at 8-16 mg/l NO_3-N) but again concentration differences were discernable as a function of location.

Groundwater nitrate-nitrogen concentrations were nearly always above the EU MAC (EC, 1998) of 11.3mg/l NO_3-N. Average groundwater nitrate-nitrogen concentration at each piezometer location, for each monitoring year, is shown in Figure 6.14 (the general area's groundwater flow, towards the River Funshion, is shown on these graphs but it was not possible to show local groundwater flow deflections). However, not all piezometers had excessive nitrate concentrations: the nitrate concentration of the inflowing groundwater, the degree of nitrate loading above any particular piezometer and most importantly, the hydrogeological controls on nitrate leaching directly above each monitoring location all influenced observed groundwater nitrate concentrations at different locations. The outlying piezometers, BHC.1 and BHC.10, show the lowest nitrate concentrations in both years monitored (see Figures 6.14 & 6.16).

The location of each piezometer was presented in association with interpolated water table contours in Figure 6.8, section 6.2.2.1. Piezometer notation was designed with consideration of groundwater flow direction onto the farm. Therefore, the first groundwater monitoring location on the farm, with respect to groundwater flow, was denoted by BHC.1 and the last piezometer on the farm is BHC.10. There is no BHC.6 because although it was thought to contain groundwater, pumping demonstrated that it was not connected to the groundwater body (it was perched water only) and so its use in this study was ruled out (Figure 5.2 shows this bore as F5).

Simply averaging all piezometer groundwater nitrate concentrations over the entire farm, the mean groundwater nitrate concentrations were 15.2mg/l NO_3-N in the first year and 11.9mg/l NO_3-N in the second year.

(a)



(b)

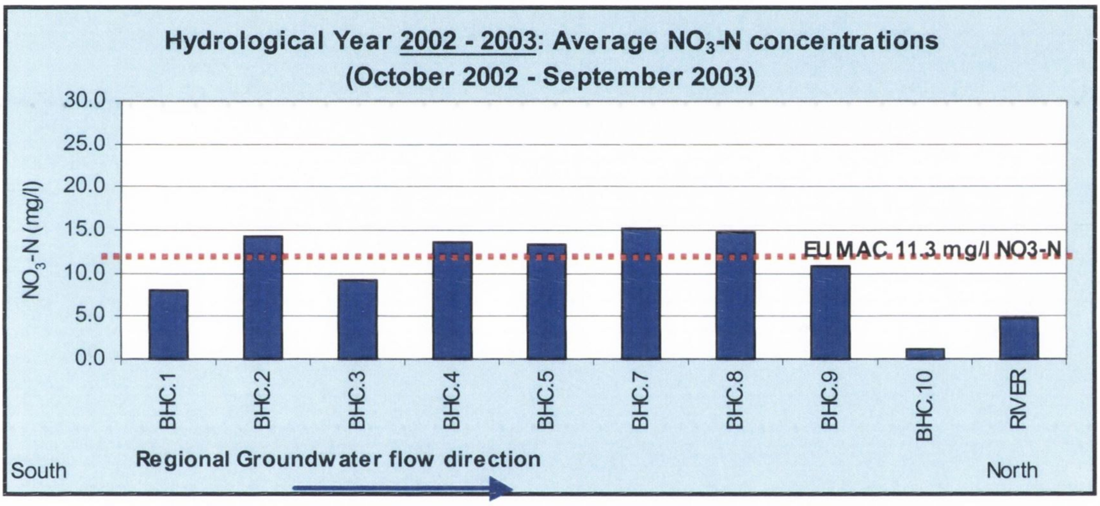


Figure 6.14 Average groundwater Nitrate-N concentrations for (a) the hydrological year 2001-2003 and (b) the hydrological year 2002-2003. (MAC (EC, 1998) is indicated by the horizontal dashed red line in each chart).

A typical example of differences between groundwater nitrate concentrations at different locations on Curtin's farm are shown in map format in Figure 6.15, which also shows associated groundwater elevations and the localised flow directions that could not be shown in Figure 6.14.

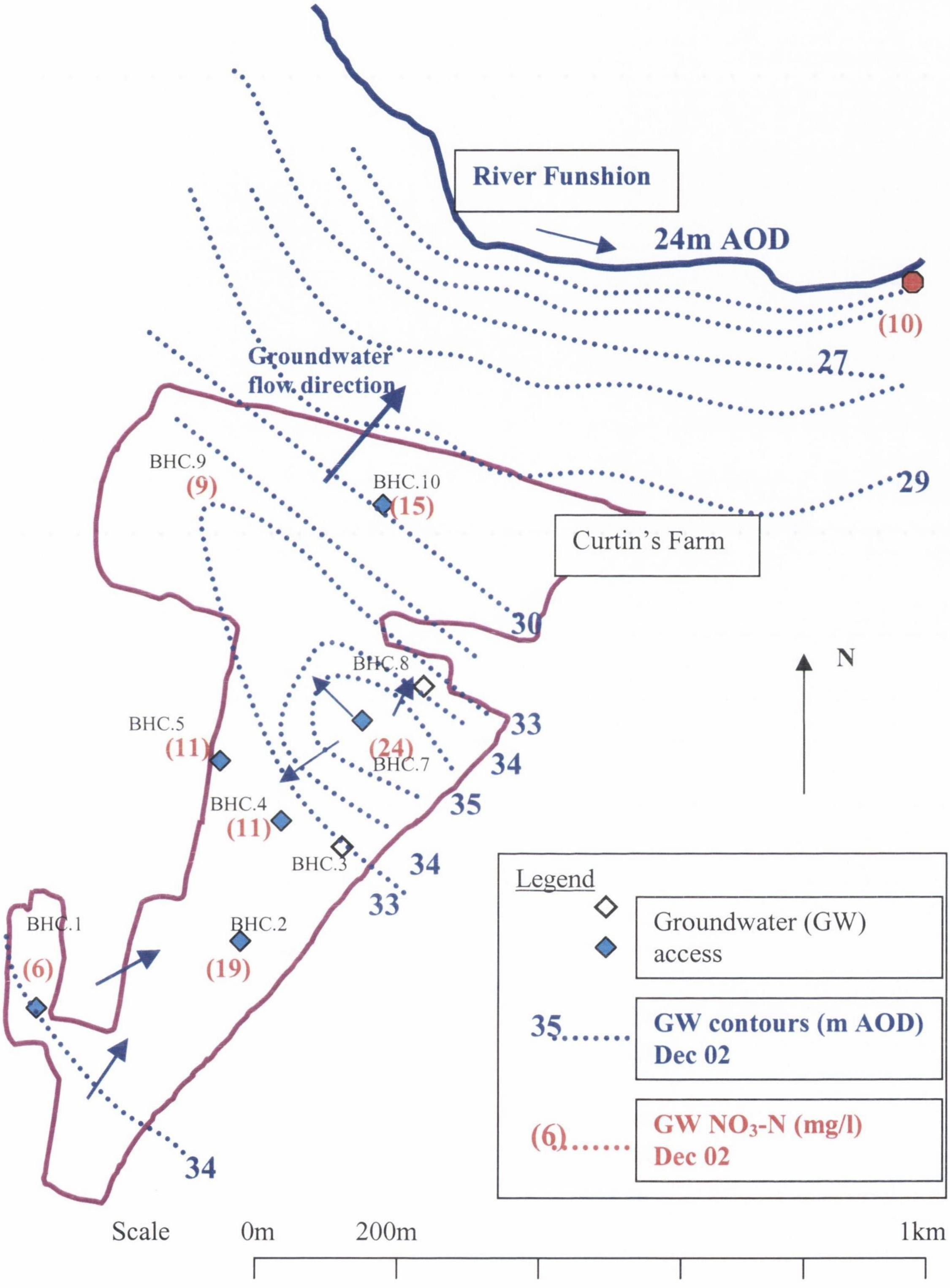


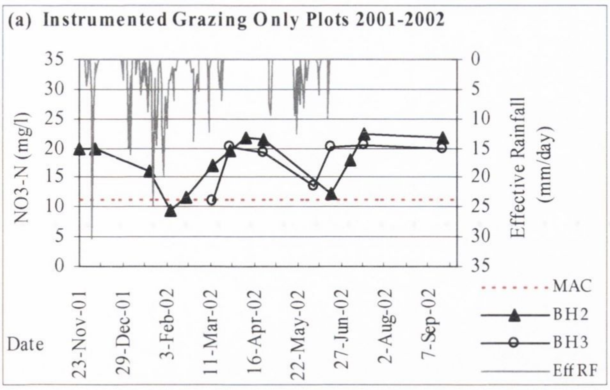
Figure 6.15 Groundwater contours, flow directions and nitrate (mg/l NO_3-N) concentrations at piezometer locations on Curtin's farm, December 2002.

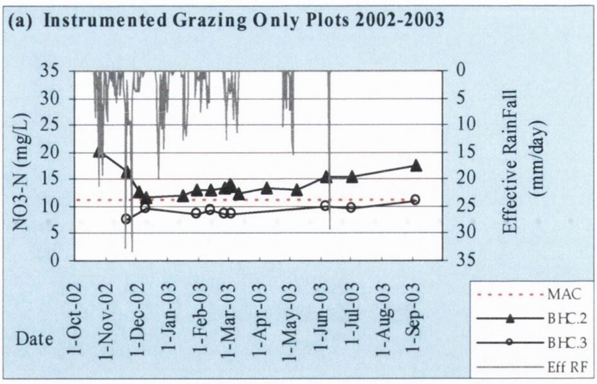
6.4.3. Temporal Nitrate Trend with respect to Agricultural Treatment

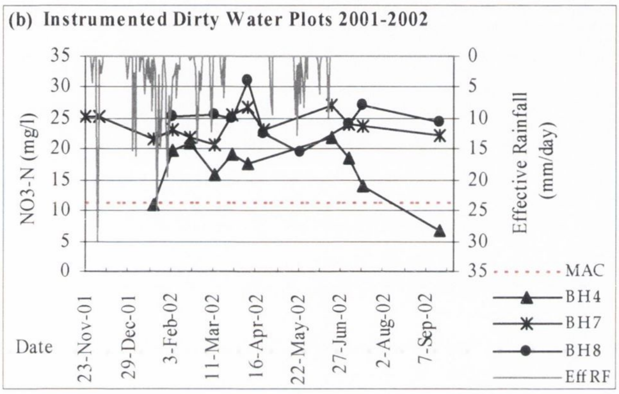
Agricultural treatment refers to one of four management scenarios under investigation; grazing only; one cut silage and grazing; two cut silage and grazing or dirty water irrigation in association with grazing.

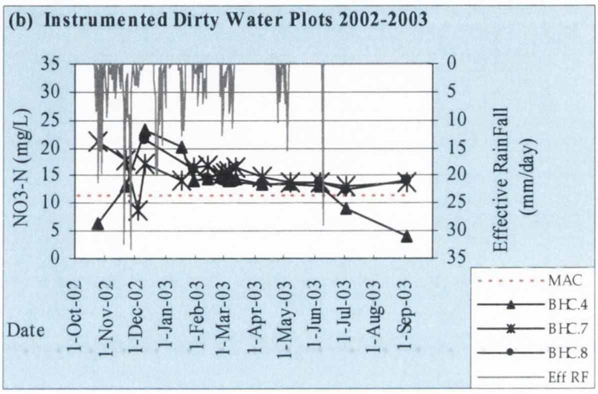
Groundwater nitrate concentrations at any particular piezometer location could vary by between 4 and 19 mg/l NO_3-N throughout the year. The temporal nitrate groundwater trends are shown in Figure 6.16; the data are presented according to agricultural treatment. However, the groundwater at any location may be influenced not only by the agricultural treatment in the vicinity of the bore but may also already be charged with nitrate from an up-gradient source. Interestingly, it can be noted that BHC.5 received no agronomic loadings but when compared with BHC.7 (dirty water plot) shows both similar concentrations and trend response (refer to Figure 6.16 (d)), the two bores are approximately 200m apart (see Figure 6.15).

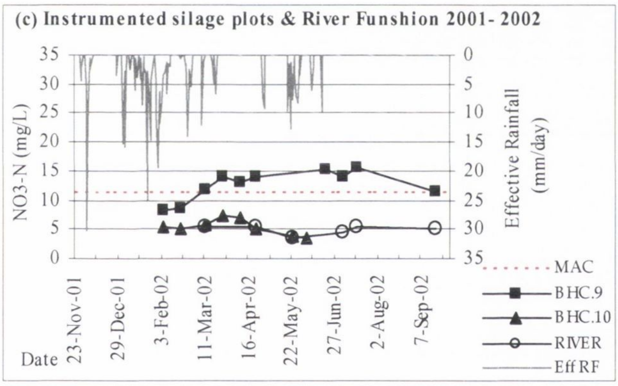
The groundwater nitrate response was discernible in correspondence to differing agricultural practice in different locations on the farm. Groundwater nitrate concentrations were observed to rise in response to significant rainfall events in spring and summer but fell proportionately with autumn and winter recharges. The highest nitrate concentrations were observed beneath the dirty water treatment area. However, all instrumented locations, except BHC.1 and BHC.10, practically always had groundwater nitrate concentrations in excess of the EU MAC (EC, 1998). The response of the groundwater, 20-30m bgl, to loadings was observed to be rapid; effective rainfall events affected a water-table rise almost instantaneously. Groundwater responses are more discernable in the graphs presented for each piezometer in section 6.4.6, whereas Figure 6.16 portrays groundwater nitrate responses together for comparative purposes.

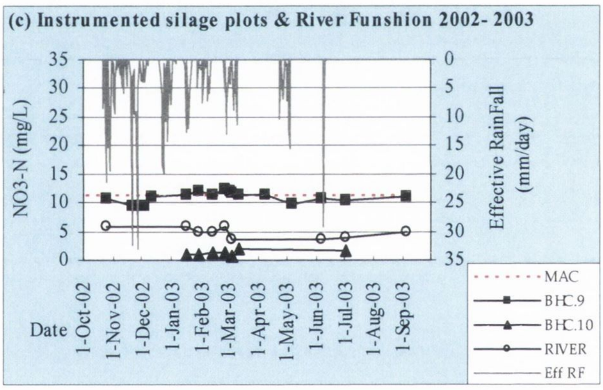


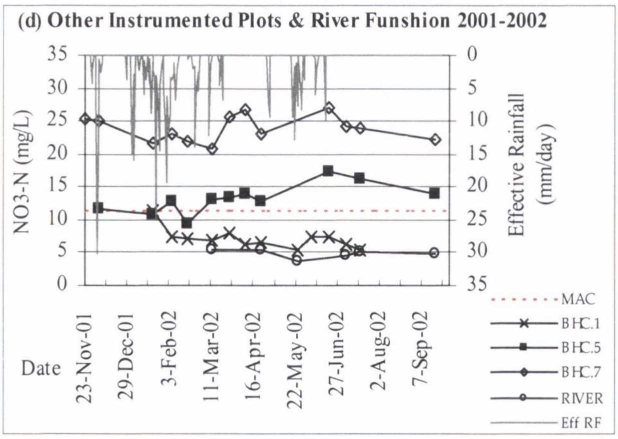












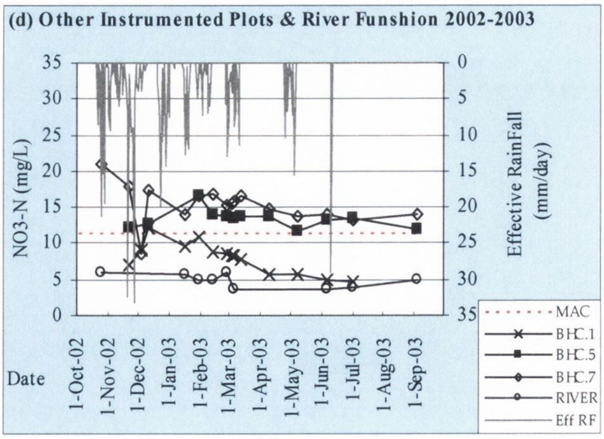


Figure 6.16 Temporal groundwater nitrate (mg/l NO_3-N) trends grouped by agricultural treatment.

6.4.4. An Observed Decline in Nitrate Concentrations in the Second Year

For the first monitoring year (2001-2002) actual nitrate concentrations in groundwater ranged from 3 to 31 mg/l NO_3-N and in the second year (2002-2003) from 4 to 23 NO_3-N, depending on the location of the borehole within the 50ha farm. The obvious decline in groundwater nitrate concentrations in the second monitoring year (Figure 6.16) may be a combined result of farm management practices and meteorological conditions. It is difficult to assign definitive answers with two years of data. However, there was more effective rainfall in the second year and the amounts that fell in the winter recharge period were dramatically different at the beginning of the second year of the investigation (section 5.5.1.7 contains full details). As has been outlined (in section 6.1.3.3) recharge did not begin in earnest until January of the first monitoring year (2001). In that first year, winter effective rainfall totalled 190mm but in the second year the winter total was 300mm. Therefore, in the second year, almost fifty percent more effective rainfall fell in the winter, acting to dilute nitrate as it was flushed from the soil. The timing of the recharge was also important: in the first year, soil nitrate could reside until January 2002, but in the second year, the residence time was much shorter.

The annual variation in groundwater nitrate concentrations at any particular monitoring point could be as little as 3.5 mg/l or as much as 19 mg/l NO_3-N. Examination of the loadings, both meteorological and agronomic, to each piezometer will contribute to understanding spatial and temporal differences in groundwater nitrate response.

6.4.5. Demarcating Seasonal Effect of Recharge on Groundwater Nitrate

Changes in the concentrations of agricultural contaminants, such as nitrate, in monitoring wells provide direct evidence of recharge responses to differences in agricultural practices (Bohlke, 2002). The hydrochemical status of the groundwater in the nine piezometers has been investigated on 30 occasions in the study. One would think that the large number of sampling events would help to shed greater insight on the sources of the nitrate occurrence in the groundwater. Of course, a good picture of the trend of nitrate concentration in the groundwater has been obtained but the temporal trends only indicate the inherent variation throughout the seasons and it is difficult to clearly demarcate the effects of recharge. Identifying whether the nitrate in the groundwater originated in the subsoil requires some form of seasonal analysis.

An interesting approach is to divide each hydrological year into the recharge and non-recharge seasons (already presented in Figure 6.9) and to analyse the relationship between groundwater nitrate concentrations in each recharge condition for each piezometer (Steele *et al.*, 2003). It is suggested that this approach can be used to identify the origin of nitrate in the groundwater system and also the processes that have influenced the observed concentrations, including other ions. Steele *et al.* (2003) infer the following:

- Plotting of nitrate data, for all monitoring piezometers, for the two different recharge conditions would result in a one-point plot if there were neither spatial nor temporal variation in groundwater concentrations.

- A straight-line plot, 1:1 relationship, of groundwater nitrate concentrations for the two different recharge conditions would suggest that the nitrate behaves conservatively and only spatial variability accounts for differing nitrate concentrations at each site. Chloride, described as a conservative ion, would be expected to behave in this manner.

- Temporal variation, indicated as deviation from the 1:1 plot, is attributable to either (i) introduction of nitrate from a nitrogen fertiliser source; (ii) dilution of existing nitrate; or (iii) denitrification of existing nitrate under non-recharge conditions.

- Evidence for addition of surface-derived nitrate is provided by a positive correlation between nitrate and phosphate concentrations during the recharge season. A positive correlation between recharge nitrate and recharge phosphorus demonstrates that the source of these two ions is from fertiliser applied nearby (if the water had migrated far from the source, one would expect more scatter of the points because of retardation of phosphate transport by adsorption and precipitation).

All piezometers on the farm respond at different rates to recharge and so the piezometric water level rises in a relatively shorter time after a significant effective rainfall event in some piezometers rather than others. This is as expected because of the differences in subsoils' depth of cover and hydraulic conductivity at each piezometer site. Therefore, in order to definitively select sampling incidences for the recharge condition, nitrate concentration and water level response graphs for each piezometer were examined individually. A rise in piezometric water levels was considered to indicate recharge and so the subsequent nitrate concentration was taken as the value to be used for the 'recharge condition' value. Sampling events in August 2002 and September 2003 were used as the nitrate concentration for the 'non-recharge condition'. The raw data (sampling dates and associated nitrate concentrations) used for analysis in the manner discussed above, as presented in Steele *et al.* (2003), are contained in Appendix R.

6.4.5.1. Recharge and Non Recharge Groundwater Nitrate Concentrations

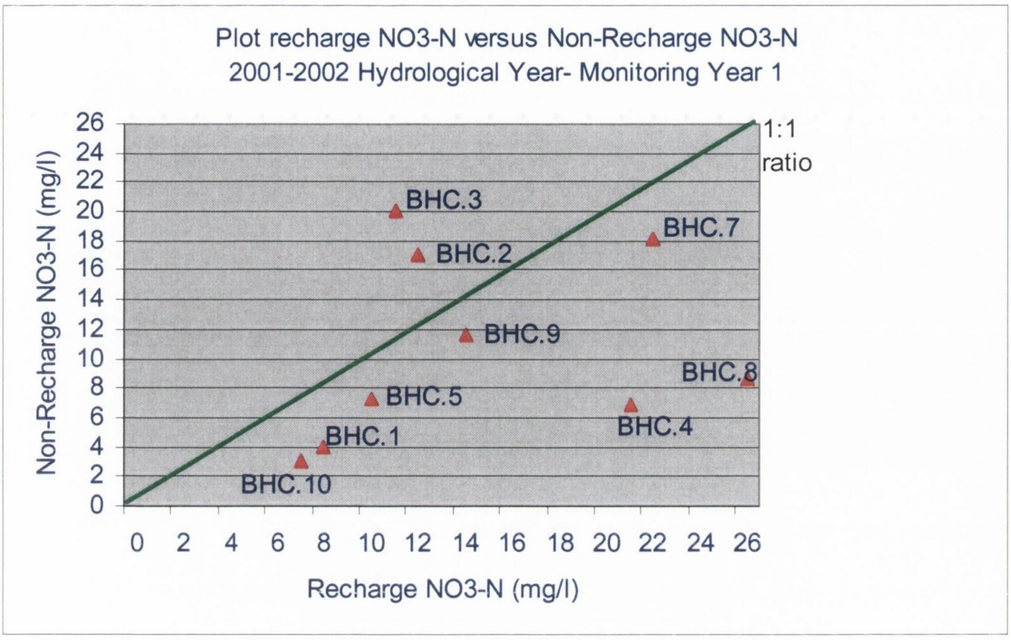
Figure 6.17 (a & b) demonstrates the temporal variation in groundwater nitrate concentration for both monitoring years. Data points, representing monitoring piezometers, that are located below the 1:1 line indicate addition of nitrate under recharge conditions and/or denitrification under non-recharge conditions (Steele *et al.*, 2003). Data points above the line indicate dilution of groundwater nitrate under recharge conditions.

Higher nitrate concentrations in summer rather than winter may indicate point sources of contamination such as septic tanks. Potential point sources of contamination on Curtin's farm were discussed in chapter five, section 5.5.2.2.1, and the relative location of the farm yard was shown in Figure 5.14. Of all project piezometers BHC.3, BHC.4 and BHC.2 are closest to the farmyard area relative to other piezometers. The possible impact of potential point sources on groundwater quality at BHC.3, BHC.4 and BHC.2 will be examined when each individual piezometer is discussed in section 6.4.6.

Peterson *et al.* (2002) offer another explanation for higher groundwater nitrate concentrations during baseflow (summer) in karst systems. They suggest that there can be a dilution effect on concentrations of nitrate during precipitation events, which can be attributed to rainfall entering a karst system via sinkholes, or moving through macropores in the soil. In either case, this hydrological short-circuiting contributes recharge whose concentrations of nitrate are surface derived only.

In the first monitoring year (Figure 6.17a) all piezometers, except BHC.2 and BHC.3, have considerably higher groundwater nitrate concentrations under recharge conditions. This contributes to the evidence that recharge carries a nitrate load to the groundwater. Further, deviation from the line indicates a large annual range in groundwater nitrate concentrations, which suggests either higher loading or higher vulnerability to contamination. In the second year (Figure 6.17b) the same recharge and non-recharge groundwater nitrate concentration responses are repeated. BHC.2 and BHC.3 again plot above the 1:1 line but the latter is so close to the line as to indicate a continuous source of nitrate at this location (see section 6.4.6.3 for further discussion).

(a)



(b)

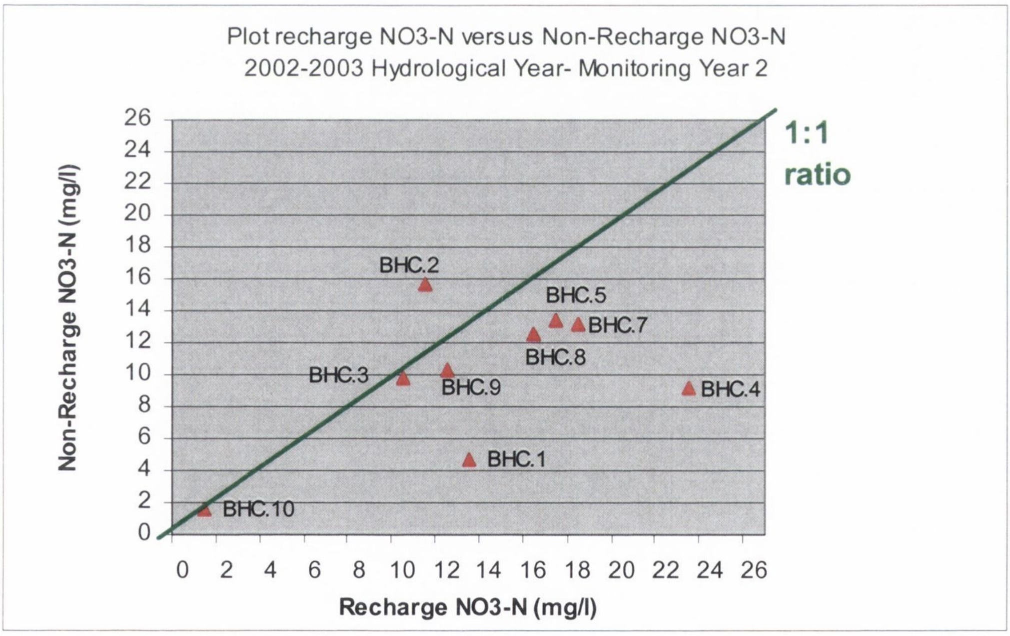


Figure 6.17 Plots of recharge versus non-recharge groundwater nitrate (mg/l NO_3-N) concentrations for (a) 2001-2002 and (b) 2002-2003.

6.4.6. Analysis of Nitrate Response at each Monitoring Location

6.4.6.1. Introduction

Whereas previous discussions considered average water level response in all piezometers on the farm in order to obtain a general picture of groundwater response to recharge, differentiation of the impact of differing forms of nitrogen loading on groundwater nitrate concentrations in each piezometer necessitates individual analysis of each monitoring location. This section considers individual piezometer response in an attempt to determine if the responses can be differentiated by transport mechanisms and/or agronomic loadings in operation in the subsoil above piezometers. In the discussion of individual piezometer response, reference will be made to all relevant results of field investigations, such as hydraulic conductivity of the soil, borehole stratigraphy, magnitude of groundwater level response, groundwater hydraulic conductivity and groundwater hydrochemistry at each location. In order to provide discussion that is uninterrupted by constant reference to source data, the reader is referred to the following sections for the following data:

- Piezometer locations – see Figure 6.15;
- Hydraulic conductivity of the soil - section 6.1.1.3;
- Phosphorus and potassium soil test results – chapter four, section 4.2.3.1;
- Borehole stratigraphy - section 6.1.2.2 & piezometer configuration Appendix B;
- Groundwater hydraulic conductivity - section 6.2.1;
- Groundwater level response - section 6.2.2 & Appendix M;
- Groundwater hydrochemistry- section 6.3 & Appendix S;
- Recharge versus non recharge groundwater nitrate concentrations- section 6.4.5.1;
- Typical groundwater contour map- section 6.2.2.1 & Figure 6.8;
- Groundwater quality of north Cork - section 4.2.9 and Appendix C & D;
- Agronomic nitrogen loadings data – section 5.5.2 and Appendix Q.

6.4.6.2. BHC.1 - Two Cut Silage Area and Grazing

This piezometer is located at a ground elevation of 55.8m AOD, in an area with 2m-depth of soil cover. Hydraulic conductivity (K_{sat}) in the upper layers of soil, calculated to be 0.013 and 0.009 m/day at 0.5 and 1m depths respectively, is lowest here relative to the five plots tested at the farm scale. A sandy layer was discovered from 1.5-2m bgl and a relatively high K_{sat} value (0.32 m/day) reflects this. Epikarst was encountered at 2m and solid rock at 3m. The bedrock is weathered from 7-10m and 19-20m bgl, otherwise it was found to be very hard, solid Waulsortian Limestone until water strike at 32m bgl. A piezometer was installed at BHC.1 with a 4m long screened interval targeting from 28-32m bgl. Three other attempts at gaining access to the groundwater in this area of the farm failed, unfortunately, due to unstable bedrock conditions.

The typical water table map shows that this piezometer generally reflects the quality of groundwater flowing into the farm. Analysis of available groundwater quality data in the general region confirms that the range of nitrate observed in BHC.1 is similar to the ranges observed at 15 other monitoring locations in north Cork.

This piezometer, BHC.1, consistently returned groundwater samples with lower nitrate concentrations than those collected at other locations on the farm. There was only one recorded breach of the nitrate MAC (EC, 1998) out of a total of 26 collected samples; this occurred in December 2002 when concentration rose, by 5mg/l to 12mg/l NO_3-N, in response to initial recharge flushing summer accumulations of nitrogen from the soil. Summer concentrations in BHC.1 were 5 mg/l NO_3-N, approximately, in each monitoring year, similar to observed nitrate concentrations in the River Funshion, adjacent to the Downing's Bridge public supply borehole 1.5km to the northeast.

Groundwater levels ranged from summer time lows of 29m bgl to wintertime highs of 19.5m bgl denoting an annual 10m range in water levels. Groundwater at Curtin's farm flows through fissures and so although the screened interval ranges from 28-32m bgl it is most probable that the same groundwater is sampled in each season despite the wide variation in water level. The maximum monthly rise in groundwater level, at this site, was observed to be 8m as a result of 200mm effective rainfall in the first month of winter recharge in October-November 2002.

Figure 6.18 shows that the groundwater nitrate concentration is positively correlated to the piezometer water level – a rise in water levels results in a rise in groundwater nitrate concentrations and summer time water level recession is reflected by decrease in groundwater nitrate concentrations.

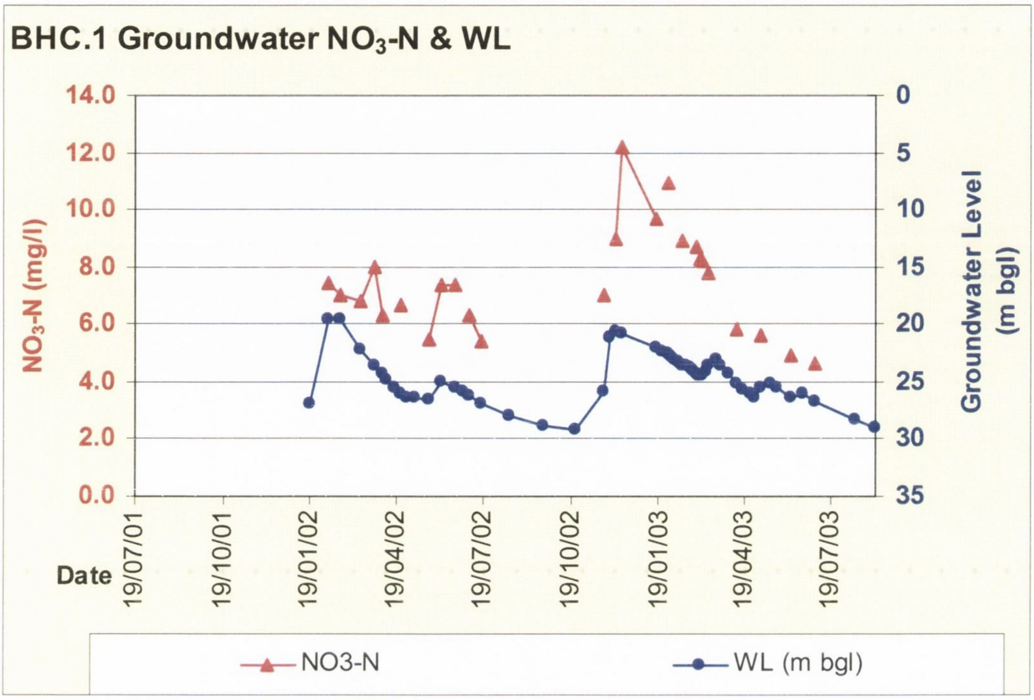


Figure 6.18 Groundwater level and nitrate concentration (mg/l NO_3-N) trend at BHC.1 in the two cut silage area.

A plot of recharge versus non-recharge groundwater nitrate concentrations highlights that nitrate is transported with recharge to the groundwater at this location (section 6.4.5.1). Groundwater nitrate concentrations during the recharge season could be as much as twice those observed at the end of the summer. Maximum winter concentrations were 8 mg/l NO_3-N in the first year, 2001-2002, and 12 mg/l NO_3-N in the second year, 2002-2003. In the first year, because the piezometer was installed in January, the first flush peak was probably missed. This would explain the increased observed maximum in the second year. Observation of the nitrate concentration trends from January in both years shows similar trends (Figure 6.18).

With respect to the response of groundwater nitrate concentrations to loadings at ground level above piezometer BHC.1, Figure 6.19 shows both hydrological (effective rainfall) and agronomic nitrogen loadings (fertiliser, slurry and grazing animal depositions) in association with the trend of both groundwater table response and nitrate response. It should be noted that although agronomic additions are the source of the mobile nitrogen leaching to the groundwater, it is the timing of effective rainfall that directly elicits a groundwater nitrate concentration response. Consider the applications of inorganic fertiliser nitrogen and organic nitrogen deposited by grazing animals in the summer of 2002. The 12mg/l NO_3-N peak observed in December 2002 is in response to 200mm effective rainfall in the previous month. The nitrate that was transported to the groundwater, by that recharge, was most likely not direct leaching of inorganic fertiliser nitrogen, which was last applied to this plot on the 28th August. All fertiliser applied elicits a grass growth response, which is proved by the grazing animal activity. Animals grazed this plot in early October and again in early November. It seems reasonable to conclude that, with the onset of recharge, the nitrate available for leaching was that which accumulated in the soil as a result of animal grazing.

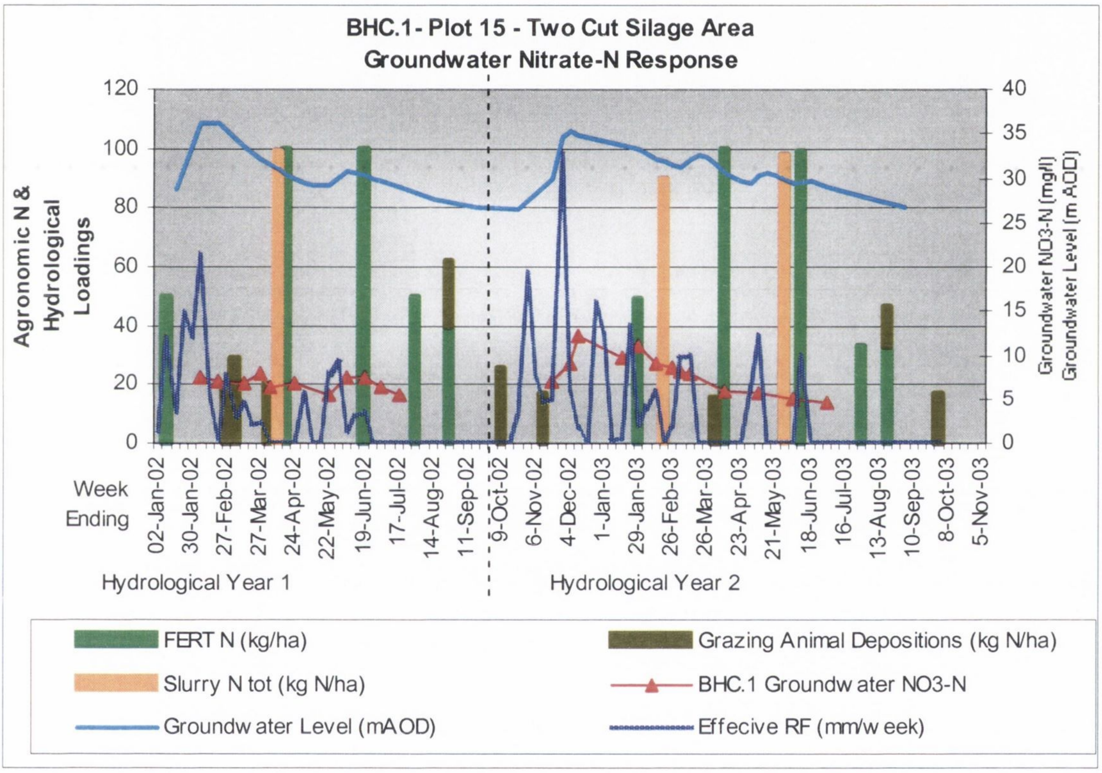


Figure 6.19 Groundwater response to both meteorological and agronomic loadings at BHC.1.

The time between the start of recharge and observed peak in groundwater nitrate level is nine weeks in the first hydrological year and six weeks in the second, resulting from monthly effective rainfall of 200mm in each instance. Obviously, the intensity of recharge is a significant factor in the time lag but nonetheless response time for peak groundwater nitrate concentration 20m bgl is dependent on 200mm effective recharge. The time lag between the 200mm effective rainfall and observed peak was less than, or approximately, 2 months in 2002. This concurs with the results of the bromide tracing experiment (section 6.5), which showed peak concentration 44 days (6 weeks) after application of bromide at ground level.

All groundwater samples were also analysed for other nutrients, namely ammonium-nitrogen, nitrite-nitrogen and phosphorus concentrations and Appendix R contains these data. Although the nutrient graphs in Appendix R show two ammonium-nitrogen peaks, only on one occasion (April 2003) is the Drinking Water Regulations (DELG, 2000) limit of 0.23 mg/l NH_4-N breached when a concentration of 0.24 mg/l NH_4-N was observed. Prior to this, an elevated potassium concentration, 8mg/l K, was observed in March 2003. These deviations from otherwise good groundwater water quality occurred after the slurry-spreading season began in the area. However, groundwater quality quickly recovered, again indicating that the groundwater system has a rapid transfer time. Groundwater travel velocity calculations suggest a turnover rate of 4-6 per year (see section 6.5.3.2).

6.4.6.3. BHC.2 - Grazing Area, south of farm yard.

This piezometer is located at an elevation of 53.8m AOD, in an area with 3m depth of soil cover. The GSI source protection zone delineated for the Downing's Bridge public supply borehole and the reference water table elevation map (Figure 6.8), constructed from water-table observations in the course of this study, suggest that groundwater flows from BHC.1, in a north-easterly direction, to BHC.2, eventually discharging to the River Funshion, which is north of the farm. As previously shown, there are some local groundwater flow deflections on the farm but the ultimate direction is towards the River Funshion. Generally, groundwater nitrate concentrations were higher at BHC.2 than BHC.1, on average by 12mg/l NO_3-N in the first year and 8 mg/l NO_3-N in the second year.

Hydraulic conductivity (K_{sat}) in the upper layers of soil, were calculated to be 0.034 and 0.085 m/day at 0.5 and 1m depths respectively, which were similar to the values returned from the same tests in another part of the farm (NUIG experimental plots, north of the farm yard). Sandy soils are known to be prone to a high level of compaction in the upper layers (Diamond, *pers. comm.*, 2003) and the hydraulic conductivity results for the 0.5 and 1m depths suggest this. A layer of relatively lower K_{sat} was encountered at 1.5m bgl (0.013m/day) but at 2m-bgl K_{sat} results similar to those in the topsoil were returned. Epikarst was encountered at 3m and solid rock at 4m. The bedrock was found to be very hard solid Waulsortian Limestone throughout the subsurface with no weathered zones encountered until approaching the water-strike zone at a depth greater than 20m bgl. The anomalies encountered were in the form of two cavities: one dry, 2m deep filled cavity was encountered from 23-25m bgl, followed by a softer (perhaps weathered but still intact) Waulsortian limestone for 5m until a very strong water strike encountered at 36m bgl in a 10m deep, filled cavity. The fill in both cavities was subjected to particle size analysis, which revealed very similar particle size distribution as samples taken from the 2m-depth in the subsoil. The sandy brown deposit in the water-bearing region was found to contain 37% sand, 20% gravel and 42% silt/clay mixture (most probably predominantly silt) and therefore can be described as a gravelly silty SAND (BS 1377, 1990).

Hydraulic conductivity in the groundwater at BHC.2 was determined, by slug test, to be 10^1 m/day. Similar hydraulic conductivity values were obtained at only two other piezometers, BHC.5 and BHC.9, and all other piezometers had lower hydraulic conductivities. Another attempt at gaining access to the groundwater in this area of the farm failed to result in water-strike.

This piezometer, BHC.2, consistently returned groundwater samples with concentrations higher than the nitrate MAC (EC, 1998). Average groundwater concentrations at this location were 18mg/l NO_3-N in the first hydrological year and 14 mg/l NO_3-N in the second year of the study. The decrease in nitrate concentration in the second monitoring year is most likely attributable to a 50% increase in effective rainfall in the second winter, which acts to dilute the nitrate load from the subsoil.

Water table elevation (groundwater levels) ranged from summer time lows of 29m bgl to wintertime highs of 19m bgl denoting an annual 10m range in water levels. The maximum monthly rise in groundwater level, at this site, was observed to be 8.7m as a result of 200mm effective rainfall in the first month of winter recharge in October-November 2002.

Increases in groundwater levels result in a reduction in groundwater nitrate concentration at this piezometer, BHC.2 (Figure 6.20). Therefore, it is concluded that recharge has diluting effect. An alternative hydrogeological hypothesis might be that these results suggest a concentration gradient in nitrate with depth below water table. However, the concentration gradient hypothesis does not apply to this karstified environment. Bedrock drilling revealed that groundwater flows in distinct fissures. Therefore, the screened interval of the piezometer monitors a distinct water-bearing fissure and the water level increase in the piezometer reflects the pressure head of water at that point.

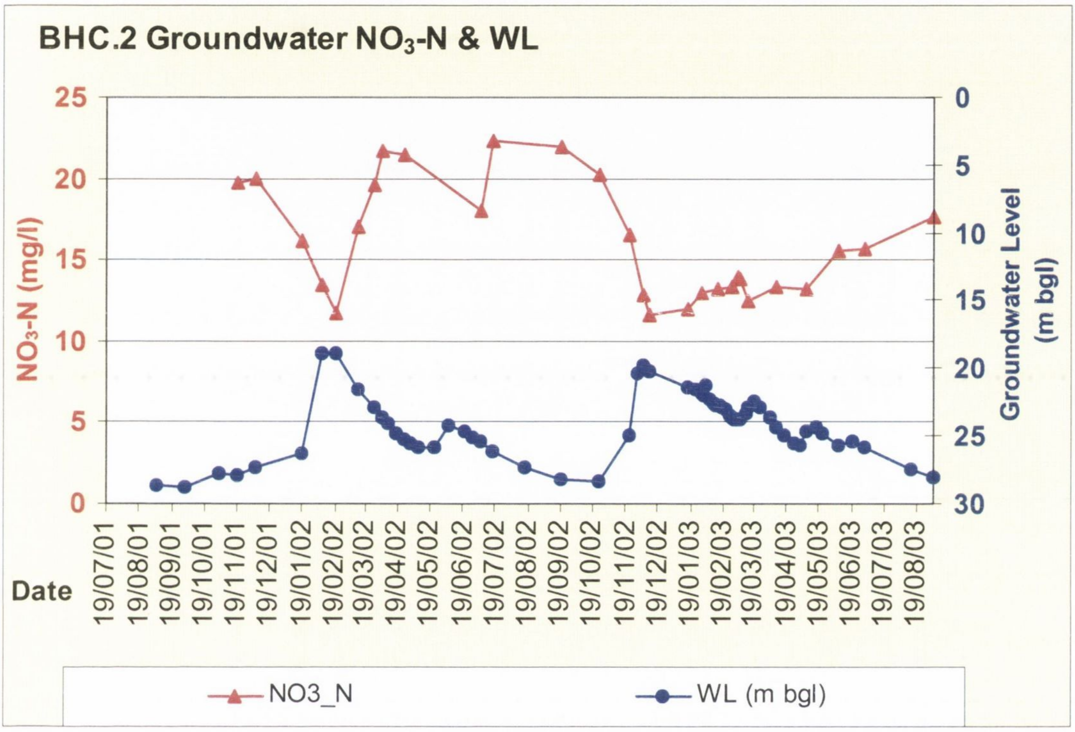


Figure 6.20 Groundwater level and nitrate (mg/l NO_3-N) trend at BHC.2 in the grazing area.

Groundwater up gradient of this piezometer has concentration ranging from 5-12 mg/l NO_3-N (BHC.1), with lowest values observed in the summer months. At this piezometer, BHC.2, plotting recharge versus non-recharge groundwater nitrate concentrations demonstrates that summer time values are higher than those observed during wintertime. This is further evidence that recharge dilutes the existing groundwater nitrate concentration. Silage is grown in the upgradient area around BHC.1 and hence slurry is spread there.

With respect to loadings, this is a grazing plot and so the only surface additions of nitrogen are fertiliser and grazing animals' depositions. No slurry or dirty water is applied to this plot. Agronomic loading records kept for the duration of the study suggest that the area in the vicinity of this borehole received inorganic nitrogen (bagged fertiliser) at a rate of 290 kg N/ha and was grazed for 19 days each year, resulting in nitrogen deposited by grazing animals being approximately equivalent to a rate of 190 kg N/ha/yr. The temporal distribution of all loadings, both agronomic and meteorological, to ground level above BHC.2 is shown in Figure 6.21 along with the response of the groundwater system.

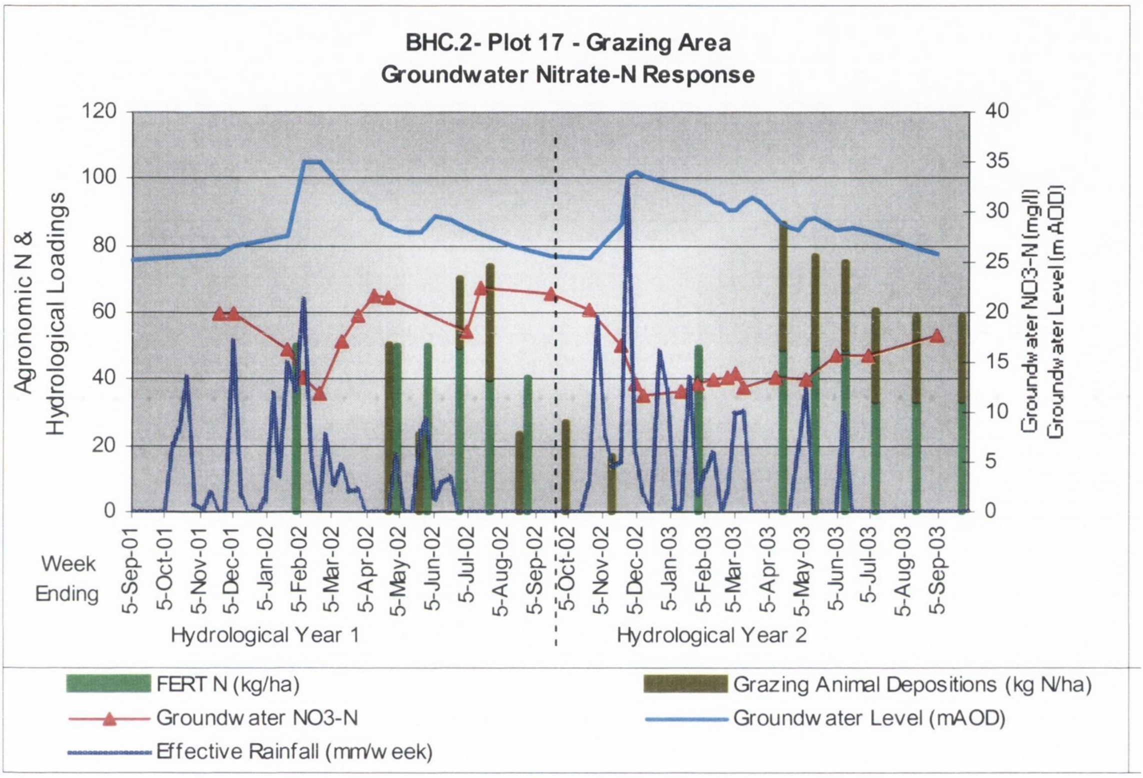


Figure 6.21 Groundwater response to both meteorological and agronomic loadings at BHC.2.

It is clear that effective rainfall has more noticeable impact on temporal variation in groundwater nitrate concentrations than agronomic loadings. Although it is also clear that the diluting effect of recharge additions does not persist and fertiliser and grazing loads do eventually result in increasing groundwater nitrate concentrations. Effective rainfall in October, November and December 2001 caused a gradual increase in groundwater levels, which was associated with a gradual reduction in groundwater nitrate concentrations from 20 mg/l NO_3-N to 11.8 mg/l NO_3-N, which is still higher than the MAC (EC, 1998). However, a 50 kg/ha application of fertiliser (Sulpha CAN) on the 30th January 2002 that was followed by 100mm effective rainfall in February resulted in groundwater nitrate concentrations of 22 mg/l NO_3-N in April 2002. The impact of late winter applications of fertiliser is therefore clearly detrimental to groundwater quality. This peak in nitrate concentration in April is not associated with an increase in groundwater levels because groundwater levels are in recession after the initial surge on the system from the winter recharges. The proposition is that the intense winter recharges surge the system because some of the recharge arrives quickly at the water table, due to by-passing of the soil matrix and so has a relatively low nitrate concentration that acts to dilute groundwater concentrations, hence the decrease in groundwater nitrate concentrations. Subsequent slow percolation through the soil matrix, in spring, results in nitrate enriched recharge to the groundwater body that does not significantly impact water table elevation but does cause increases in groundwater nitrate concentrations. This response pattern analysis is supported by the work of others (e.g. Peterson, et al., 2002), which has been discussed in section 6.4.1. The pattern is again repeated in early summer when, in June 2002, an increase in water levels is followed immediately by a decline in groundwater nitrate concentrations. However, groundwater concentrations peak in July at 22 mg/l NO_3-N, a level that is higher than those observed in April. Concentrations do not decrease significantly throughout the summer of 2002. This suggests that percolation though the subsoil matrix slowly continues to reach the groundwater body and steady state nitrate concentrations persist at approximately 20mg/l NO_3-N.

At the start of the second hydrological year 200mm effective rainfall fell in one month, November 2002, and 50% of this fell in one week at the end of the month. This recharge elicited the same characteristic response in the groundwater: peak in water table elevation accompanied with decline in groundwater nitrate concentration, to 11.6mg/l NO_3-N, but spring fertilisation and grazing additions, in association with recharge, cause a gradual rise in groundwater concentrations to 17mg/l NO_3-N.

Examination of the presence of other nutrients in groundwater at this location, BHC.2, may shed light on the transport mechanisms in operation. Each of the lowest points on the groundwater nitrate concentration curve was accompanied by a peak in ammonium-nitrogen concentrations (see Figure 6.22). Ammonium-nitrogen is a transitory species of nitrogen cycle activity and does not persist in a groundwater environment. Therefore, the presence of ammonium-nitrogen further supports the above propositions of recharge to groundwater by dual mechanism: initial by-pass flow succeeded by matrix flow. The ammonium peak in early spring could be a result of the Sulpha CAN (Calcium Ammonium Nitrogen) fertiliser applied in late January. A clear temporal progression of nitrogen cycle activity can be observed in Figure 6.22, through the spring and summer of 2002. The initial source of the ammonium could be the hydrolysis of urea – the late

April and May 2002 fertiliser applications were in the form Urea. Additionally, the first grazing of the year, in the area around BHC.2, took place just before the 50kg/ha Urea fertiliser application in April. This first grazing was particularly intensive, lasting five full grazing days, resulting in an equivalent loading rate of 50kg N/ha. More than 5000 urinations could have been deposited in the plot in which BHC.2 is located in those five grazing days. The ammonium, nitrite and nitrate trend all suggest that grazing and fertilisation activity in late May and June 2002, followed by effective rainfall events, had a significant impact on groundwater nutrient concentration response.

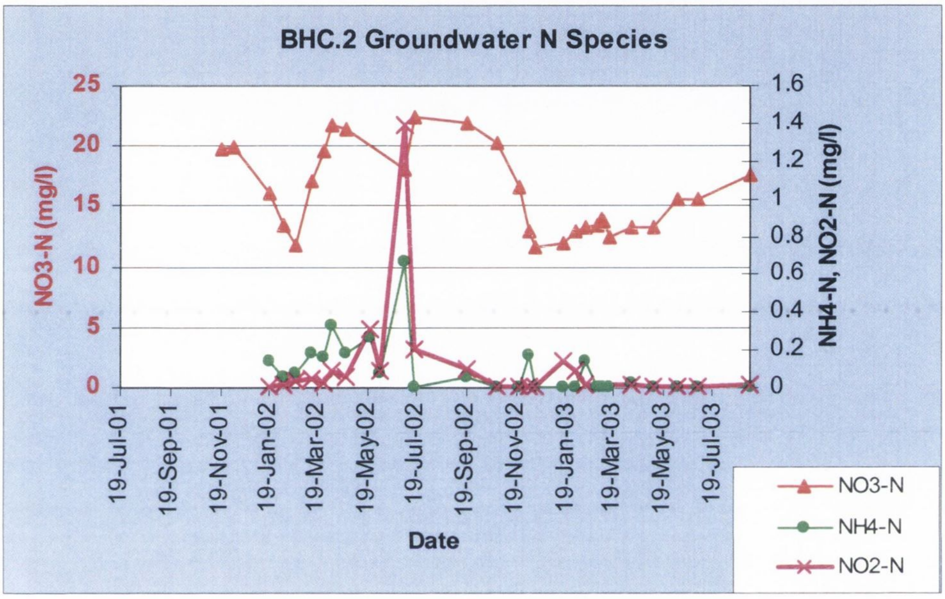


Figure 6.22 Trend of different nitrogen species in groundwater at BHC.2

With respect to the phosphorus status of the groundwater abstracted from BHC.2, increases in groundwater levels resulted in peaks of phosphorus (see Figure 6.23). I propose that the relationship between groundwater phosphorus peaks and water level increases is further evidence of the fact that on some occasions contaminant transport is by preferential or by-pass flow. Phosphorus carried from the soil surface to the groundwater body may have by-passed the soil matrix. Dills & Heathwaite (1996) suggested preferential flow as a mechanism for phosphorus to bypass the soil's natural sorbing capacity (see section 6.7 for further discussion of this issue). The effect of preferential flow on groundwater nitrate concentrations is quite opposite to the phosphorus response because nitrate may not be readily available at the soil surface, it is within the soil matrix that nitrate is created by the nitrogen cycle. Despite fluctuations, there is only one major time period when phosphorus concentrations rise above the 0.03mg/l P indicator concentration, which is in January 2003, when elevated concentrations persist for two consecutive events.

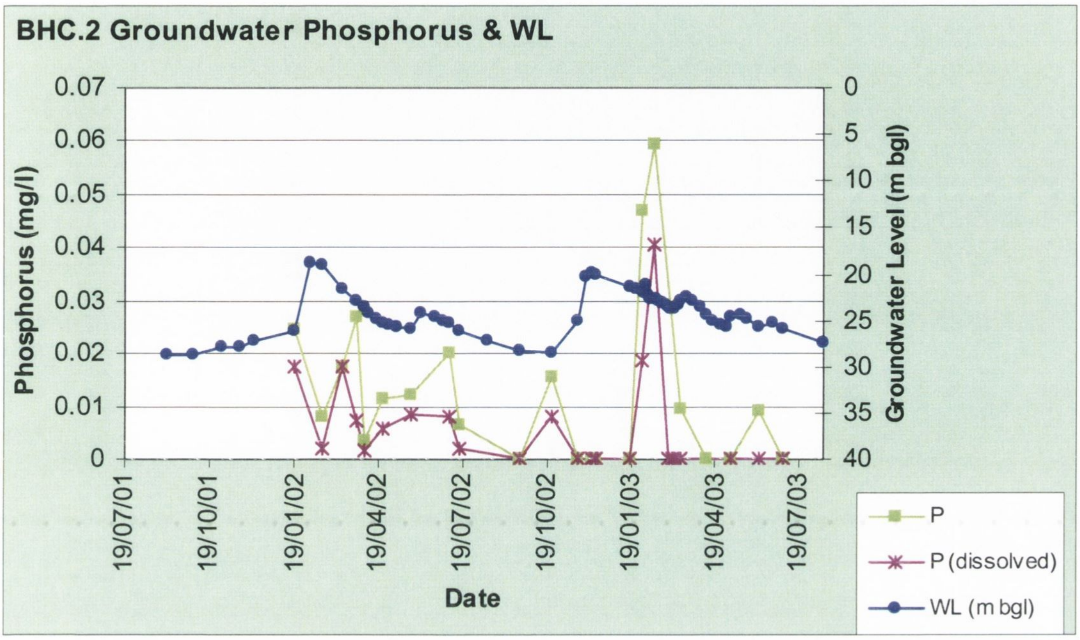


Figure 6.23 Groundwater phosphorus concentrations at BHC.2.

6.4.6.4. BHC.3 - Grazing Area, east of Farm Yard

BHC.3 is situated in a grazing treatment 150m east of the farmyard, at an elevation of 53.2m AOD, in an area with 3m depth of soil cover. The bore was drilled by a mineral exploration company using coring techniques that resulted in a 50mm diameter bore to 59.5m depth bgl. Piezometer installation was neither possible nor required: the core drilling technique results in a stable open bore. The groundwater is protected from contamination from subsoil by a grouted sleeve. Despite the difference in borehole completion, the two-groundwater access points located in the grazing only treatment (BHC.2 & BHC.3) demonstrate similar water levels trend and groundwater nitrate concentration. In the first year of the study 90% of groundwater samples from BHC.3 exceeded the MAC (EC, 1998) but in the second year there were no MAC violations. Four other piezometers are situated in the same farm area as BHC.3, which is north of the farmyard. Figure 6.24 shows that rising groundwater levels affect groundwater nitrate concentrations but summer concentrations are generally higher than winter values.

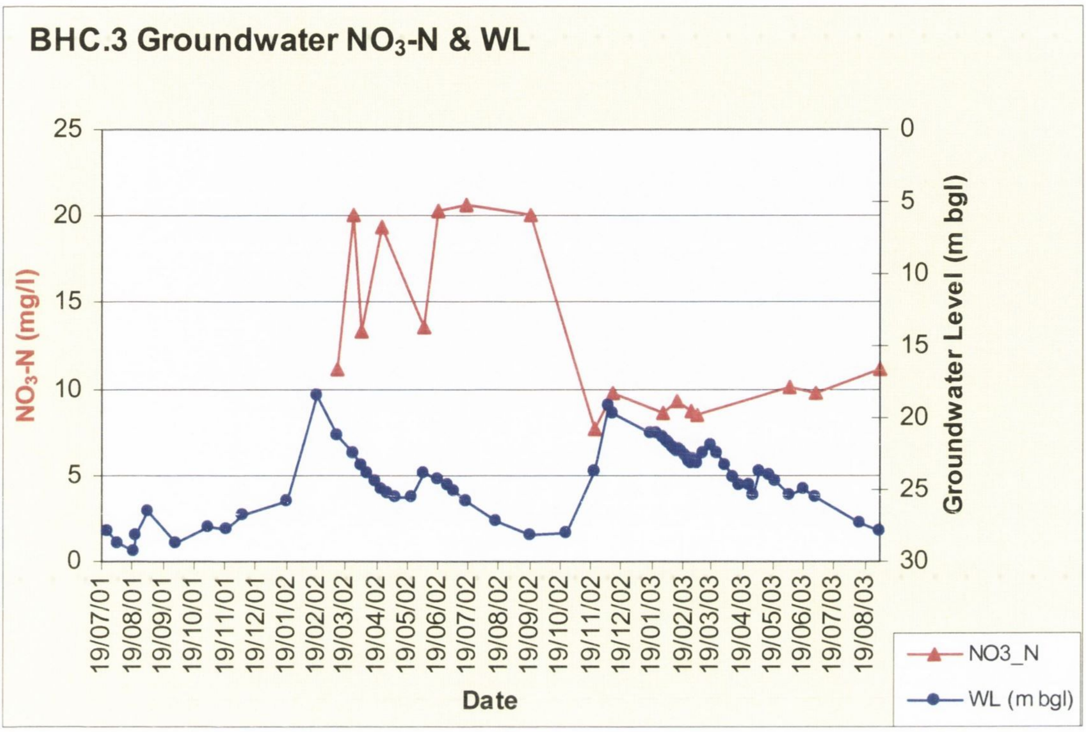


Figure 6.24 Groundwater level and nitrate concentration (mg/l NO_3-N) trend at BHC.3.

Average groundwater concentrations at this location were 16mg/l NO_3-N in the first hydrological year and 9mg/l NO_3-N in the second year of the study. The decrease in average nitrate concentration in the second monitoring year is most likely attributable to a 50% increase in effective rainfall in the second winter, which acts to dilute the nitrate load from the subsoil. Peak nitrate concentrations at this location were 20.6 mg/l NO_3-N and 11.1 mg/l NO_3-N in the first and second years, respectively.

Water table elevation (groundwater levels) ranged from summer time lows of 29.5m bgl to wintertime highs of 18.5m bgl indicating an annual 11m range in water levels. The maximum monthly rise in groundwater level, at this site, was observed to be 8.2m as a result of 200mm effective rainfall in the first month of winter recharge in October-November 2002.

In the first year of the study, groundwater nitrate concentrations were observed to fluctuate greatly in response to recharge at this piezometer, BHC.3. In the second year, the response of the groundwater levels to recharge was similar to the pattern of the first year but nitrate concentration response was very muted. While an 11.8mg/l NO_3-N range variation was observed in the first year, the groundwater at this very same location exhibited a drastically lower range of 3.5mg/l NO_3-N in the second year. Plots of recharge versus non-recharge groundwater nitrate concentrations suggested that recharge somewhat dilutes groundwater nitrate at BHC.3 (see Figure 6.17). The only nitrogen additions in the immediate vicinity of BHC.3 are fertiliser and grazing animal depositions although the dirty water area is adjacent.

With respect to agronomic loadings, the plot overlying BHC.3 received inorganic fertiliser N at rates of approximately 300, 250 and 340 kg N/ha in the years 2001, 2002, and 2003 respectively. The plot was grazed for a total of 17-18 grazing days each year, resulting in an approximate organic N loading rate equivalent to 180 kg N/ha, if the load is distributed evenly on the area grazed. It is acknowledged in the loading section of this work that this is a conservative method of estimating the impact of grazing animal depositions but some attempt must be made to compare fertilisation rates with grazing animal depositions. The effect of temporal loadings to the plot overlying BHC.3, in terms of N and effective rainfall, in addition to groundwater nitrate and water table response can be examined in Figure 6.25.

With reference to Figure 6.25, it is difficult to discern whether it is the inorganic nitrogen (fertiliser) or organic nitrogen (grazing animal depositions) that might be leaching. However, it is only really necessary to consider either one due to the fact that the nitrogen deposited by the grazing animal is a recycling of the nitrogen in herbage that was originally contained in the applied fertiliser (see section 5.5.2.6). In any case, the groundwater nitrate trend demonstrates a more discernable response to effective rainfall (hydraulic loading) than to nitrogen applications at the surface.

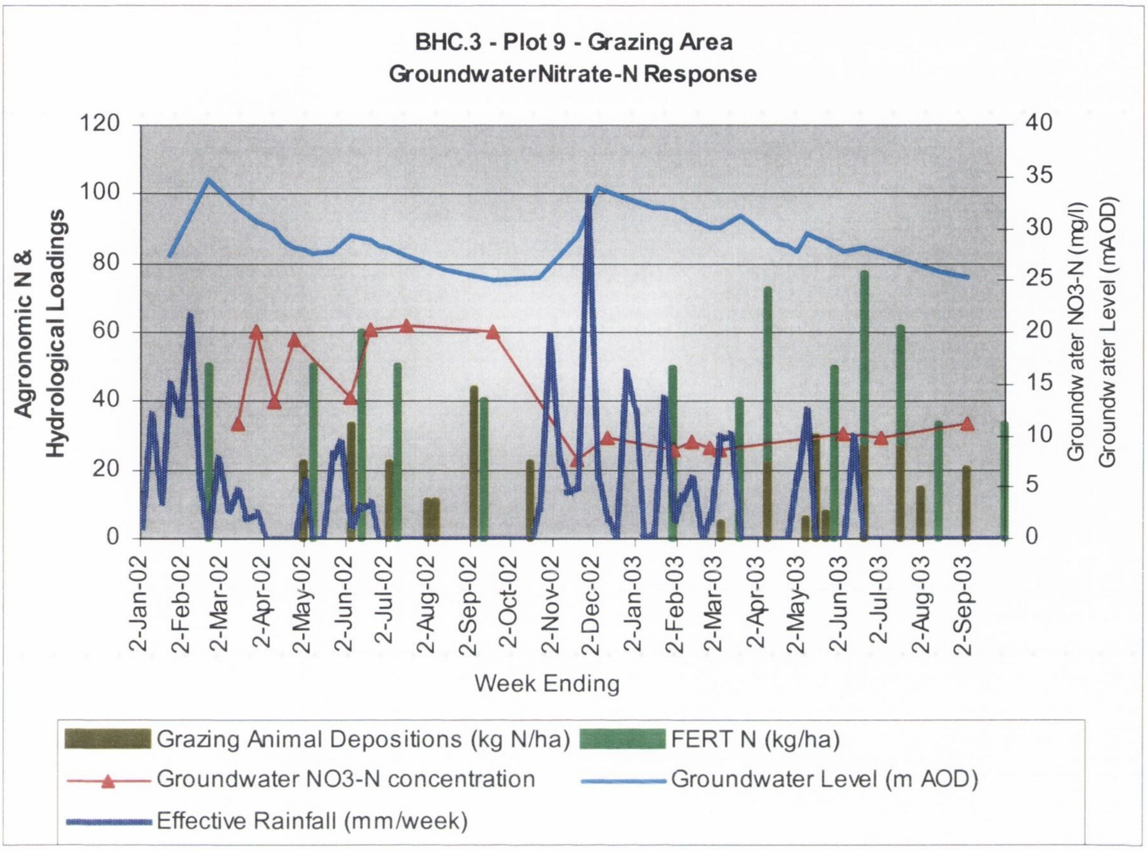


Figure 6.25 Groundwater response to meteorological and agronomic nitrogen loadings at monitoring location BHC.3.

Consideration of analytical results for other hydrochemical parameters reveals that while other forms of nitrogen, namely ammonium-nitrogen and nitrite-nitrogen concentrations are mostly negligible in the groundwater removed from BHC.3, there are surprisingly high concentrations of potassium at this location. Generally the groundwater beneath the farm conforms to the Drinking Water Standards limit of 12 mg/l K and the GSI trigger value of 5 mg/l K. However, BHC.3 (and BHC.4) consistently breach the 12mg/l K concentration. Although the median value was 15.5mg/l K, a range of 11-73mg/l K was detected at BHC.3, with highest values observed in August 2002 and September of both monitoring years (70 and 40mg/l K in September of 2002 and 2003, respectively). These autumn values are extremely high and alert grave concern. Potassium is thought to be relatively immobile in soil and subsoil and background groundwater concentrations in Ireland are usually less than 3mg/l K (Daly *et al.*, 1989). Potassium levels in the topsoils of

Curtin's farm are approximately 80 mg/l K in the grazing and silage areas. However, in the dirty water treatment area topsoil potassium levels measure 200-300 mg/l K. Super saturation of potassium in the soil could result in its leachate. Strangely, the autumn potassium contamination incidences are detected at a time when there had been no effective rainfall recharge to the system in the previous three months. This could suggest to some that the contamination might have a point or underground source but this is unlikely, in my opinion, because the slurry tanks are empty and the dirty water tank is constantly drawn from by the irrigator. However, over 60mm of rainfall occurred in the previous month and perhaps some recharge occurred but the monitoring programme missed its effect on groundwater levels. Dirty water irrigation in the central farm area can be shown to be connected to two groundwater contamination incidences (see section 6.4.6.5 and 6.7).

Daly & Daly (1982) point to the significance of a K:Na ratio greater than 0.3 as an indicator of contamination from dirty water, farmyard and other wastes derived of plant origin. The K:Na ratio for groundwater abstracted from BHC.3 was greater than 0.3 for every sampling event. Similarly consistent K:Na ratio results were obtained at BHC.4. Other piezometers sporadically returned groundwater samples with K:Na ratios greater than 0.3, but mostly in the first year. BHC.7, located in the dirty water area had a particularly bad record for K:Na ratios in the first year but all samples returned in the second year conformed to a ratio of greater than 0.3, indicating improvement in some area of farm management.

Results for chloride, sulphate, magnesium and calcium at BHC.3 reveal similar concentrations to those in groundwater abstracted at other monitoring locations on the farm, all within accepted guide values.

Dissolved phosphorus concentrations at BHC.3 were observed to rise to 0.08mg/l PO_4 on the 19th June 2002 in response to 74mm effective rainfall in the previous month, which caused a 1.6m rise in groundwater level at this location in the first week of June. A second serious peak in phosphorus concentrations occurred on the 12th February 2003 when both dissolved and particulate concentrations peaked at 0.045 and 0.056 mg/l PO_4 respectively, again in response to 75mm effective rainfall in the previous month. High concentrations of phosphorus were observed in some other, but not all, piezometers. One potential source could be slurry, which was spread in the area around BHC.1, upgradient with respect to groundwater flow, on the 5th April 2002. The spread of slurry was followed by approximately 70mm effective rainfall in the following month. Another possible source of elevated phosphorus might be dirty water irrigated in plots close to BHC.3. The high concentrations of phosphorus in the topsoils of the farm have already been referred to in chapter four, section 4.2.3.1, Figures 4.3 & 4.4. Whether phosphorus migration is by leaching from over-saturated soils, or by by-pass flow from the land's surface, is discussed in section 6.7.

6.4.6.5. BHC.4 - Dirty Water Area

BHC.4 is situated on the perimeter of a dirty water plot 50m north of the farmyard, at an elevation of 54.06m AOD, in an area with 2.5m depth of soil cover. Piezometer installation was not possible because of a 10m deep cavern encountered at 33.5m bgl. Groundwater hydraulic conductivity at this location was observed to be 10^{-1}m/day, which was low relative to other locations, especially considering the encountered cavern.

Despite the difference in borehole completion BHC.4 and its closest neighbouring piezometer, BHC.5, both demonstrate complementary water level trends. BHC.5 is the located approximately 150m northwest of BHC.4. Groundwater samples from BHC.4 persistently breach the MAC (EC, 1998) on all occasions except in the late summer months. The subsoil has higher gravel content than other locations but sand is the predominant component: the classification is silty gravelly SAND according to BS 1377 (1990). Subsoil hydraulic conductivity was not investigated in this plot (11RED) in which BHC.4 is sited, but results from the other instrumented dirty water plot suggests increased hydraulic conductivity compared with other areas on the farm that are not used for dirty water irrigation. Soil phosphorus levels are high in this area.

The maximum monthly rise in groundwater level, at this site, was observed to be 8.6m as a result of 200mm effective rainfall in the first month of winter recharge in October-November 2002. Figure 6.26 shows that groundwater nitrate concentrations generally mimic changes in water table elevations.

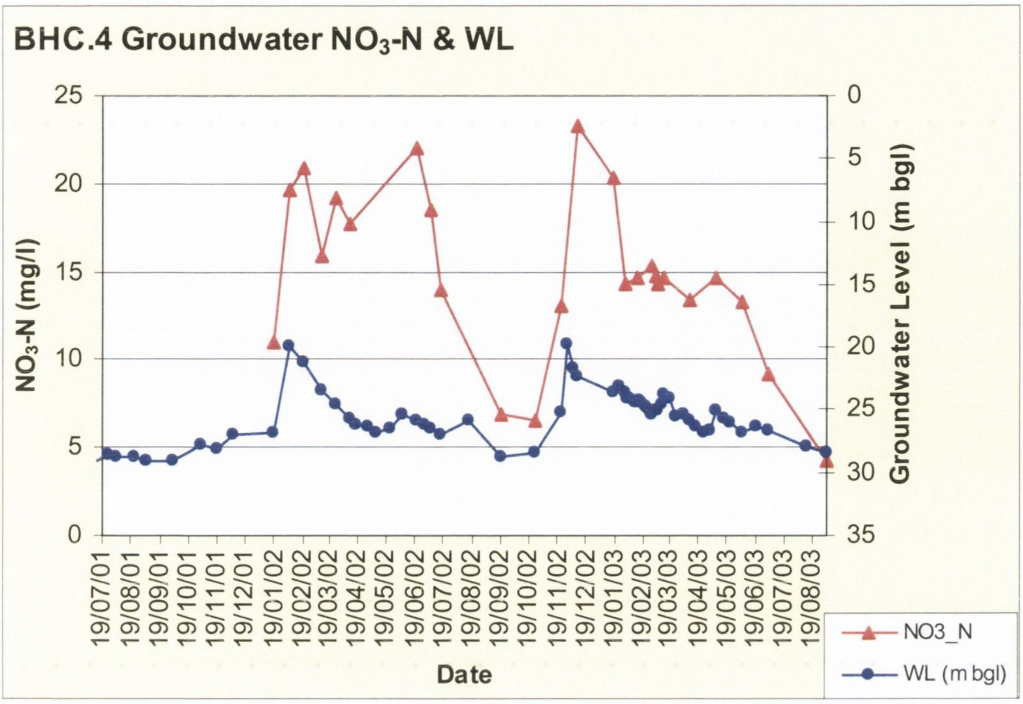


Figure 6.26 Groundwater level and nitrate concentration (mg/l NO_3-N) trend at BHC.4.

Increase in water level results in increase in groundwater nitrate concentration within one month in the first year and six weeks in the second hydrological year. The initial peaks in nitrate concentration do not persist. Annual groundwater nitrate concentration fluctuation is 16mg/l NO_3-N with pre-recharge autumn lows of less than MAC (EC, 1998) raising to nearly twice the MAC in January and May of 2002 again in the next recharge season in November of 2002. The plot of recharge versus non-recharge nitrate shows that nitrate is transported by recharge (section 6.4.5, Figure 6.17). With respect to the cause of the nitrate peaks, Figure 6.27 shows meteorological and nitrogen loadings in association with groundwater nitrate response and groundwater level response at BHC.4.

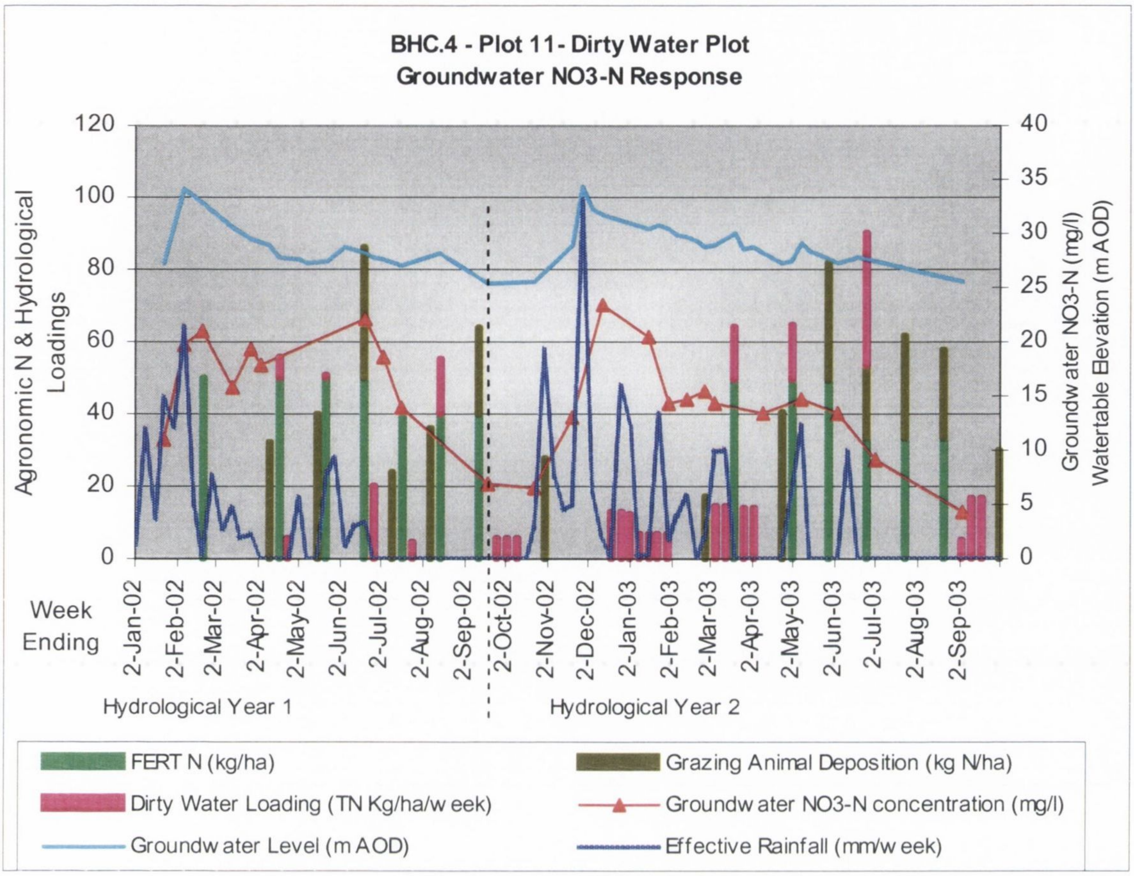


Figure 6.27 Groundwater response to meteorological and agronomic loadings at BHC.4.

At this piezometer, like all others, there is a clear response when effective rainfall and nitrogen loadings occur in close proximity to each other. From Figure 6.27, in May 2002 the effect of 50mm effective rainfall, which fell in the same week as the plot was grazed and then fertilised, is clear. A 0.8m rise in groundwater levels is accompanied by a small rise in nitrate concentrations. However, once the non-recharge season commences and there is no more effective rainfall, groundwater nitrate concentrations fall steadily throughout the summer.

In the second hydrological year, with the onset of recharge, the first 100mm effective rainfall, in October 2002, effects an approximate doubling of the groundwater nitrate concentrations from levels of approximately 6mg/l before recharge to 13mg/l by the end of November, breaching the MAC (EC, 1998). A further 100mm of effective rainfall at the end of November appears to again double the groundwater nitrate concentrations to levels of 26 mg/l by the end of December, which is more than twice the MAC (EC, 1998). However, groundwater nitrate concentrations fall steadily again after the first flush of nitrate from the subsoil system. These results, duplicated in successive years, and in more than one piezometer, confirm the rapid transfer times in this karst system.

Consideration of analytical results for other hydrochemical parameters reveals that ammonium-nitrogen concentrations are persistently greater than 1mg/l NH_4-N in both summers 2002 and 2003 (Appendix R). Groundwater phosphorus concentrations were elevated at this location. The observed median groundwater phosphorus concentration in groundwater abstracted from BHC.4 was 0.033mg/l PO_4 (see section 6.3.3.2 and Table 6.13). Potassium and sodium concentrations were also always elevated at this location. Most piezometers yielded EC values between 800 and 900μS/cm, which are within the IGV standards. However, this piezometer consistently breached the EPA IGV for groundwater EC, 1000μS/cm, during the monitoring period. Generally the groundwater beneath the farm contains conforms to the Drinking Water Standards limit of 12 mg/l K and the GSI trigger value of 5 mg/l K. However, BHC.3 and BHC.4 consistently breach the 12mg/l K concentration. The median value at BHC.4 was 31mg/l K and maximum values were observed in August and September 2002 (over 100mg/l K persisting over two sampling events). These autumn values are extremely high and alert grave concern because although they indicate potential point source pollution from the farmyard, the source is not obvious because the underground slurry tanks would be empty at this time of the year. Examination of the potassium trend graph for all piezometers (Appendix R) suggests that this potassium contamination incident originated in BHC.7 and travelled to numerous boreholes (BHC.4, 5, 8, and 9) and the River Funshion. The bromide tracing experiment validated hydrogeological connectivity between the piezometers mentioned (see section 6.5.3.2). The dirty water had been irrigated in early August and the contamination incidence was observed in September. Attention has already been drawn, in section 6.2.2.1, to the work of Sapek (2000) who reported groundwater concentrations up to 390mg/l K observed beneath agricultural pasture.

The K:Na ratio for groundwater abstracted from BHC.4 was greater than 0.4 for every sampling event. The usual indicator or trigger values reveal a contaminated groundwater but maximum potassium and ammonium concentrations occur at a time when nitrate concentrations are lowest. These results highlight the effect of groundwater solute concentrations being influenced from multiple sources and directions is at this monitoring location.

6.4.6.6. BHC.5 - Experimental Plot (No agricultural activity)

This piezometer was located alongside a perimeter of the farm in the corner of a plot set aside from agricultural production because of an NUIG subsoil investigation. There were some nitrogen additions during the groundwater-monitoring period but not in the vicinity of the piezometer. No animals grazed the plot. Ground level elevation is 51.8m AOD. This piezometer was positioned with the intention of targeting groundwater flowing into the farm and also because nitrogen additions were to be minimal. Even though nitrate concentrations were lower here than at other locations, it was later established that groundwater quality here was affected by nitrogen loadings in the dirty water area, which is targeted by BHC.7 (this evidence is presented in section 6.4.6.8 and 6.5.5)). The average annual concentration was 13mg/l NO_3-N and the variation observed in a year was 10mg/l NO_3-N.

The subsoil depth at this plot was 2.5m. The topsoil is described as sandy GRAVEL in topsoil layer and also at 2m bgl. The hydraulic conductivity in the subsoil was measured to be similar to that observed in the plot where BHC.2 is sited: in the topsoil K_{sat}= 0.03m/day; 0.08m/day at 1m and 1.5m; and much higher in the layer above the epikarst region at 0.68m/day. The compacted topsoil is expected in sandy soils (Diamond, *pers. comm.*, 2003).

During drilling, weathered zones were encountered at 5 and 19 m bgl but water strike occurred at the same region, 28m bgl, as other piezometers. Like most bores,a piezometer was fitted with a screened area targeting 26-29 m bgl, which was protected from direct infiltration with bentonite seals.

Water levels in BHC.5 show similar magnitude of responses to effective rainfall as BHC.4, which is its closest neighbour, but groundwater nitrate response was different. Figure 6.28 shows the response of groundwater nitrate at BHC.5 in association with increases in groundwater levels. The clearest response relationship is discernable in November 2002, when a groundwater elevation peak is followed 2 months later by a groundwater peak of 16.5mg/l NO_3-N. However, the source of this nitrate must be identified.

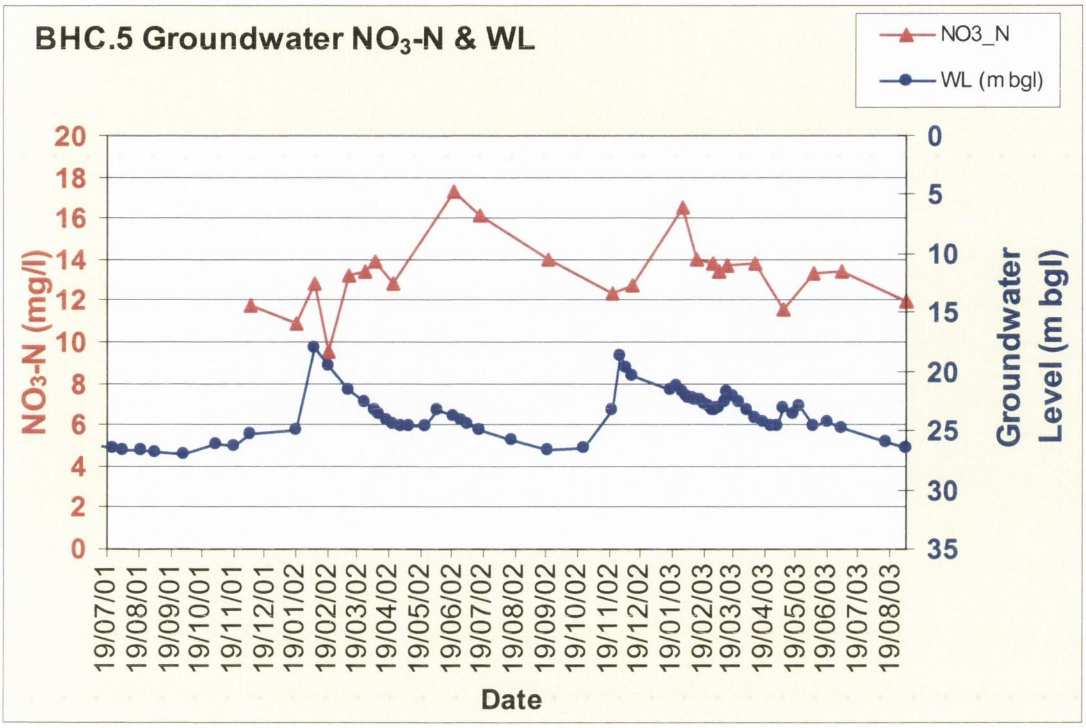


Figure 6.28 Groundwater level and nitrate concentration (mg/l NO_3-N) trend at BHC.5.

Initial small increase in groundwater levels in November 2001 caused a 2mg/l NO_3-N increase in groundwater concentrations six weeks later. However, 200mm effective rainfall in January 2002 caused a 4m increase in groundwater level elevation by February and this rise in water level caused an initial 5mg/l reduction in groundwater nitrate concentration. However, the decrease in groundwater nitrate concentration did not persist but increased steadily to a maximum of 17mg/l nitrate in May 2002. A two-month time lag between the month of maximum effective rainfall (200mm) and peak groundwater nitrate was observed in both hydrological years. Although the recharge versus non-recharge analysis (section 6.4.5) signifies that nitrate is transported to the groundwater with recharge, the initial decrease in nitrate concentrations and subsequent slow increase after recharge also suggests dual mechanism solute transport through the subsoil.

The dirty water area (plot 12) was observed to have an effect on the nitrate concentrations at BHC.5. The bromide tracing study proved the link between BHC.7 and BHC.5 (section 6.5). The temporal groundwater nitrate trend at BHC.5 and BHC.7, which targets the dirty water plot 12, shows the connection between the two piezometers in Figure 6.29.

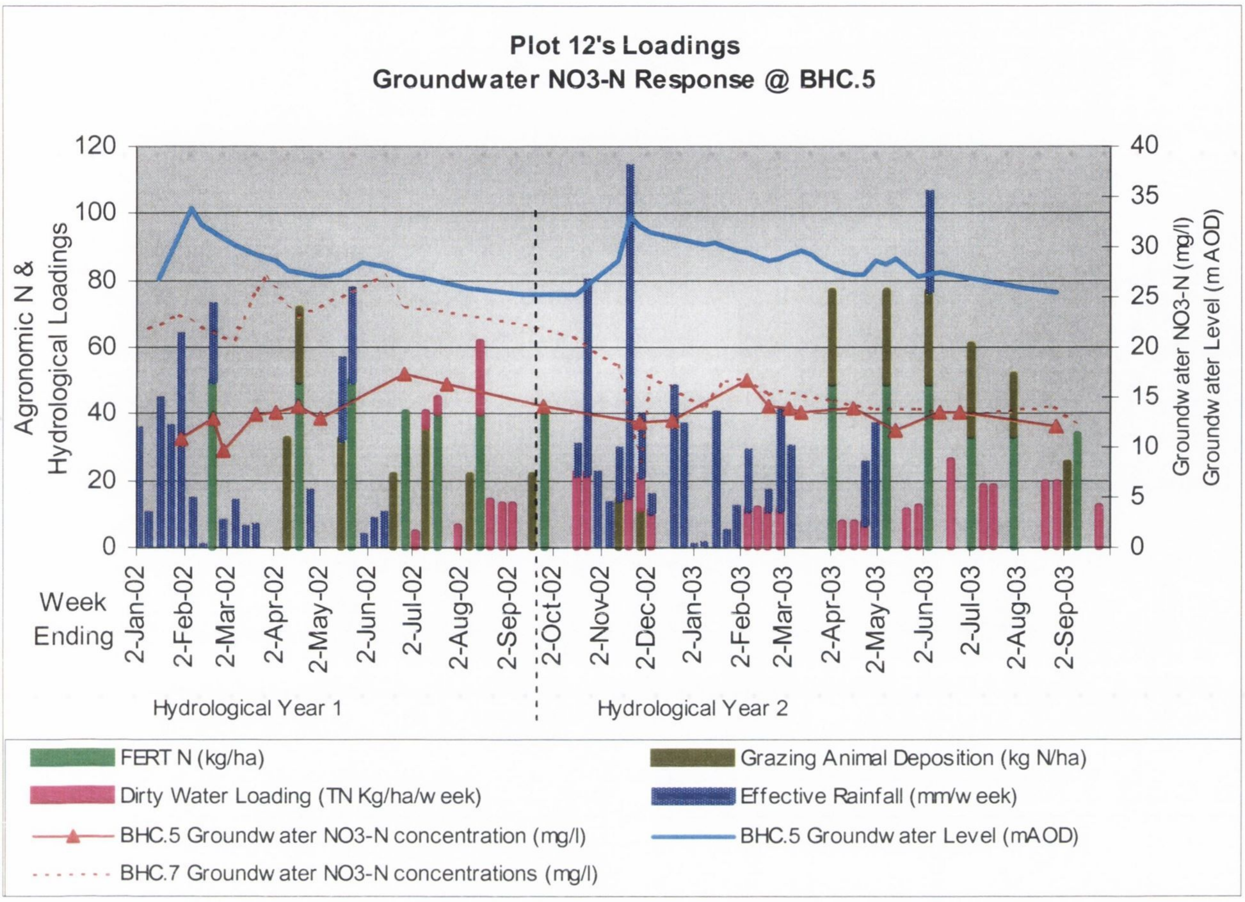


Figure 6.29 Groundwater response to meteorological and agronomic loadings at BHC.5 (groundwater nitrate concentration trend in BHC.7 is also shown).

Although there were some detections of the ammonium ion in the groundwater abstracted from BHC.5 other parameters such as potassium and sodium conform to good quality standards. However, chloride concentrations were elevated at this location. Richards (1999), in a study of an intensive dairy farm's effect on groundwater quality, related elevated groundwater chloride concentrations to dirty water applications.

6.4.6.7. BHC.7 - Dirty Water Area

This piezometer targets the dirty water area and the ground elevation was surveyed to be 53.9 m AOD. Soil cover was measured to be 2-2.5m-depth and the predominant soil type through the soil profile was gravelly SAND (BS 1377, 1990). Whilst subsoil hydraulic conductivity investigations at four other locations on the farm reveal compacted topsoil conditions, this site was different. Hydraulic conductivity (K_{sat}) was measured to be 0.57m/day in the topsoil layer at BHC.7's plot 12,which is ten times higher than at other sites. At the 1m-depth in the K_{sat} was measured to be 0.166m/day, which was double that measured at other sites. Water table elevation observations suggest a mound of groundwater beneath BHC.7 and groundwater hydraulic conductivity measurements suggest a 10^0 m/day K value, which is significantly lower than other locations and suggest low groundwater storage in this area. These subsoil and groundwater hydraulic conductivity measurements, coupled with the dirty water irrigation activity justify the observed groundwater mounding. Groundwater nitrate concentrations are highest in this area. Maximum observed concentrations were 27 mg/l, over twice the MAC (EC, 1998), and median values are 1.5 times the MAC. Groundwater at this location was shown to travel to other monitoring piezometers (refer to section 6.5) and this finding highlights the inherent uncertainty of attempting to differentiate groundwater-monitoring results by agronomic treatment.

Borehole drilling for installation at BHC.7 revealed solid Waulsortian limestone throughout the entire subsurface until an approximate 1m-depth weathered zone at 30m in which water strike was achieved. Progression down the hole revealed a deposit filled cavity at 34m and so drilling was stopped. The piezometer screen targets 29-32m bgl. The fill in the cavity was subjected to particle size analysis, which was found to contain 39% gravel, 33% sand, and 28% silt/clay mixture (most probably predominantly silt) and therefore can be described (using BS 1377, 1990) as a silty, very sandy GRAVEL (see Appendix F, page 511, volume two of this thesis).

Groundwater levels at this piezometer demonstrated highest ranges and fluctuations. Groundwater levels at other piezometers always remained at least 18m bgl but here, at BHC.7, winter recharge could cause water levels to rise within 13m of ground level. In both monitoring years, 200mm effective rainfall in the wettest month of each year resulted in 15m water level rise within weeks.

An analysis of recharge versus non-recharge groundwater nitrate concentrations (section 6.4.5) shows that concentrations are higher in winter rather than summer and this is borne out by Figure 6.30. Groundwater level peaks result in nitrate peaks.

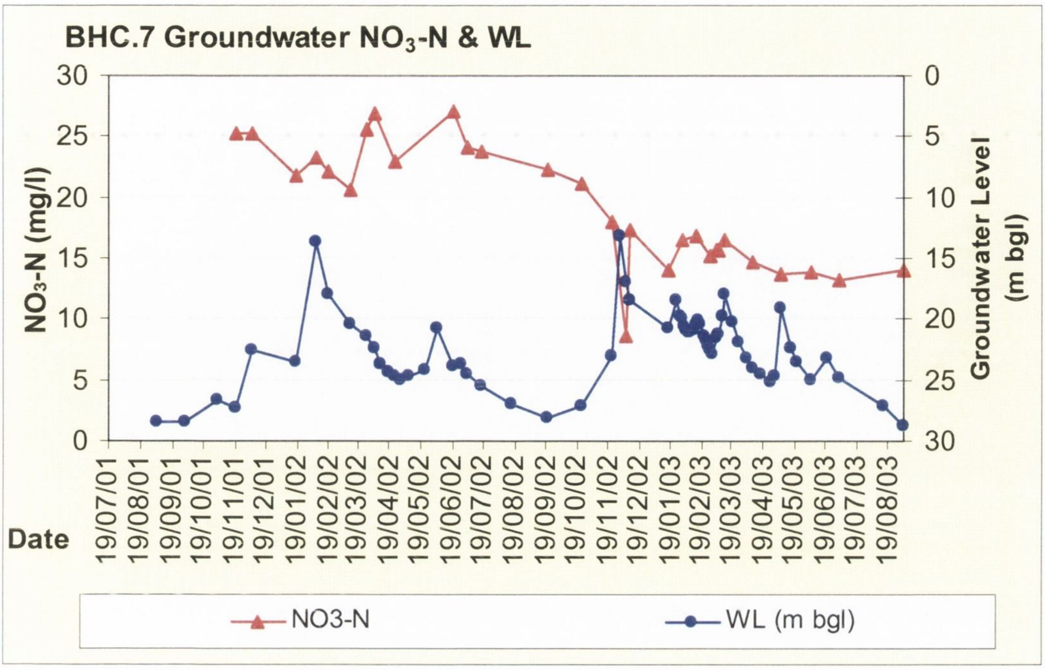


Figure 6.30 Groundwater nitrate concentration (mg/l NO_3-N) and water level trend at BHC.7.

There was a significant decrease in groundwater nitrate concentrations in the second year of the study. In the first year a groundwater nitrate concentration peak of almost 27mg/l NO_3-N, in April, occurs two-months after the groundwater level peak in January. That springtime peak of 27mg/l NO_3-N occurs after a 50kg/ha application of fertiliser followed by 50mm of effective rainfall over a two-week period. Figure 6.31 shows the response of the groundwater system to meteorological and nitrogen loadings. Again, the pattern observed at other locations is repeated, effective rainfall after nitrogen application results in an increase in groundwater NO_3-N concentrations. The overall reduction in concentrations in the second year concurs with observations at other locations. Winter effective rainfall in the second year was double that recorded in the first year, which means that the same available nitrate load was diluted, potentially two-fold. The responsiveness of the system is thereby demonstrated: the nitrate response in the groundwater is more distinguished by the effects of recharge than by individual nitrogen fertilisation events.

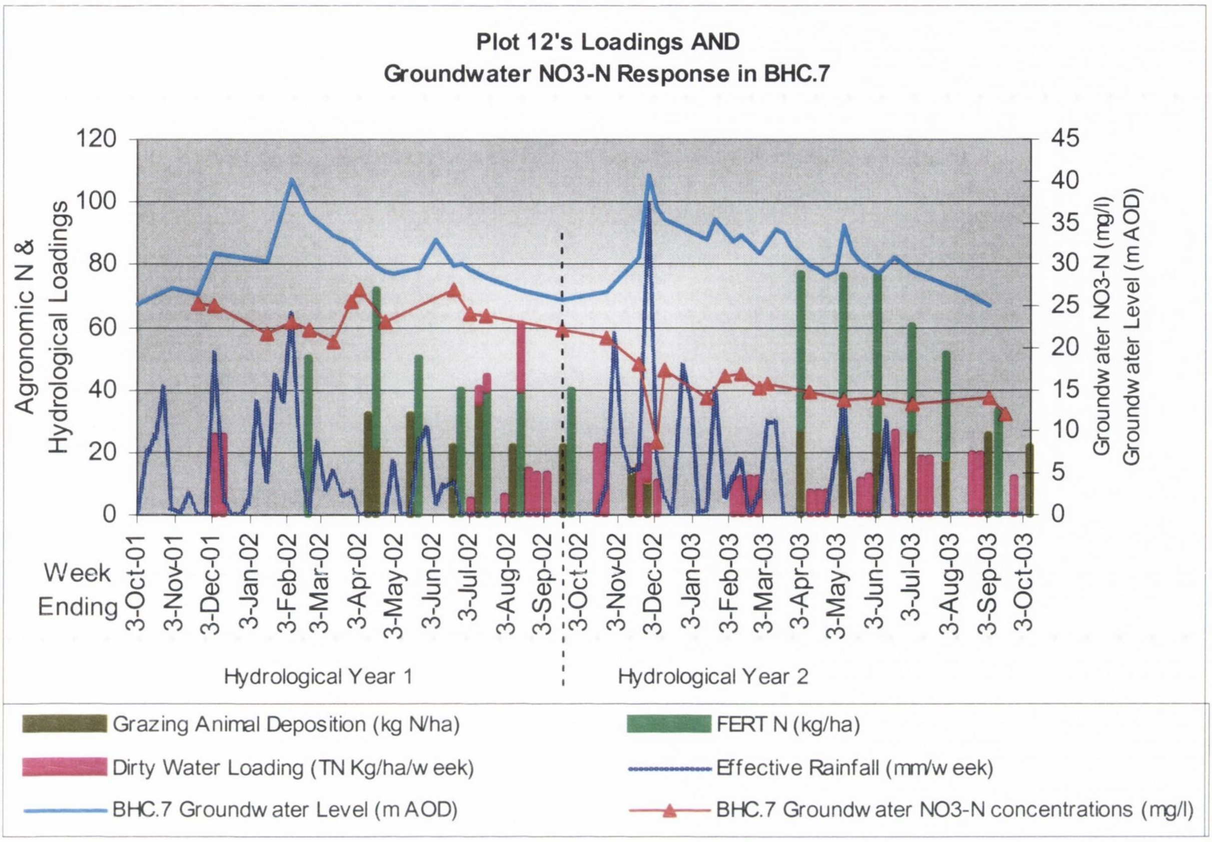


Figure 6.31 Groundwater response to meteorological and agronomic loadings at BHC.7

Other indicators of groundwater quality at this location demonstrate both ammonium and phosphorus peaks corresponding with groundwater elevation peaks (Appendix R), which signifies preferential flow from the subsoil in the overlying plot because the mounded groundwater conditions negates inflow from other locations. Potassium concentrations are generally within the IGV limit except for the two contamination incidences in autumn 2002 and spring 2003 (see previous discussion in section 6.4.6.5). Both incidences concur with recent dirty water irrigation in the plot. The only K:Na ratio breaches of the IGV (EPA, 2003a) at BHC.7 occurred in August and September 2002. However, the rapid response of the system ensured that the K:Na status of the groundwater returned to acceptable standards in the succeeding recharge period when values were consistently less than 0.3 (refer to Appendix R).

A bromide tracing experiment was focussed on the plot in which BHC.7 is sited. Results (section 6.5) proved the rapid response of the system, the potential for preferential flow in the overlying subsoil at this site, and radiating groundwater flow directions from BHC.7 to other monitoring locations.

6.4.6.8. BHC.8 - Experimental Area

BHC.8 is situated approximately 150m northeast of BHC.7, at an elevation of 54.77m AOD, in an area with 4m depth of soil cover. The bore was drilled by a mineral exploration company using coring techniques that resulted in a 50mm diameter bore to 59.5m depth bgl. Piezometer installation was neither possible nor required: the core drilling technique results in a stable open bore. The groundwater is protected from contamination from subsoil by a grouted sleeve. Despite the difference in borehole completion, BHC.8 demonstrates similar water level trend and groundwater nitrate concentration as BHC.7. Groundwater samples from BHC.8 exceeded the EU MAC (EC, 1998) for most sampling occasions. Figure 6.32 shows how rising groundwater levels influence groundwater NO_3-N concentrations.

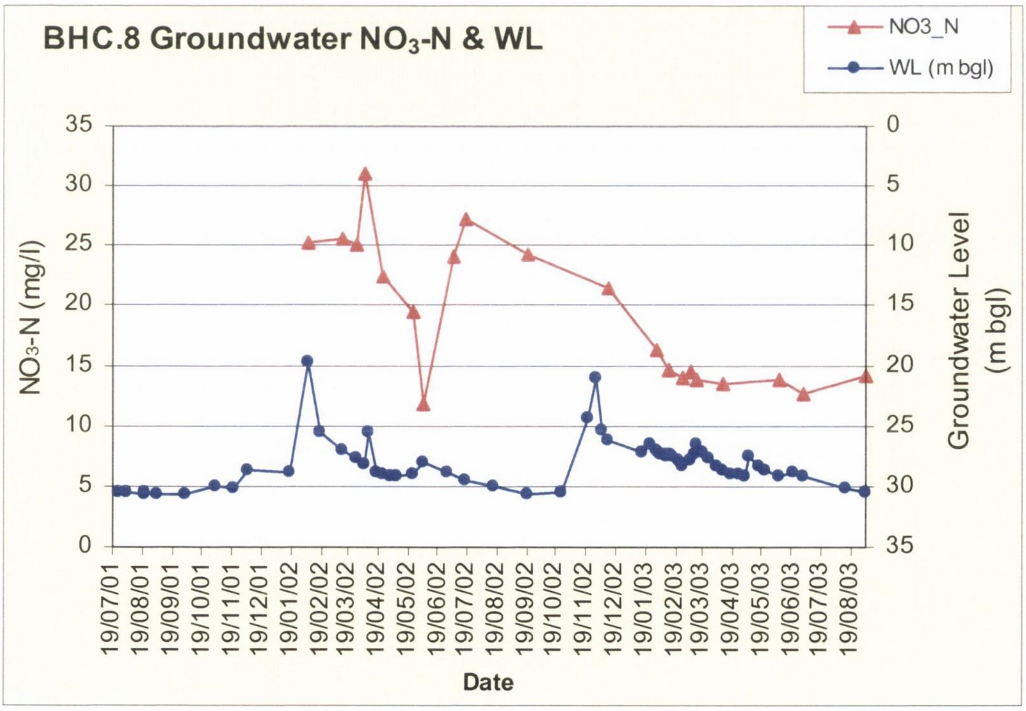


Figure 6.32 Groundwater level and nitrate concentration (mg/l $N0_3$-N) trend at BHC.8.

Groundwater levels, in BHC.8, respond to meteorological loading. In the first hydrological year, a total of 100mm effective rainfall in October and November results in a 2m rise in groundwater levels. In the following two months, 200mm effective rain in December and January, affected a further 9m rise in groundwater levels observed in early February. Based on observations at all other piezometers, 50mm effective rainfall causes an average rise of 1m in groundwater level. Indeed, 50mm effective rain in the month of May is reflected by a 1m increase in groundwater levels in BHC.8 in the following month, June 2002. There is no SMD at this time. Water levels decline throughout the summer when there is no meteorological loading. Over 200mm effective rainfall in October and December 2002 is reflected in a 9m rise in water levels, similar to the response in the previous year. Therefore, the system responds rapidly to recharge. What effect does the influx of recharge have on the groundwater body nitrate concentrations at this location?

The first peak in groundwater nitrate concentrations is observed in April 2002, on which date the groundwater concentration was 31mg/l NO_3-N. This 6mg/l increase in April, perhaps as a response to the first flush of recharge in January, occurs three months after the recharge and two-months after the peak in groundwater level observed in February. There was no recharge between the two sampling events, in late March and early April, when the 6mg/l NO_3-N increase was observed. It seems reasonable, therefore to conclude that the time lag for nitrate migration at this location is at least four months from ground level to groundwater at over 25m bgl. Groundwater nitrate concentration decreases quite significantly from April to June, in response to the large rainfall in January, again suggesting a four-month phase shift in response to meteorological loading. The plot overlying BHC.8 was used to isolate sick animals, individually, during the experiment. Therefore animal grazing was not intensive, fertiliser was very rarely applied and neither slurry nor dirty water was applied. Groundwater nitrate concentrations reduced dramatically throughout the remainder of the experiment although they were still 14 mg/l NO_3-N, which is well above the MAC (EC, 1998), at the end of the experiment. The water table map suggests that the mound of groundwater in the central farm area, beneath the dirty water plot where BHC.7 is sited, influences flow towards BHC.8 and this might explain the high groundwater nitrate concentrations here.

In the first year of the study, a groundwater elevation peak in early February is followed by a 5mg/l NO_3-N concentration increase at a two-month time lag. This suggests initial recharge carries little nitrate from the soil matrix. In the second year, there is little response of the groundwater levels to recharge and similarly nitrate concentration response was negligible. The 20mg/l NO_3-N range observed in the first year was caused by sharp decline in groundwater nitrate concentrations that persisted for three consecutive sampling events. Figure 6.32 reasonably validates the adopted methodology regarding plotting recharge versus non-recharge groundwater nitrate concentrations (section 6.4.1) in that in Figure 6.17a recharge is implicated in transporting nitrate to groundwater at BHC.8. However, Figure 6.17b suggests, by close proximity to the 1:1 line, that there is little temporal variation in groundwater nitrate at BHC.8 in the second year. Nitrogen additions in the immediate plot overlying BHC.8 are negligible because the plot is used only on occasions and never supports intensive grazing. The dirty water area is adjacent however. BHC.8 is also situated within 200m of some private residences, which are served by septic tank systems. However, the groundwater flow gradient suggests BHC.8 to be up gradient of these systems. The significant decline in groundwater nitrate concentrations in the second year also supports our understanding that it is the combination of meteorological and agricultural activity that is the most significant influence on groundwater nutrient status.

It is difficult to discern the effect of temporal nitrogen loadings on groundwater nitrate concentrations. The loadings to the adjacent dirty water plot 12, which it is hypothesised influences BHC.8's groundwater nitrate, are presented in Figure 6.33. The temporal trend of groundwater levels and nitrate concentrations are shown for both BHC.7 & 8 on the same plot, to show the similarity and connectivity between these piezometers. Groundwater hydraulic conductivity, measured at BHC.8 was determined to be 10^0, similar to that measured at BHC.7.

With regard to the other nutrients monitored, peaks of ammonium-nitrogen (NH_4-N) and nitrite-nitrogen (NO_2-N) were observed only once, within two weeks of each other, and phosphorus showed only one strong signal response, and that was in early spring 2003. In late March 2002, nitrite concentrations reached 0.1mg/l NO_2-N. Two weeks later, ammonium concentrations of 0.1mg/l NH_4-N were recorded, in early April. Heavy rains had fallen in the previous months and the auxiliary nitrogen species occurred in the same time frame as the spike concentration of 31mg/l NO_3-N, nicely indicating progression in the nitrogen cycle. Phosphorus was observed in the groundwater, in both dissolved and particulate form, in both late January and early February 2003. On the 29th January particulate phosphorus concentrations in the groundwater were 0.07mg/l PO_4 and of that the dissolved fraction was 50%, at 0.037mg/l PO_4. Two weeks later, on the 12th February, particulate phosphorus levels had risen further, to 0.09 mg/l PO_4 and on the same day dissolved phosphorus in the groundwater was 0.04 mg/l PO_4.

Neither potassium, sodium, chloride nor sulphate concentrations are elevated in the groundwater samples abstracted from BHC.8, except during the two dirty water influenced groundwater contamination incidences previously mentioned.

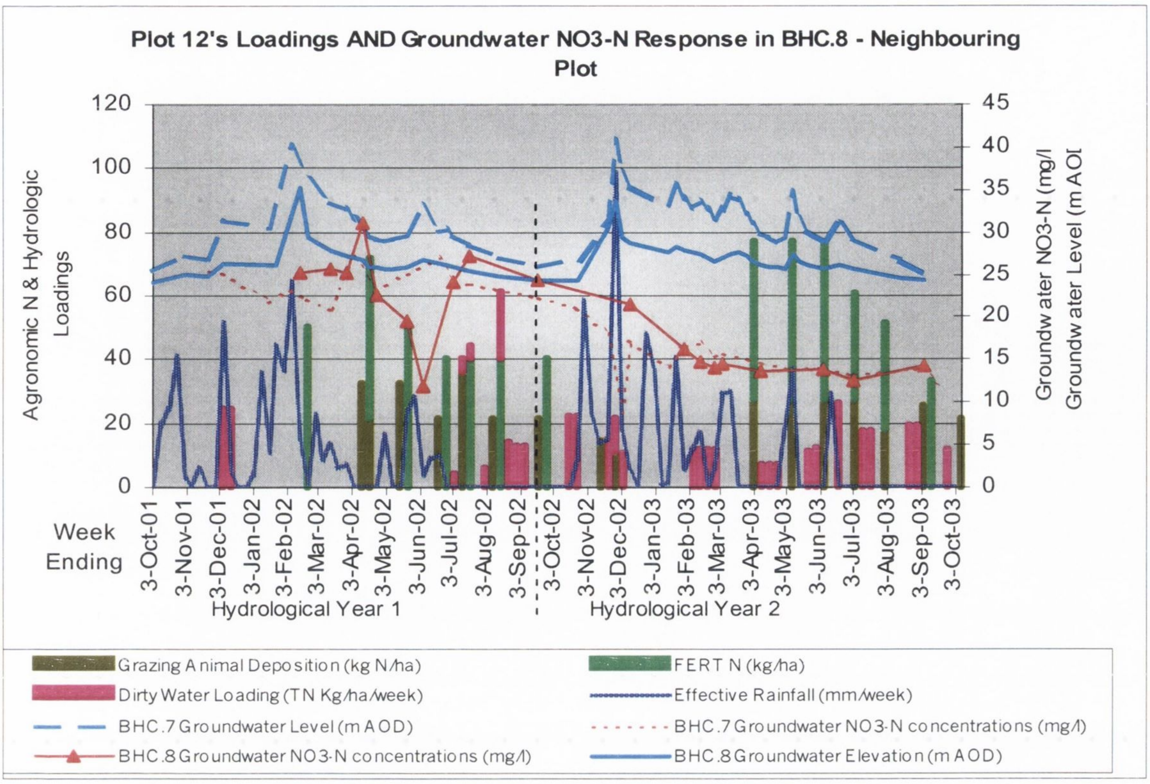


Figure 6.33 Groundwater response to meteorological and agronomic loadings at BHC.7 & BHC.8.

6.4.6.9. BHC.9 – One Cut Silage Area

It is clear that the responses observed in other locations on the farm are repeated here: groundwater levels respond within one month of recharge. This piezometer was drilled later than others so it is difficult to comment definitively on the behaviour at the beginning of records in January 2002. However, both winter and spring recharges greater than 50mm/month caused increases in groundwater levels. Water levels fall by three metres during the summer 'non-recharge' period. A six-metre rise in groundwater levels occurs as a result of the first 200mm effective rainfall in the first month of recharge in October/November 2002. There are spring and early summer responses to recharge also, on the 19th March and on the 6th May 2003. There was little effective rainfall in March and April 2003 and SMD grew to 30mm. There was 55mm effective rainfall in the ten days prior to the May rise in groundwater levels which leads us to conclude that groundwater response to rainfall is very quick at this location with time-lags of less than one month. Field tests for hydraulic conductivity found very sandy layers at depths of 1.5 and 2m bgl in this location that would allow rapid transport from the subsoil to the groundwater. Observed groundwater nitrate concentration trend is shown in Figure 6.34.

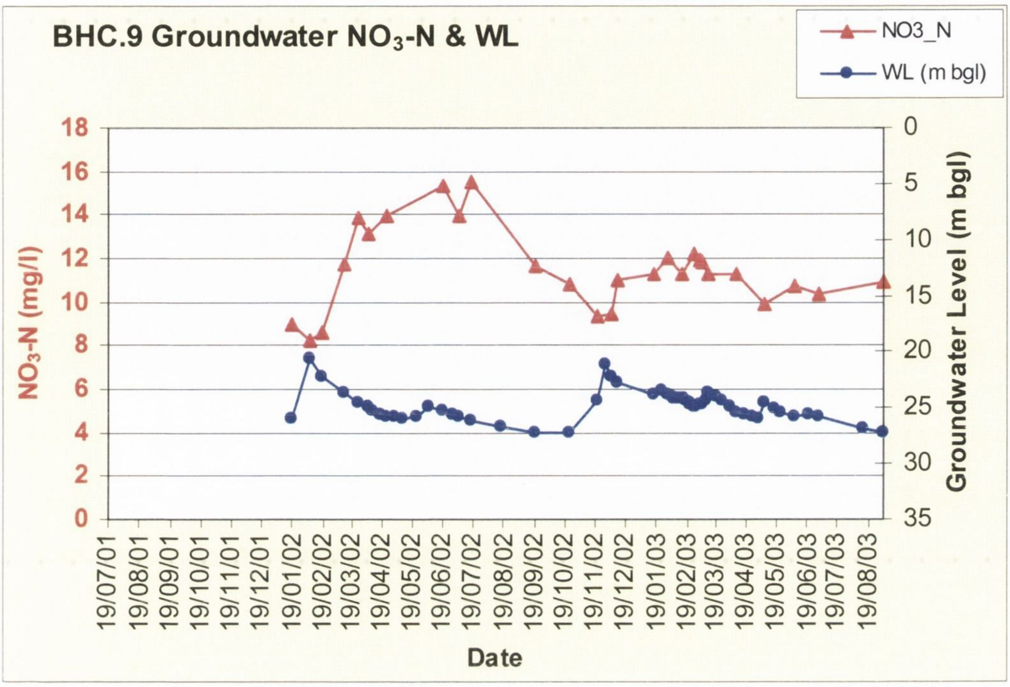


Figure 6.34 Groundwater level and nitrate concentration (mg/l NO_3-N) trend at BHC.9.

Recharge is seen to transport nitrate to the groundwater at this piezometer (Figure 6.34). There appears to be a one-month time lag between recharge and water level peak and a further month lag before groundwater nitrate concentrations begin to rise. This might indicate that the first recharge arriving at the groundwater body has a lower concentration than the later additions. Perhaps soil moisture residing at depth, held under tension, has been denitrified but recharge additions in spring would be rich in nitrogen, from late winter and spring fertiliser and slurry additions, and so cause continual increases in groundwater nitrate concentration until recharge ceases and water levels decline throughout the summer. Groundwater nitrate concentrations were at their maximum (15 mg/l NO_3-N) in BHC.9 in June 2002 declined to 9mg/l NO_3-N in October 2003, before recharge again influenced the system. In the second hydrological year, recharge had significantly less impact on nitrate concentrations and this most likely is because 50% more effective rainfall fell in that second winter, relative to the first. Groundwater concentrations rose by only 3mg/l NO_3-N and were relatively stable throughout the second monitoring year.

The response of groundwater at BHC.9 to loadings is shown in Figure 6.35. Results of the tracing experiment (section 6.5) highlighted the transport connection between BHC.7, in the dirty water area, and this location. Therefore, observed nitrate concentrations in BHC.7 are also shown in Figure 6.35. This connection complicates interpretation of the analysis of observed hydrochemistry at BHC.9 and surface loadings in the vicinity of that piezometer.

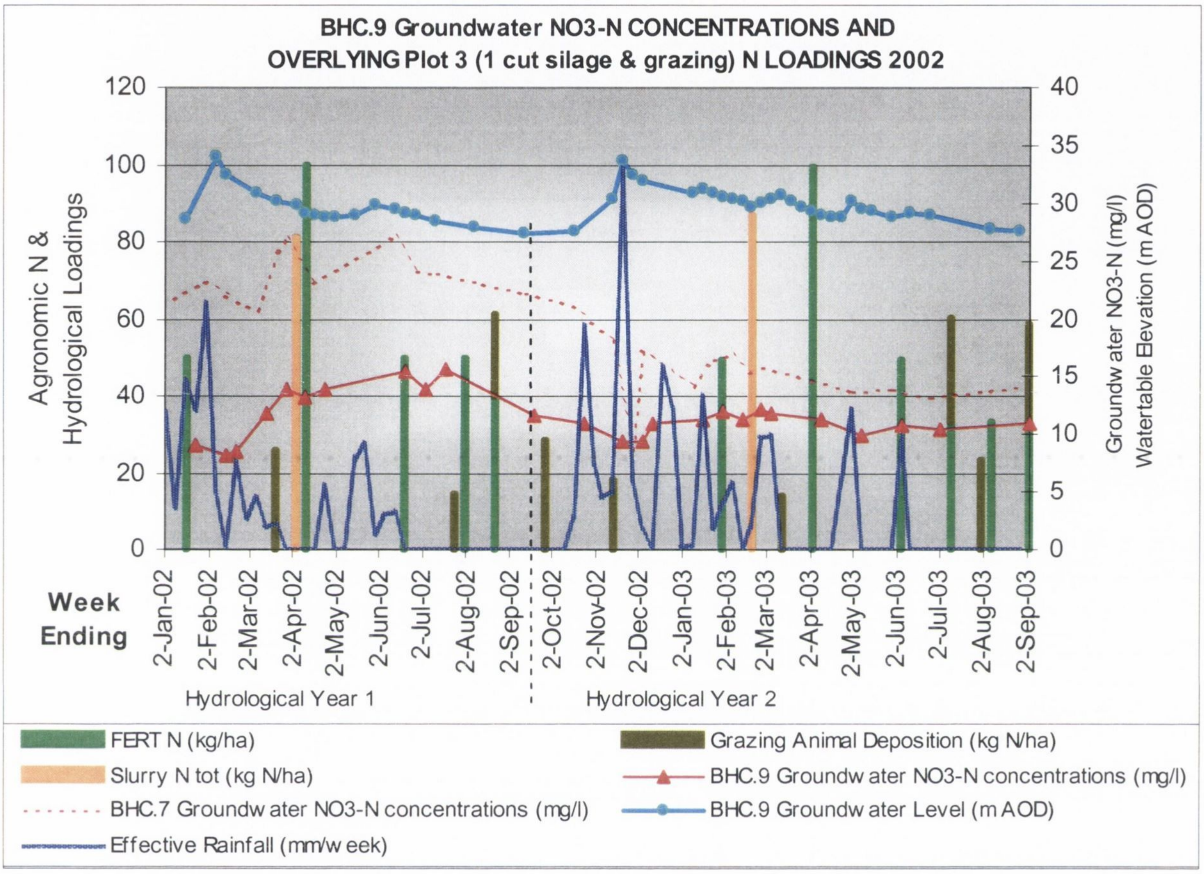


Figure 6.35 Groundwater response to meteorological and agronomic nitrogen loadings at BHC.9.

6.4.6.10. BHC.10 - One Cut Silage and Grazing Area

This piezometer is located at an elevation of 57.23m AOD, in an area with 3m-depth of soil cover. Hydraulic conductivity of the soil was not measured in the field above this piezometer but soil analysis by particle size distribution tests suggest the soil to be a sandy GRAVEL to gravelly silty SAND. Two other attempts at gaining access to groundwater in this field resulted in failure due to continuous weathered broken bands of limestone. A third attempt did result in water strike but the piezometer appears to have been compromised in some way because in the second hydrological year very few samples were obtained. Piezometer purging, at the time of groundwater sample collection, usually resulted in the piezometer drying up. Therefore, for the second year it is not possible to comment on piezometer response to loadings. The bedrock was found to be very hard, solid Waulsortian Limestone throughout the subsurface with only one weathered zone encountered, from 17 – 18m bgl. Solid bedrock then continued until a very small water strike at 34.5m bgl. Testing of hydraulic conductivity in the groundwater revealed that this piezometer, BHC.10, has a much lower K value (10^{-3} m/day) than all other piezometers on the farm.

This piezometer, BHC.10, consistently returned groundwater samples with concentrations significantly lower than the nitrate MAC (EC, 1998). The piezometer is located only 500m from the River Funshion and groundwater concentrations at BHC.10 were very similar to those observed in the river, in the first year. Phosphorus concentrations also support the proposition that the groundwater at this location is hydraulically connected to the river (see Appendix R).

In the summer of 2002 the water level dropped below the screened interval, which prevented sample collection. Upon rewetting at the start of the second hydrological year the piezometer was only sporadically active and if samples were returned groundwater nitrate concentrations ranged from 0.8-1.8 mg/l (Figure 6.36). These values are suspicious and unusual for the study farm. Perhaps an anaerobic environment existed and denitrification was occurring due to geologic conditions. The piezometer was not investigated further because it appears that there was some localised failure at the screened area during the drying-rewetting of summer 2002.

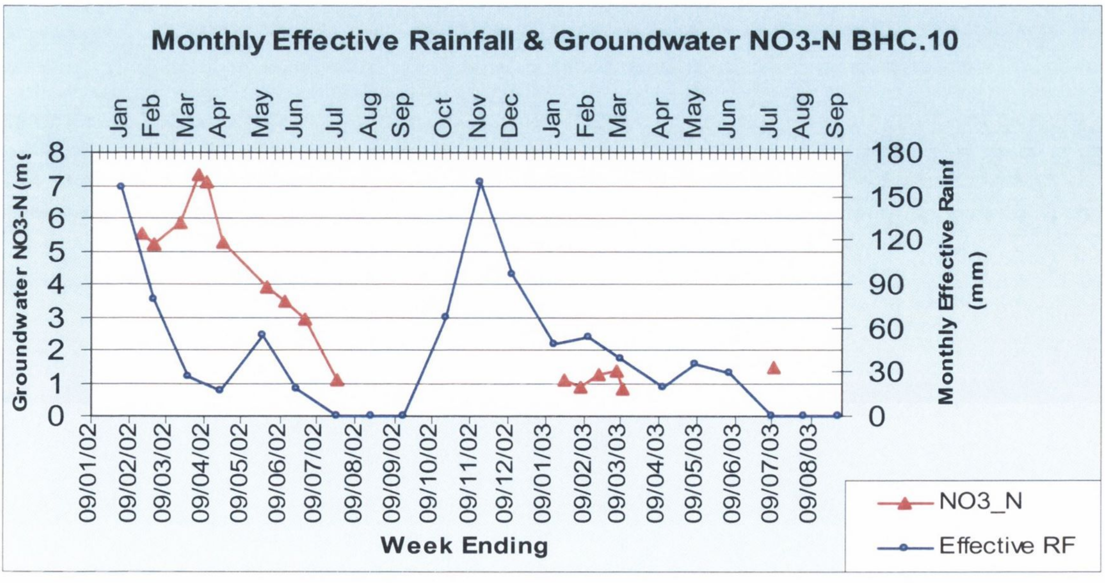


Figure 6.36 Effective rainfall and groundwater nitrate concentration at BHC.10.

6.4.7. Groundwater Nitrate Response To Grazing Animals

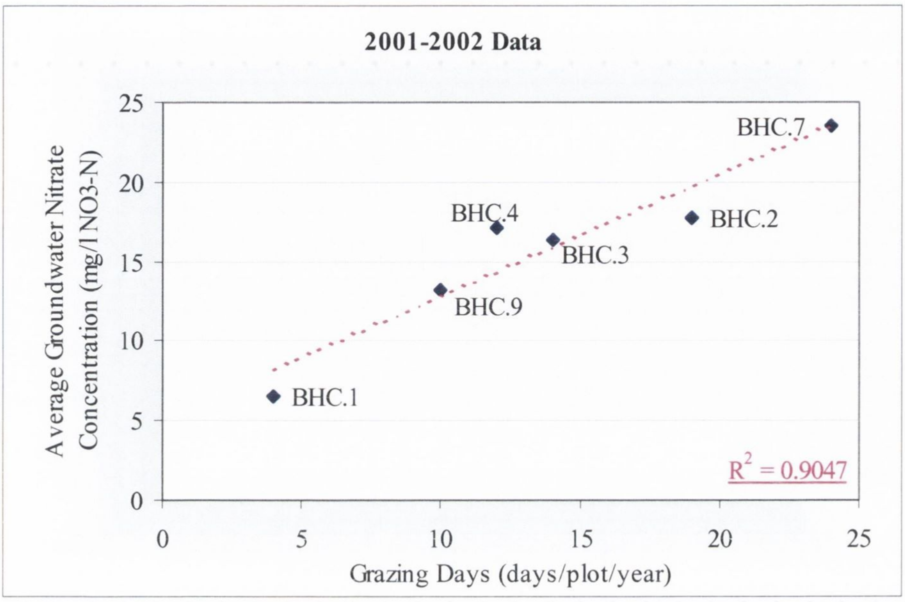
It is obvious from the previous discussions (section 6.4.6) that it is difficult to discern which specific nitrogen loading is the most significant with respect to groundwater nitrate status. Indeed, all nitrogen applications occur in such close proximity and a related. While previous loadings analysis concentrated on summation of nitrogen loading rates by agricultural management zone (refer to section 5.5.2) and determination of daily/weekly nitrogen loading rates (section 6.4.6), a simpler issue appeared in the form of the wide variation in the number of days that each plot was grazed in any year (see chapter five, section 5.5.2.4, Figure 5.15). These data were collected for calculation of grazing animals deposited nitrogen loadings. First analysis of this data seemed to show that grazing activity and the groundwater nitrate trends are related, at least for some piezometers.

6.4.7.1. Grazing day Relationship

A positive correlation was found between cow grazing day numbers, for a particular plot in one grazing season, and the average groundwater nitrate concentration recorded in that plot's associated piezometer in the following recharge period (see Figure 6.37 a & b). In this analysis BHC.5 was not included because its plot was not grazed and the uncertainty regarding BHC.10 has already been discussed (section 6.4.6.10). The raw data are presented in the Appendix U.

It is clear from Figure 6.37 that increased grazing intensity results in a higher availability of nitrate to be lost as leachate. The literature supports correlation between grazing days and nitrate leaching. Cuttle & Scholefield (1995) and Cuttle *et al.* (1992) observed a positive correlation between sheep grazing day numbers and nitrate concentration in drainage waters. Animal populations in catchments have been shown to be a dominant influence on nitrate leaching (Hack-ten Broeke, 2000). Whitehead (1995) reports that as the intensity of grazing is increased, there is increased consumption of the herbage available, which results in a larger proportion being returned to the soil via animal excreta. Sapek (2000) found that intensively used pastures with excessive grazing intensity was one of the "hot spots" responsible for farm input to groundwater pollution by solutes, especially nitrogen, phosphorus and potassium.

(a)



(b)

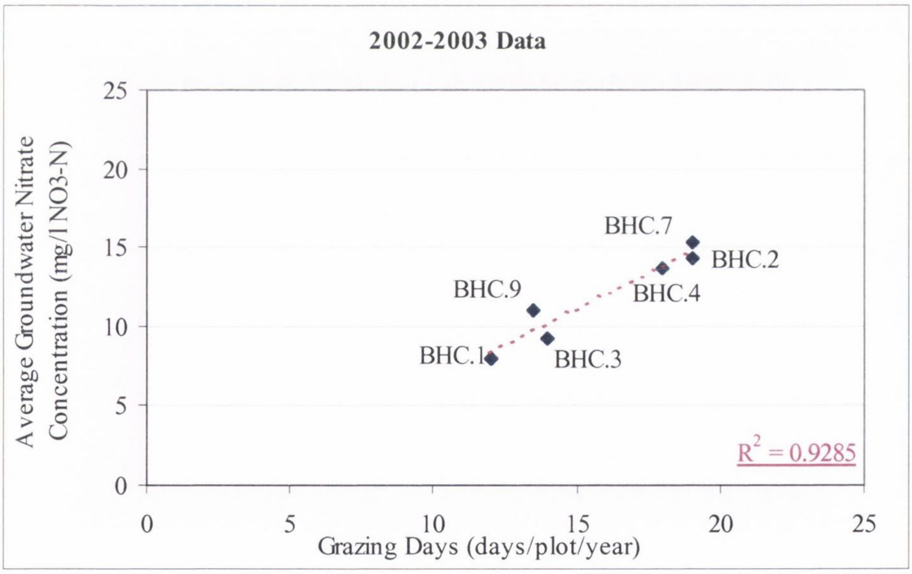


Figure 6.37 The relationship between a plots' grazing day numbers and average groundwater nitrate concentration observed in that plot's piezometer in the following year for (a) 2001 grazing day and 2001-2002 average groundwater nitrate concentration data and (b) 2002 grazing day data and 2002-2003 average groundwater nitrate concentration data (trend lines have been added and the R^2 of the trend line is also shown).

I consider the relationship between grazing days and observed groundwater nitrate concentrations as an indicative, rather than absolute, measure of the impact and significance of grazing animal's depositions in the field. One would not expect a purely linear relationship because the thickness of subsoil and its ability to conduct leachate varies from one piezometer site to another. Using the GSI vulnerability assessment methodology, it is the nature of the cover that determines intrinsic vulnerability but the above relationship shows that increasing grazing animal intensity increases the potential for nitrate delivery to the groundwater. The organic nitrogen-loading rate is therefore a crucial factor in managing nitrogen loss to groundwater. This finding validates the requirements of the Nitrate Directive (EC, 1991a) to restrict grazing intensity in vulnerable areas.

The grazing season extends from February (full herd out by late March-April) until the end of November (see section 5.5.3.2.1 for more grazing details). Based on the weekly analysis of grazing animal depositions (based on 85 kg N/cow/yr) approximately forty five percent of the grazing animals' annual nitrogen load is deposited in spring and early summer when there is significant effective recharge. Approximately fifty percent of grazing animals' annual nitrogen load is deposited during the non-recharge season, July to the end of October. The literature (refer to section 2.4) suggests that excess nitrogen additions (slurry, dirty water, fertiliser or grazing animal loads; all of which have been quantified) deposited in the 'subsoil bank' during the non-recharge summer period may be available to loss with the onset of the autumn/winter recharge season.

6.5. Tracing Experiment Results

6.5.1. Overview

Because groundwater response was observed to be rapid in all piezometers, verification was required to demonstrate that solutes observed in the groundwater actually originated at the ground surface above the piezometers. A tracing experiment was designed (the methodology and instrumentation were described in section 5.4). The tracer was applied in the field containing BHC.7 and the relative location of the tracer site was shown in Figure 5.7. Bromide migration to eight ceramic cups was also investigated; these cups were located in the same farm field as BHC.7 (see section 5.4.4). The results of monitoring and associated discussions are presented here.

In summary, the tracer tests highlighted that the time of travel for solutes from ground surface, through the subsoil, to the groundwater body was in the order of months, approximately 44 days to peak groundwater concentration, under spring recharge and a single irrigation of dirty water (15mm). Indeed, bromide was transported in the groundwater to three other piezometers before the bromide peaked at 1m-depth in all the active ceramic cups in the subsoil of the field in which the tracer was applied. This suggests that bromide moved preferentially to the groundwater body and was more quickly transported through karstified bedrock than through the subsoil matrix.

Summary results are presented in Table 6.14. Results of all analyses for piezometer BHC.7, all other piezometers and the ceramic cups are presented in Appendix S. Bromide breakthrough behaviour was different for each of the eight ceramic cup locations but the peak concentrations all occurred around the same time in June (approximately 140 days after bromide application). The observed occurrence of bromide in all eight ceramic cups is shown in Figure 6.38 to demonstrate that the trend of bromide concentration is similar, despite cup 5 being more responsive.

Table 6.14 Summary results for all monitoring instruments of the Bromide tracing experiment (1mm Br applied on 29th January 2003).

[+] Note: This column lists instrumentation as they are arranged in the field (see Figure 5.8)

Sampler I.D.[+]	**Depth (bgl)**	**Media Investigated**	**Dirty Water Applied**	**Dirty Water Depth**	**Time of Bromide first arrival (Date)**	**Velocity to first arrival**	**Recharge to first arrival[+]**	**Time to peak Bromide**	**Recharge prior to Peak[+]**	**Peak Br concentration**
Cup 5	1m	Subsoil	30th Jan 2nd Feb*	32mm	16 days (13 Feb)	0.062 m/day	66mm	144 days	182mm	748 mg/l
Cup 6		Subsoil	31st Jan	16mm	106 days (15 May)	0.009 m/day	165mm	>141 days	>195mm	141 mg/l
Cup 7	1m	Subsoil	1st Feb	16mm	44 days (13 Mar)	0.023 m/day	115mm	141 days	195mm	271 mg/l
Cup 8	1m	Subsoil	2nd Feb	16mm	23 days (20 Feb)	0.043 m/day	50mm	only 1 sample	unknown	>0.3 mg/l
BHC.7	**30m**	Groundwater	**8th Feb**	**16mm**	**18 days (15 Feb)**	**1.66 m/day**	**50mm**	**44 days**	**115mm**	**5.04 mg/l**
Cup 4	1m	Subsoil	22nd Feb	16mm	126 days (4 June)	0.008 m/day	165mm	148 days	148 days	247 mg/l
Cup 3	1m	Subsoil	23rd Feb	16mm	148 days (24 June)	0.007 m/day	195mm	only 1 sample	unknown	>76 mg/l
Cup 2	1m	Subsoil	24th Feb	16mm	44 days (13 Mar)	0.023 m/day	115mm	121 days	121 days	214 mg/l
Cup 1	1m	Subsoil	25th Feb	16mm	30 days (27 Feb)	0.033 m/day	56mm	>106 days	>106 days	>128 mg/l

Bromide Migration to other Groundwater Monitoring Locations on Curtin's Farm

Sampler I.D.	**Depth (bgl)**	**Media Investigated**	**Dirty Water**	**First Observance of Bromide (Date)**	**Total Effective Rainfall Recharge to first arrival**	**Calculated Groundwater Velocity**	**Peak Br concentration**
BHC.4	33.5m	Groundwater	See details above for cups and BHC.7. DW was only applied in the traced plot.	44 days (13 Mar)	115mm	~8 m/day (see section 6.5.3.2)	5.9 mg/l
BHC.5	27.5m	Groundwater		44 days (13 Mar)	115mm		0.34 mg/l
BHC.9	33m	Groundwater		98 days (6 May)	170mm		5.71 mg/l
BHC.10	30m	Groundwater		51 days (19 Mar)	116mm		0.4 mg/l

*Note: ceramic cup number five accidentally received a double dosing of dirty water.

Bromide applied to the ground surface at the end of January responded to recharge and first appeared at the 1m monitoring depth in 16-148 days in response to recharges, for the corresponding periods, of 66-195mm respectively. Bromide appeared in the groundwater (piezometer BHC7) 18 days after application at ground level in response to a total of 50mm recharge and it persisted for a further 26 days. The observed concentration of bromide in the groundwater peaked at ~5mg/l Br^- some 44 days after the bromide was applied, during which time 115mm of effective recharge (some rainfall and some dirty water) entered the subsoil.

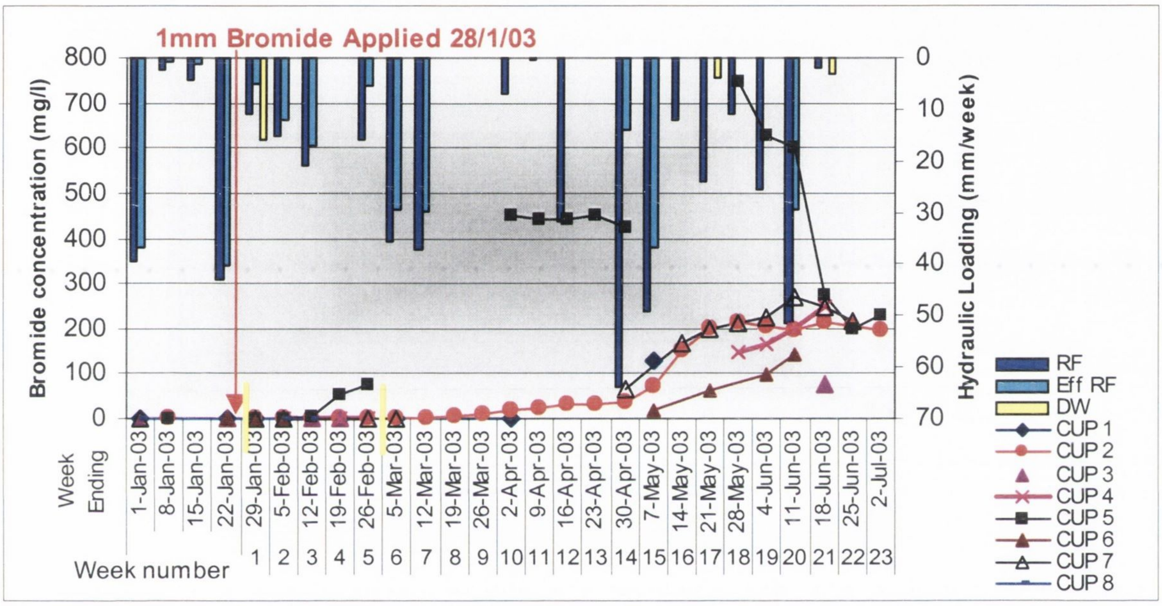


Figure 6.38 Bromide tracer trend behaviour at 1m-depth in the subsoil ceramic cups and hydraulic loadings for the duration of the experiment (a discontinuous line in this graph, such as observed in the 'cup 5' concentration trend, denotes that the sampler/cup did not yield a sample during that time period). ['RF'= rainfall, 'Eff RF' = calculated effective rainfall, 'DW' = dirty water irrigation].

Table 6.15 presents the loadings and bromide responses sequentially for the entire bromide experiment.

Table 6.15 Sequence of events in the Bromide Tracing Study.

Day Number	Significance	Cumulative Hydraulic Loading
Day 1	1mm Bromide Tracer irrigation	1mm Br
Days 3 - 5	16mm dirty water irrigation to cups 5, 6, 7, 8 & 5$^+$	24mm
Day 16	Bromide breakthrough in cup 5$^+$	66mm$^+$
Day 18	Bromide breakthrough in groundwater at BHC.7	50mm
Day 23	Bromide breakthrough in cup 8	50mm
Days 26 - 28	16mm dirty water irrigation to cups 1, 2, 3 & 4	
Day 30	Bromide breakthrough in cup 1	56mm
Day 44	Bromide breakthrough in cup 2 & 7 Bromide **peak** in Groundwater at BHC.7 Bromide appears in BHC.4 & BHC.5	115mm " "
Day 51	Bromide appears in BHC.10	116mm
Day 62	39 cows graze the field for 1 day (1st graze)*	116mm
Day 64	Cup 5 active again after 4 dry weeks	116mm
Day 91	39 cows graze strip over cups 1-4 (2nd graze)*	140mm
Day 92	39 cows graze centre of field	no cups
Day 93	39 cows graze strip over cups 5, 6, 7 & 8	140mm
Day 98	Bromide reappears in BHC.4 & BHC.5, also BHC.9	170mm
Day 106	Bromide breakthrough in cup 6	170mm
Day 108	4mm dirty water irrigation to cups 5, 6, 7 & 8 (a)	186mm
Day 115	4mm dirty water irrigation to cups 1, 2, 3 & 4 (a)	186mm
Day 121	39 cows graze strip over cups 1-4 (3rd graze)* Bromide **peak** in cup 2	186mm
Day 122	39 cows graze centre of field*	no cups
Day 123	39 cows graze strip over cups 5, 6, 7 & 8*	192mm
Day 126	Bromide breakthrough in cup 4	192mm
Day 128	Bromide reappears in groundwater at BHC.7	192mm
Day 138	3mm dirty water irrigation to cups 5, 6, 7 & 8 (b)	222mm
Day 141	Bromide **peak** in cup 7	222mm
Day 143	3mm dirty water irrigation to cups 1, 2, 3 & 4 (b)	222mm
Day 144	Bromide **peak** in cup 5	222mm
Day 148	Bromide breakthrough in cup 3	222mm
Day 155	Groundwater bromide has persisted in BHC.7 since Day 128 (at low concentration: Mean = 0.33 mg/l Br)	204mm

Explanatory Notes

- **Total Hydraulic Loading** = Br + effective rainfall+dirty water + urination load since Day 1
- $^+$cup 5 (only) accidentally received a second 16mm dosing of dirty water (see Table 6.14)
- * Potentially each urination could charge a cup with 6mm urine, and so it is added here
- Note reference (a) SMD calculated to be 5mm when that 4mm of dirty water was applied
- Note reference (b) SMD calculated to be 10mm that 3mm dirty water added

6.5.2. Behaviour of the Bromide Tracer in the Subsoil

Recharge from rainfall was observed to have had significant influence on the trend of bromide tracer concentrations observed in subsoil pore-water samples collected by ceramic cups. It is also obvious that one cup, 5, responded earlier and with far greater amplitude of tracer concentration than all other cups. The field technician described cup 5 as the most active of all 96 cups used over the two-year monitoring period of the nitrate leaching experiment. This cup also accidentally received a second dose of dirty water, on the 2nd February three days after the first dirty water irrigation (refer to Table 6.14). Only cup 5 received the initial double dosing of dirty water and because it was not part of the experimental design the results were not duplicated.

Figure 6.38 clearly demonstrates that three distinct recharge-defined periods operated during the tracing experiment. A wet time-period occurred at the beginning where most of the rainfall contributed to recharge because there was little or no soil moisture deficit (SMD). Secondly there was a dry spell in the middle time-period where there was no effective rainfall/recharge and the SMD grew. Finally, there was a time-period of heavy rainfall in which showers were often intense but with little calculated effective recharge. In the first period, only cup 5 responded significantly. Although bromide was observed to breakthrough to 1m-depth in four other cups (1, 2, 7 and 8) the concentrations were less than 1mg/l in each case. In the second period: from mid March to the end of April there was a relatively dry spell where there was no rain for four weeks and the SMD reached 39mm. There was no effective rainfall in seven weeks. At this stage in the experiment only cups 2 and 5 returned samples (refer to Appendix S). During this dry period the concentrations of bromide in the pore water samples returned from cup 2 rose slowly but continuously from approximately 0.5 to 32mg/l Br. The concentration in cup 5 was over ten times greater at 440 mg/l Br. The bromide concentrations from both cups levelled off until recharge began again. In the final period when the rain began again, the showers were intense and on two occasions, the 13th and 24th April, the daily rainfall was ~30mm. All cups became active together and bromide concentrations rose in seven cups despite only 51mm effective rainfall at the end of April and early May. Clearly, meteorological recharge is not the only driver on the system. Dirty water was applied and cows grazed. The system is inherently noisy making it difficult to define a consistent message from the non-uniform response of the monitoring instruments and the loadings to the system.

Essentially, there are three distinct hydrological loadings to the subsoil system. Rainfall is a permanent source that occurs in sporadic events. Urinations from grazing animals (at the grazing densities in the field) are another source of driving hydrological load. Under the Curtin's farm management system, the dirty water irrigator, the third hydrological loading source, moves into a field directly after it has been completely grazed. Because these three loadings happen so close together it is difficult to distinguish which of these loadings is the crucial driver for the tracer migration through the subsoil. It is possible, though, to convert all these loadings to approximate comparable depths of application that can be cumulated to distinguish the depths of recharge that affect changes of solute concentration in the subsoil and the groundwater. Rainfall and dirty water already are referred to in millimetre (mm) depths. The approximate equivalent depth of application arising from a single urination from a grazing animal was determined to be 6mm (refer to section 5.5.2.7 for calculation details). The way in which fields are grazed on Curtin's farm ensures that at least 50% of the field's area is affected by urine deposition. Therefore, for this analysis, whenever the field is grazed a recharge of 6mm was added as a potential impact on each cup.

The response of different subsoil ceramic cups to recharge may highlight the main controls on the leaching of solutes. All meteorological and agronomic loadings and bromide response details for each cup are tabulated in Appendix S. In total, cup 5 received 32mm of dirty water in the first week of the experiment and then 34mm effective rainfall, totalling **66mm** recharge in three weeks, to effect a breakthrough concentration of 2.7mg/l Br in the **third week** of the experiment. The concentration rose to 52 mg/l Br and to 76 mg/l Br in fourth and fifth weeks, despite only a further 6mm effective rainfall. This highlights the action of infiltration pathways under gravity on the leachate process, as well as known processes in solute transport such as dispersion/diffusion. Then the cup did not return any samples at all until week nine. A concentration of 452 mg/l Br was observed in week nine when the cup demonstrated response to two consecutive weeks of 30mm effective rainfall, totalling **60mm** recharge, at a time lag of, again, **three weeks**.

The bromide concentration in cup 5 then plateaus for five weeks and despite no additional recharge to the system the cup returns five consecutive samples, while six of the seven other cups are dry. Cup 5 then dries up and returns no samples from week 15 to 18 until a value of 748mg/l mg/l Br is recorded in the sample collected on the 29th May, week 18. The question arises as to what might have caused the re-emergence of water in this sampler and the 70% increase in bromide concentration. Three things happened in the time period in which the cup was inactive: the cows grazed the plot for 2.5 days; there was 51mm effective rainfall; and the plot was irrigated with 4mm of dirty water. Figure 6.39 strongly indicates that the bromide concentration in cup 5 follows the same incremental stepwise pattern as recharge: **51mm** of effective rainfall falling in weeks 14 and 15 affects leachate down to 1m depth, in the cup-sampler in week 18, and at a concentration of 748mg/l mg/l Br.

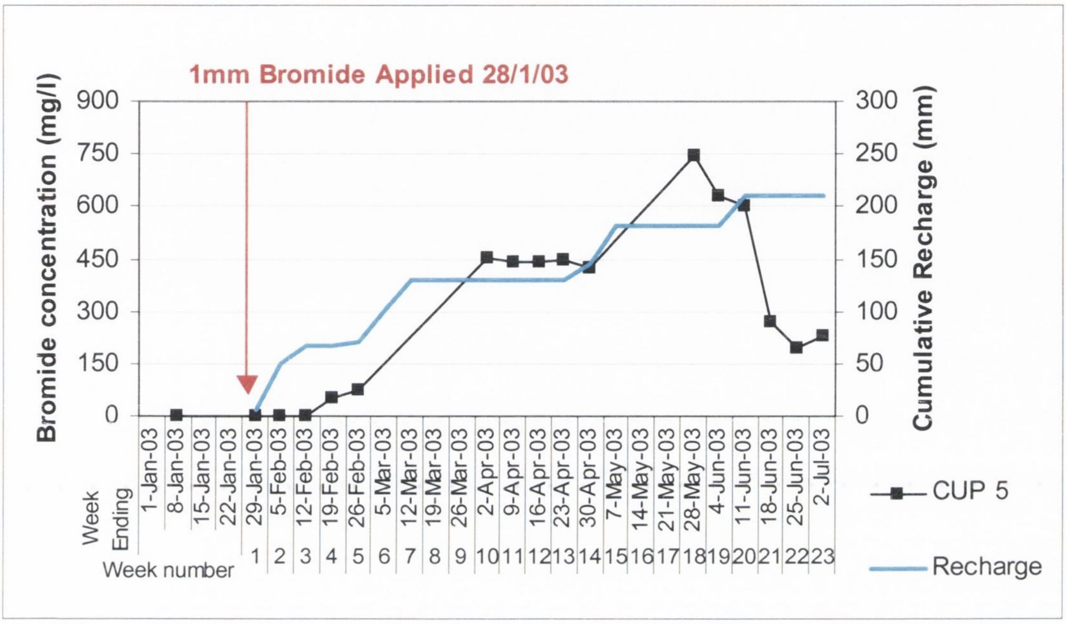


Figure 6.39 Bromide tracer trend for cup 5 and cumulative recharge (applied dirty water and weekly effective rainfall) since experimental day 1, 28th January 2003.

As in the two previous cases of recharge-induced bromide leaching to this cup, 5, a **three-week** time lag was observed between recharge and increased bromide concentration in the cup. Thereafter, further recharge acts only to dilute the bromide concentration in cup 5, suggesting that the bromide front has passed the 1m-depth after 23 weeks. No more samples are returned from the cup because of summer weather conditions. However, there are three instances where similar recharge, ~60mm in two weeks, resulted in bromide concentration augmentation at 1m depth in the soil profile with a three week time lag. The fact that cows grazed the plot, for the first time in the experimental period, for one full day on the 31st March and then two-days later the bromide concentration, in a previously dry cup 5, was 452 mg/l Br may be coincidental. There is a possibility that a urine patch deposited in the area around the sampler may have provided the necessary hydraulic loading - although there is no evidence. Nevertheless, the grazing and urine deposition is a normal part of the agricultural routine and is a contributor to nitrate leaching, which is an integral part of the bromide tracing experiment.

Adding the response behaviour of the other cups to that for cup 5 results in Figure 6.40, which shows similar trends of bromide behaviour, albeit delayed, and with lower concentrations. It can be observed from Figure 6.40 that all cups show response by weeks 14 and 15 after bromide application. Indeed, it is not until early May that all the cups start to respond together.

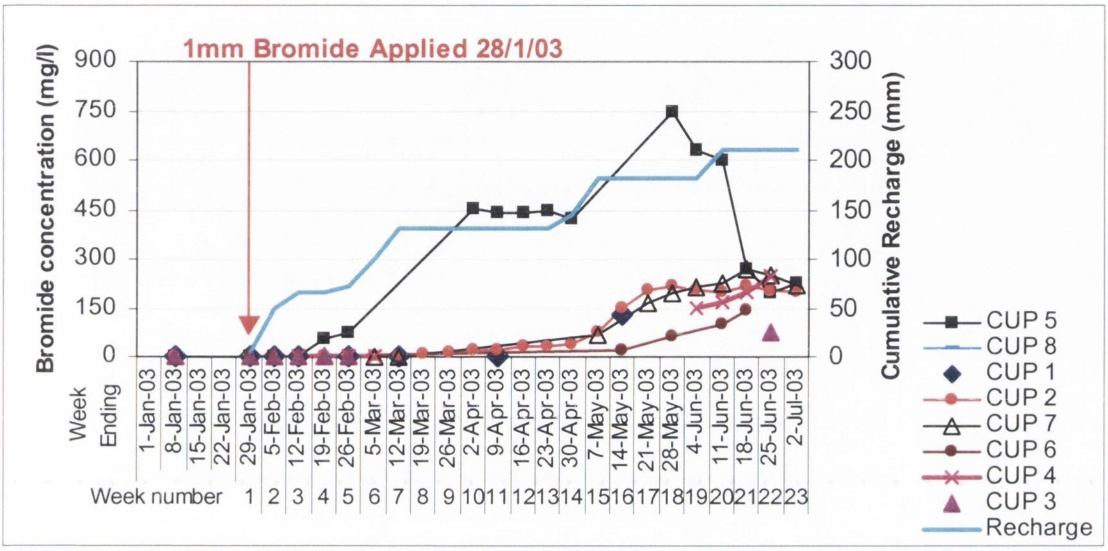


Figure 6.40 Bromide tracer trend for all cups and cumulative recharge (applied dirty water and weekly effective rainfall) since experimental day 1, 28th January 2003.

Removing the data for cup 5 from Figure 6.41 will allow closer examination of the early bromide tracer trend behaviour data for the other seven cups.

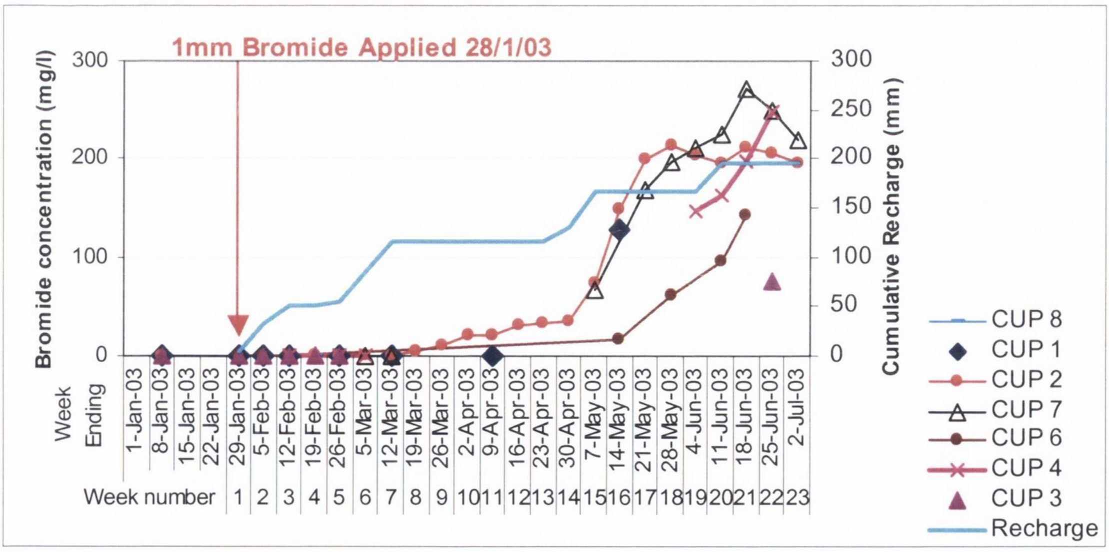


Figure 6.41 Bromide tracer trend for cups numbered 1-4 and 6-8 and cumulative recharge (applied dirty water and weekly effective rainfall) since experimental day 1, 28th January 2003. (The order of the legend relates to the times of first arrival for those cups: cup 8 showing first and cup 3 last).

6.5.3. Behaviour of the Bromide Tracer in the Groundwater

6.5.3.1. Observed Bromide in the Groundwater

With regard to the groundwater abstracted from the piezometer at the centre of the tracing investigation, BHC.7, the 'time of first arrival' of bromide to 28m bgl was 18 days (14/2/03) after its application on the ground surface (Figure 6.42). Bromide was observed in the groundwater abstracted from BHC.7 on seven occasions from the 14/2/03 to 5/3/03. Bromide concentrations were low on these seven occasions, ranging from 0.25-1.15 mg/l Br. Groundwater abstracted from BHC.7 on the 10th of March had no detectable bromide. However, intense rainfall was experienced on that day (12.6mm of actual rainfall was recorded, which was calculated to be 11.4mm effective rainfall). The maximum groundwater bromide concentration at BHC.7 was then recorded on day 44 (12/3/03) in association with a water table peak, which was a response to approximately 65mm effective rainfall in the first two weeks of March. Further sampling events did not result in detection of bromide in BHC.7 until early June (5/6/03) when a summer recharge event caused another rise in groundwater levels. Bromide was again detected on the 19th June and the 1st of July.

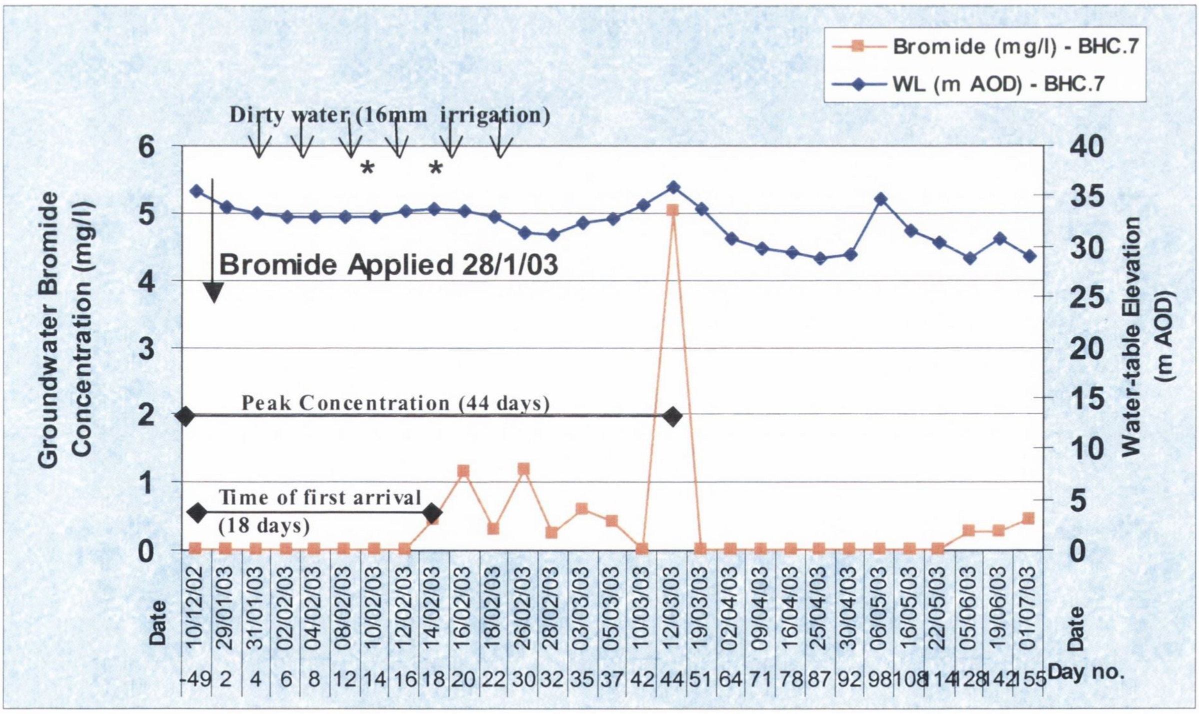


Figure 6.42 Bromide concentration in groundwater piezometer BHC.7 and associated water table elevation trend.

The impact of effective rainfall on the concentration of bromide in the groundwater abstracted from piezometer BHC.7 can be examined in Figure 6.43 (in this Figure all data were averaged on a weekly basis for the purposes of clear representation of the effect of cumulative effective rainfall). The cumulative effective rainfall pattern is stepped and at the beginning of the experiment the bromide appears to respond much more quickly. The 50mm recharge in late April seems to be reflected by a stepped increase in groundwater bromide concentration in late June and the effective rainfall of early June causes a further increase in bromide in early July.

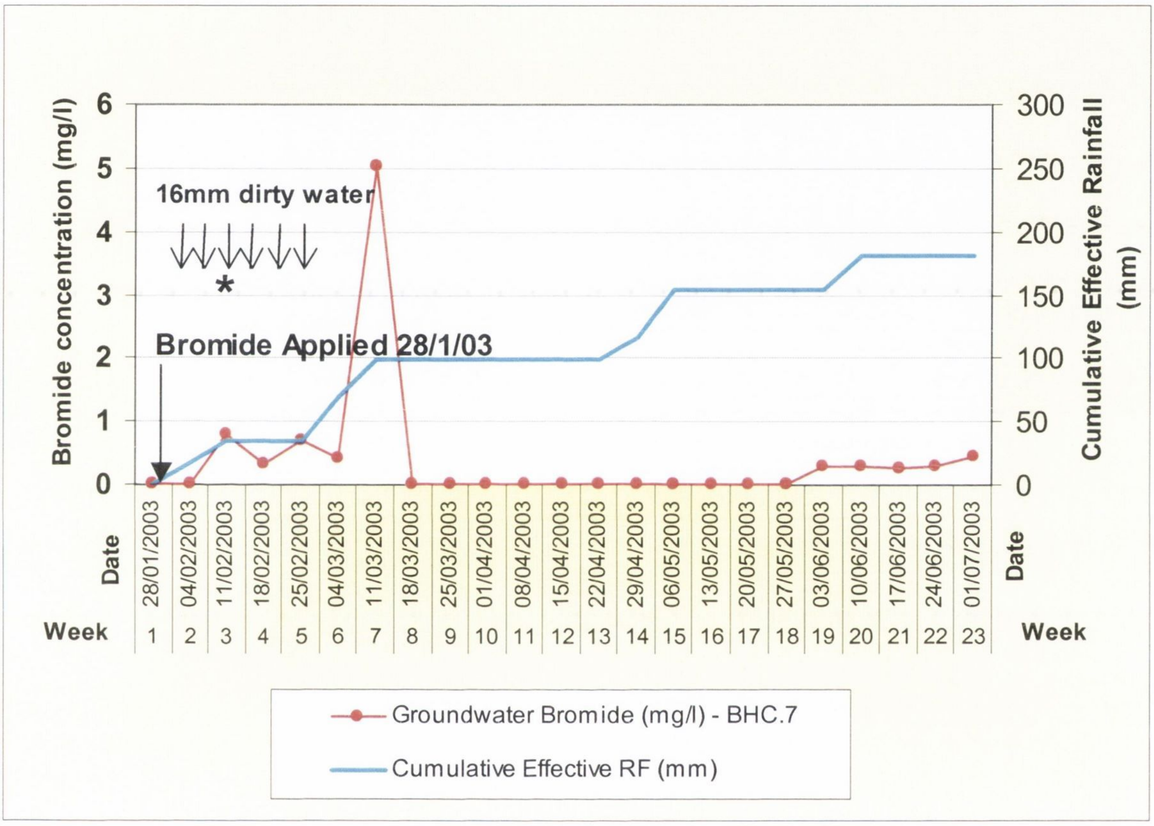


Figure 6.43 Average weekly groundwater bromide concentration at BHC.7, weekly cumulative effective rainfall for the monitoring period and dirty water irrigation in the field in which BHC.7 is sited.

6.5.3.2. Tracer Transport in the Groundwater

In the two weeks before 10th March (day number 42 after bromide addition) 80mm rainfall was recorded, which was estimated to result in 65mm of effective rainfall. These heavy rains in early

March caused water levels in all piezometers to rise by 0.5m on average, but by more than 1m in BHC.7 (Appendix J). Figure 6.44 shows the observed occurrences of bromide in the groundwater abstracted from all piezometers on the farm. On the 12th March (day number 44 after bromide addition) bromide appeared in samples collected from the groundwater abstracted from piezometers BHC.4 and BHC.5.

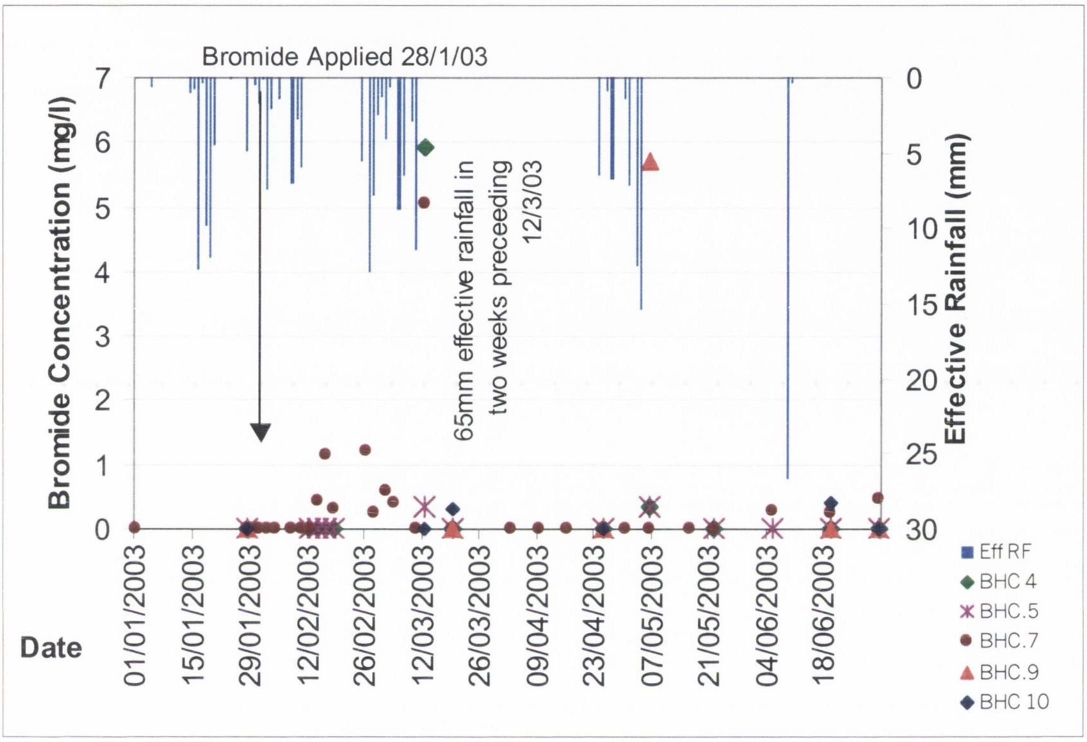


Figure 6.44 Observed appearance of bromide in all piezometers.

Therefore, with conservative estimations, the minimum horizontal velocity in the aquifer under the central farm area could be calculated as follows:

- Bromide was first detected in BHC.7 on the 18th day after bromide application at ground surface (see Figure 6.42);

- Bromide was then detected in BHC.4 and BHC.5 on day number 44 after bromide addition (see Figure 6.44);

- If the bromide observed in BHC.4 and BHC.5 was that which was detected in BHC.7 on day 18 then it follows that the horizontal travel time in the aquifer could be calculated based on tracer migration over a distance of 200m in 26 days (day 44- day 18). This suggests a travel time of 7.7 m/day.

However, a groundwater velocity of ~8m/day is remarkably slow for some kinds of Irish karst aquifer. Other Irish investigations of karstified bedrock have demonstrated that groundwater velocities can vary from 5-10m/hr in low flow conditions (Coxon & Drew, 1986) to 100-200m/hr in highly karstified conditions (Coxon & Drew, 2000). An alternate, more subjective, methodology for groundwater velocity calculation at Curtin's farm could take the following form:

- The concentration of bromide in groundwater abstracted from BHC.4 on the 12th March (day 44) was 5.9 mg/l Br, which would appear to be more closely related to the second, larger, wave of bromide (5.04 mg/l Br detected in BHC.7 on the 12th March). It might be considered unlikely that the almost 6mg/l Br observed in BHC.4 on the 12th March related to the approximately 1mg/l Br observed on three consecutive occasions at the time of first arrival at BHC.7 (days 18 – 22). The impact of 65mm effective rainfall, in the first two weeks of March, could have been to energise bromide migration to BHC.4. It is possible that the detection of bromide at BHC.4 (on day 44) directly resulted from the arrival of bromide at BHC.7 between the 10th and 12th of March (see Figure 6.44). Therefore, the calculation of horizontal travel time in the aquifer could be as follows:
    - Both BHC.4 and BHC.7 returned spikes of bromide concentrations of 5-6mg/l Br on the 12th March;
    - Therefore, it could be argued that travel times, for 200m, were less than 2 days.
    - The potential horizontal travel time in the aquifer could then be calculated to be 100–200m/day.

However, this 100-200m/day travel time is highly unlikely given the recession characteristics of BHC.4 & BHC.7 (see sections 6.4.6.5 & 6.4.6.7). The previous work of Coxon & Drew (1986 and 2000) studied conduit flow systems in the west of Ireland. Conduit groundwater flow velocities are likely to be higher than those in the weathered fissures beneath Curtin's Farm. Therefore the lower groundwater velocity of ~8m/day will be accepted in this work.

By the 19th March (day number 51) bromide was also observed in piezometer BHC.10 but unfortunately the samples abstracted from BHC.9 were lost in the field. However, in the last weeks of April and first week of May heavy showers effected bromide transport again in the aquifer. Water levels rose by 1.8m, on average, in all piezometers but a water level rise of 5.5m was observed in BHC.7. This water level rise observed on the 6th May resulted in bromide appearing in groundwater samples taken from three piezometers: BHC.4, BHC.5 and BHC.9, all approximately equidistant from BHC.7. Groundwater flow direction radiates from BHC.7 towards BHC.4, BHC.5, BHC.9, & BHC.10 (see Figure 6.45 for groundwater flow directions). In this way the tracer experiment confirmed the conceptual groundwater flow model. Appendix S contains the bromide concentration results returned from groundwater sampling in all piezometers.

6.5.3.3. Piezometric Water Levels During Tracer Experiment

The behaviour of all piezometer water levels to recharge during the tracing experiment is presented in the bromide experiments results appendix (Appendix S) in the form of water level changes between each monitoring day. Water levels in the piezometers dropped continuously for most of the experiment, but only on four occasions did the water levels rise and these occasions are highlighted in Appendix S. On the first occasion it is not effective recharge, but the presence of the dirty water irrigator in the tracing plot that caused a rise in groundwater levels in some of the piezometers. Bromide was found in 80% of those piezometers that demonstrated a rise in water levels in response to dirty water irrigation in the central farm area. On the other three occasions, effective rainfall was significant and caused a rise in groundwater levels in all piezometers. The evidence is strong that agricultural practice in the immediate vicinity of each piezometer affects the recharge at that piezometer depth. This is borne out by the fact that effective rainfall recharge events did not result in the same degree of transport of the bromide in the groundwater body as that affected by the dirty water transport as well. A water table elevation map is presented for a typical occasion during the bromide tracing experiment in Figure 6.45. The groundwater mounding at BHC.7 is particularly evident in this map, groundwater elevations were elevated 4m at this location.

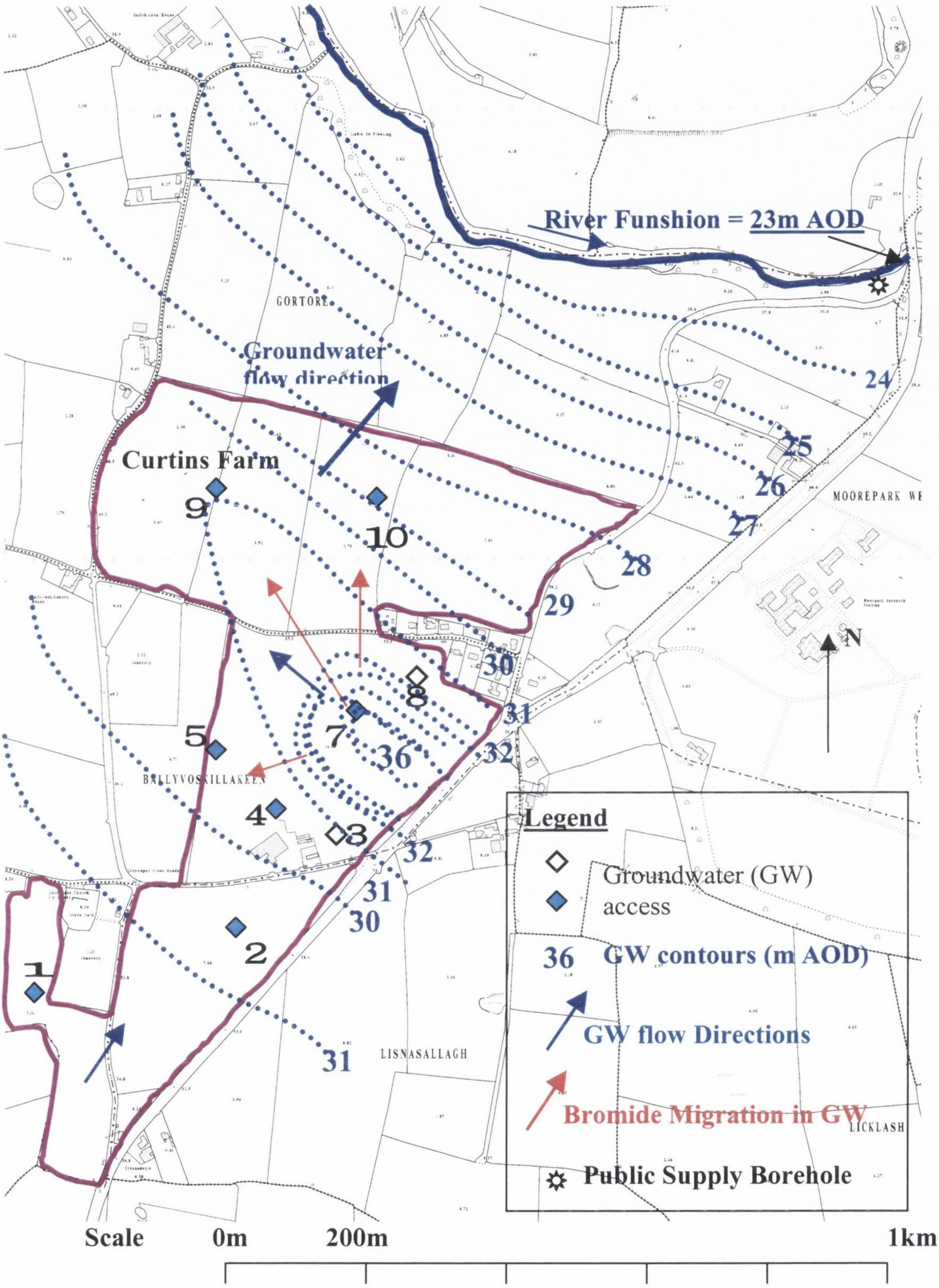


Figure 6.45 Water table elevation contours for the 12th March 2003, during the tracing experiment, when bromide was observed in other piezometers.

6.5.4. Discussion of Tracing Results

It can be reasoned from Table 6.15 that approximately 50mm recharge was enough to effect a breakthrough of the bromide tracer in three cups as well as the groundwater directly beneath the study field, in the first 30 days of the experiment. That 50mm comprised 16mm dirty water application and 34mm effective rainfall. A further 50mm of recharge, from effective rainfall, resulted in three more significant events. Bromide breakthrough occurred in two more cups; the observed peak bromide concentration for groundwater in the piezometer at the centre of the investigation and the appearance of bromide in groundwater samples taken from two piezometers located ~200m from the area dosed with the tracer. Following these events, a further 100mm recharge ensured that all cups had some degree of tracer breakthrough, or even peak concentration. However, bromide appeared in other down-gradient piezometers before its breakthrough in three of the five subsoil cups.

Of the eight cups at 1m-depth under investigation, three were insufficiently active, in a hydrological sense, to allow comment on anything other than breakthrough. Three other cups demonstrated peak activity around the same time in late May/early June. Bromide concentrations in two other cups approached expected peaks in a similar time frame to the other three cups but had failed to show diminishing bromide concentrations before the cups dried up in July. However, of the five cups in which the trend in tracer concentrations could be examined all cup concentrations peaked after the bromide peak was observed in the groundwater body at 30m below the ground surface.

Bromide was transported in the groundwater from BHC.7 to BHC.4 and BHC.5, ~200m horizontal distance, and observed to peak in these other piezometers two months before the bromide arrived at most of the 1m-depth ceramic cups in the subsoil of the field in which the tracer was applied. This suggests that bromide moved preferentially to the groundwater body and was more quickly transported through fissure karst than through the subsoil matrix. This effect does not preclude piston flow in the soil/subsoil matrix - it merely supersedes it initially. The literature certifies that solute transport may proceed simultaneously in two different modes: one by complete displacement of existing soil water, the relatively slow moving piston flow, and the other by short-circuiting through the vertical soil column, commonly referred to as by-pass or preferential flow (Quisenberry & Phillips, 1976; Iqbal & Krothe, 1995 & 1996; Peterson *et al.*, 2002). A US tracing experiment detected the applied bromide throughout 6.5m of fractured till and in the underlying aquifer almost immediately after the first rainfall after tracer application (Schuh *et al.*, 1997).

The piston-type passage of the bromide plume through the 1m-depth in the subsoil, in response to effective recharge events in early May and early June, is reflected in a second and third groundwater bromide response in early June and July respectively. The piston-flow observed movement of bromide suggests a time lag of between one and two-months between 1m depth in the subsoil and the 30m-depth screened interval of the groundwater body. Already, the data for cup 5 highlighted a one-month lag time between surface recharge and impact at the 1m-depth (notwithstanding a possible increased local hydraulic loading) and the data results from cups 1, 2, 6 and 7 imply a two-month response lag to recharge. Therefore, there is already strong evidence of a travel time in the upper 1m of subsoil of 0.5-1m/month. If this travel time was replicated for the remaining 1m depth of subsoil, to the top of the epikarst at 2m, then the subsoil data validates the second and third groundwater response, when considering the piston-transport mechanisms governing the behaviour of the bromide tracer in this later portion of the experiment.

Interestingly, no cup shows response to over 30mm of rainfall in week twelve (13th April), when there was a calculated SMD of >30mm and consequently no calculated effective rainfall. Generally, all cups seemed to respond together in the first week of May, experimental week 15, after which they consistently showed increases in bromide concentration. The average weekly rainfall during the experiment was 20mm. On two occasions in April there were ~30mm/day rainfalls, mostly in heavy showers. These heavy rainfalls may not receive enough recognition in the role they might play in recharge, as incorporated in the meteorological balance approach of this study. The soil moisture accounting methodology does not allow for the role of rainfall intensity or preferential flow, and these are shortcomings of the methodology. On the 12th April the SMD was 37mm and the following day 29mm of intense rain fell. On the 23rd April the SMD was 19mm and the following day 33mm of rain fell in intense spring showers. Further research is required to specifically investigate the role of these intense showers on contaminant transport.

On the 29th of April, experimental week 14, 39 cows began to graze the field under investigation. The field, as part of normal grazing management on the farm, was divided into three, with only one third of the field open to the cows on the first day, two-thirds on the second day and finally the entire field on the third grazing day. Therefore, grazing density is three times heavier on the first rather than the last day. The strip of land above cups numbered 1-4 was grazed first. They progressed through the field in two and a half days until the strip of land housing cups 5-8 was grazed on the 1st May.

What is worth noting, from Table 6.15, is that despite differing times of first arrival of bromide in each of the seven cups, five show significant response at the same time in early May, week 15 (Figure 6.40). Cups 1 and 2 respond in the same week as cups 5, 6 and 7 even though those latter cups were irrigated with dirty water one month earlier. These five cups are responding to a loading other than the dirty water: it is a response to the two intense rain days of April and/or the cattle grazing at the end of April.

Investigations have previously found that substantial amounts of nitrate can be observed, under previously marked urine patches, to have travelled to below 1m-depth in the subsoil in November despite a soil water deficit of about 15mm (Garwood & Ryden, 1986). Percolation through macropores in the 'dry' soil, followed by the hydrolysis of urea and nitrification of the resultant ammonium are possible reasons for the migration of nitrate to greater than 1m in soil moisture deficit conditions (Whitehead, 1995) and this is supported by the presence of ammonium with a peak concentration at a slightly shallower depths in the soil profile (about 1m) than that of nitrate (Ryden *et al.*, 1984, cited in Whitehead, 1995). These issues have been discussed in detail in section 2.4.

The tracer experiment confirmed the conceptual groundwater flow model: that groundwater flow radiates from BHC.7 was proven. Travel times were also computed and these were within ranges measured in other Irish karst aquifers (e.g. Coxon & Drew, 1986; Drew *et al.*, 1995; Coxon & Drew, 2000).

6.5.4.1. Significance of Depth of Dirty Water Irrigation

It is clear that no cup, other than number 5, displayed a massive response to the dirty water applied at the beginning of the experiment. From this it may be inferred that the usual irrigation depth of 16mm may not be sufficient in itself to cause significant leaching of solutes to 1m-depth in the soil. The evidence from cup 5 suggests that a dirty water irrigation of 32mm, in association with natural recharge, can significantly affect initial pore water bromide concentrations at 1m. It is the total hydraulic loading, whether natural rainfall or dirty water, that appears to govern travel time.

6.5.5. Tracer Monitoring Results in the Context of other Field Monitoring Results

Permeability tests carried, out in the course of this investigation, on the subsoil in five different fields on the farm reveal that the plot in which the tracer was applied has a higher hydraulic conductivity, in the upper 1m, relative to other plots. Generally, at the upper 0.5 and 1m depths investigated the relative saturated hydraulic permeability was at least an order of magnitude greater in the traced area than two other plots located less than 200m away (refer to section 6.1.1.3 for details). Investigations at the 1.5m depth revealed subsoil conductivity values similar to, or less than, that measured in the other plots. Bohlke (2002) suggests that indirect effects of infiltration of agriculturally contaminated water with high ionic strength of acidity include increasing weathering rates. Rates of leaching may therefore be enhanced by physico-chemical and biological changes in the subsoil caused by increased acidity and the ionic strengths of agriculturally impacted or derived recharge. The fact that the rate of solute migration may be higher in the tracer area than other parts of the farm does not negate the validity of the tracer experiment. Recharge that falls on the traced area travels with the groundwater to other parts of the farm carrying solutes with it. During the course of this tracing experiment alone there were five days in which natural rainfall exceeded the depth of water deposited by the dirty water irrigator and three occasions when daily rainfall was 30mm or more.

6.6. Preliminary Testing Of Proposed Modelling Strategy At Curtin's Farm

The work presented in this section represents a preliminary testing of the chosen modelling strategy, which was justified in section 3.9. Recommendations for future modelling strategies are discussed in section 6.6.5.

6.6.1. Curtin's Farm Conceptual Leaching Model

At its most abstract, a model is a unification of learnt concepts of the aquifer (Price, 1996), or the system under investigation. As noted in section 6.1.1.1, Curtin's farm subsoils comprise a mixture of coarse and fine-grained materials, namely till, and are directly influenced by the underlying bedrock, which is limestone. Limestone fragments tend to dominate the till which, when described using BS 1377 (1990), varies from silty SAND with frequent/abundant gravels to angular sandy GRAVELS with clay (GSI, 2000). Laboratory analyses of subsoil samples returned during borehole drilling in the course of this experiment concur with the GSI soils classification. The overburden depth is 2.5m, on average, but undulates in depth from 0-4.5m, consistent with the karst terrain. Bedrock outcrops abound in the area and rock is visible at the surface at four locations, at least, on the 50ha farm.

The hydraulic conductivity of the subsoil is high. Results from my investigations suggest saturated hydraulic conductivities (K_{sat}) of 0.14m/day in the topsoil, 0.07m/day at 1m-depth and approximately 1m/day in the subsoil layer at 2m-depth, on average. Others (Gibbons *et al.*, 2003) suggest K_{sat} values of 0.4m/day in the topsoil (0-3m-depth), 0.2m/day at 1.5m-depth and over 1m/day in the subsoil layer at 2m-depth: the epikarst, top of weathered limestone bedrock, is approximately 2.5m below ground level. The bromide tracing experiment, the results of which were presented in chapter six, section 6.5, revealed an average travel time of 0.3m/day to the 1m-depth in the subsoil. Of course, the travel times measured in the bromide experiment are not fully saturated values. For the reasons outlined in section 5.2.1.2, the highest values of K_{sat} measured at Curtin's farm (i.e. that measured by Gibbons *et al.*, 2003) will be used in the simulations discussed in this section. The surface infiltration capacity was also measured by Gibbons *et al.* (2003) to be 250mm/day.

The GSI methodology for assessment of groundwater vulnerability to contamination (GSI, 2003) rates a site on the basis of the depth of subsoil overlying bedrock and the permeability of that material. The methodology requires that a site of this nature, having an average overburden cover of less than 3m and high hydraulic conductivity, be assigned an 'extreme' vulnerability rating.

In essence, all groundwater is hydrologically connected to the land surface and the effectiveness of this connection determines the relative vulnerability to contamination (Fitzsimons *et al.*, 2003). Groundwater beneath Curtin's farm quickly receives water and solutes from the land surface and is hence a vulnerable groundwater. The bromide tracing experiment confirmed that travel time from the land surface to the groundwater body could be less than one month in winter recharge conditions. Analysis of groundwater level response to recharge showed that in each hydrological year, piezometer water levels demonstrated a significant response to RF_{eff} within one month of the onset of recharge. In the first month of recharge, groundwater levels rose by approximately 1m as a consequence of the first 80mm RF_{eff}. Overall in both years investigated, approximately 200mm/mth RF_{eff} fell in the wettest month of each year and this affected the same groundwater level response: groundwater levels, in the piezometers, rose by approximately 8m in each case.

The hydraulic conductivity measured in the groundwater body, presented in Table 6.16, concurs with both literature values (Brassington, 1995) for the secondary permeability of limestone bedrock and the results of the bromide tracing experiment.

Table 6.16 Relative magnitude of groundwater hydraulic conductivity measured by piezometer slug test.

K (m/day)	**10^{-3}**	**10^{-1}**	**10^{0}**	**10^{1}**
Piezometer	**BHC.10**	**BHC.3** **BHC.4**	**BHC.1** **BHC.7** **BHC.8**	**BHC.2** **BHC.5** **BHC.9**

Slug tests in piezometers indicated that the groundwater hydraulic conductivity is as great as 10^1 m/day in piezometers BHC.2; BHC.5; and BHC.9, which mark groundwater conduits observed during drilling. The values of hydraulic conductivity for BHC.5 and BHC.9 are very similar: 17.8 and 15.5 m/day respectively. The results of the tracer experiment indicate a good hydraulic connection between BHC.7, BHC.4, BHC.5 and BHC.9. Indeed, bromide was transported laterally in the groundwater from BHC.7 to BHC.4 and BHC.5, ~200m horizontal distance, and observed to peak in these other piezometers three months before the bromide front, moving vertically, peaked at 1m-depth in all the active ceramic cups in the subsoil of the field in which the tracer was applied. The hydraulic conductivity of the aquifer tested at BHC.7, the target piezometer of the bromide experiment, was 2.8m/day. This suggests a lower transmissive capacity for groundwater at this location on the farm, which leads to the groundwater mound observed in constructed water table contour maps generated in this study (see Figures 6.8 & 6.45 for a representative water table contour map).

Of the five ceramic cups, installed at 1m-depth in the subsoil, in which the trend in tracer concentrations could be examined, all cup concentrations peaked after the bromide peak was observed in the groundwater body at 30m below the ground surface (see section 6.5.4). This suggests that bromide moved preferentially to the groundwater body and was more quickly transported through fissure karst than through the subsoil matrix.

Results of all pertinent field investigations are presented in summary format in Table 6.17. These data were used to prepare the diagrammatic representation of the learnt hydrological controls on solute movement at the site, Figure 6.46. The modelling strategy adopted was justified in chapter three, section 3.9. Collated nitrogen loading data (section 5.5.2.6) were used as input to the root-zone nitrate leaching NCYCLE model (Scholefield, 1991). Output from the NCYCLE model was used to define subsoil porewater nitrate concentrations for use with the second step of my modelling strategy: RAM (ESI, 2000). The RAM model requires definition of the contaminant concentration in the subsoil. The subsoil and hydrogeological characterisation results (see section 6.1) were also employed within the hydrogeological risk model RAM application.

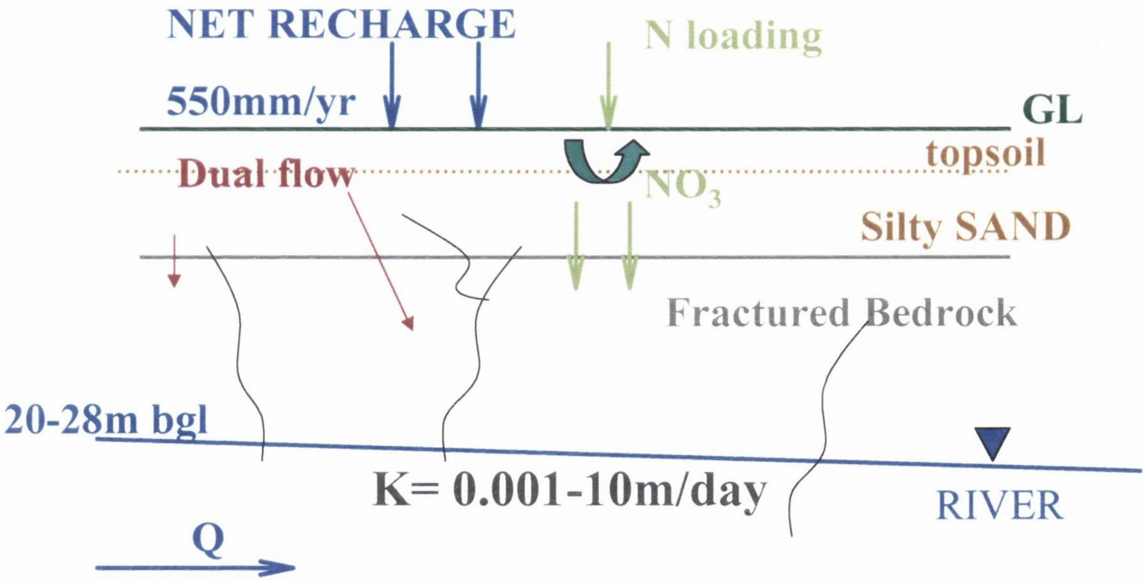


Figure 6.46 Schematic conceptual solute transport mechanisms at Curtin's farm.

Table 6.17 Curtin's farm - conceptual model data.

Overburden

Predominant soil type: Silty SAND (see section 6.1.1)

Depth range: 0-4m (see Figure 6.2)

Average subsoil depth 2.5m (calculated)

K_{sat}: Topsoil = 0.4m/day (Gibbons *et al.*, 2003)

K_{sat}: Subsoil = 0.2 – 1m/day (Gibbons *et al.*, 2003)

Surface infiltration capacity: 250mm/day (Gibbons *et al.*, 2003)

Porosity: 37% (Gibbons *et al.*, 2003)

Matrix vertical flow rate: 0.008m/day (Gibbons *et al.*, 2003)

Evidence of by-pass flow from ground surface to groundwater (section 6.5.4)

Bedrock (results of the investigation reported in this dissertation)

Karstified Waulsortian Limestone

Water Table ~25m bgl

Water Table seasonal range = 20-28 m bgl

Secondary permeability

Groundwater hydraulic conductivity = 10^{-3} - 10^{1} m/day

Evidence of some caverns @ 30m bgl

Good hydraulic connectivity between some piezometers (see section 6.5.3.2)

Horizontal groundwater velocity: 100-200 m/day (see section 6.5.3.2)

Vertical travel times: 1- 10m/day (see section 6.5.3.2)

Recharge Calculations (see section 5.5.3)

2001-2002: recharge volume = $2.32 * 10^{5}$ m^{3}

2002-2003: recharge volume = $2.32 * 10^{5}$ m^{3}

6.6.2. Soil Zone Modelling

Linkage between the unsaturated and saturated zones can be achieved by defining loading rates into the groundwater by regression analysis using measured field data for nitrogen fertilisation and leaching as a function of soil type and land use (CEC, 1991).

Actual subsoil nitrate leaching data was available for the 1m depth in the subsoil at Curtin's farm, as noted in section 1.5, which was supplied by M. Ryan of Teagasc. However, this subsoil leaching data for Curtin's farm was difficult to interpret because of the trends in cup concentration data, the indeterminable effects of preferential flow and residence time.. Replicate cups in each field behaved with wide variation in response to the same loadings. The problems with representative sampling of the unsaturated subsoil zone are well documented (e.g. Stockdale, 1999) and these issues have already been discussed in chapter three, section 3.5.3. Therefore, the actual Teagasc subsoil nitrate leaching data required careful analysis prior to its use as validation data for the NCYCLE simulations, which is the first step of my modelling strategy.

6.6.2.1. Definition of Subsoil Nitrogen Load

With regard to matrix or macropore flow being a flow mechanism that most significantly influences observed groundwater nitrate concentrations at Curtin's farm, analysis of the loads observed in the subsoil may shed some light on the issue. The farm-scale subsoil investigation (led by M. Ryan of Teagasc, Johnstown Castle) provided concentrations of nitrate returned in pore water samples taken from ceramic cups installed at 1m-depth in the soil profile, at 96 locations at Curtin's farm. Teagasc converted these pore water nitrate concentrations, which had been returned from the subsoil, to loads (kg) using antecedent effective rainfall data (knowing the concentration (mg/l) and the volume of recharge (litres) it is possible to use the data to provide loadings (mg, which can then be converted to kg). The loads were approximated to rates (kg/ha) so that they could be compared with the actual applied nitrogen loadings. All fields on the farm receive inorganic nitrogen (bagged-fertiliser). A grass growth response is observed after application of fertiliser nitrogen and this grass is consumed by grazing animals (see section 6.4.6). The grazing animals excrete much of the nitrogen they consume (see section 2.4). Analysis of nitrogen excretion loads from grazing animals showed that they excrete approximately 70 to 80% of nitrogen that was applied to the grass as inorganic fertiliser (see section 5.5.2.4). Some fields receive additional organic nitrogen loading in the form either dirty water or slurry. In this thesis, for the purposes of comparing calculated applied agronomic nitrogen load with the nitrate load observed in the subsoil, I considered the total organic load as that assumed to be available for loss, given that there is a grass growth response to fertiliser application (see sections 5.5.3 and 6.4.6). The whole tenet of the Nitrates Directive (EEC, 1991a) is the organic nitrogen loading rate. Therefore, I compared the total organic nitrogen loading rate data with 1m-depth pore-water nitrate concentration data to create Table 6.18. The load of nitrate returned from the soil is reported as a proportion of the organic load nitrogen that was applied to the field. NCYCLE simulations suggest that at these nitrogen loading rates 30%, approximately, will be lost by leaching.

Table 6.18 Proportion of applied organic nitrogen loading observed in porewater samples from ceramic cups at 1m depth, with respect to agricultural management zone (raw data supplied by M.Ryan, farm scale subsoil investigation, Teagasc/EPA research report in press).

Agricultural Management Zone	**Average Proportion of Organic N loading observed in Ceramic Cups at 1m deep**	
	2001-2002	**2002-2003**
Grazing Only s	15	7
Dirty Water & Grazing	18	11
One-Cut Silage & Grazing	5	1
Two-Cut Silage & Grazing	25	17

The nitrate loss loading rates calculated from the monitored subsoil leaching data seemed unrealistically low (in particular the for the 1 cut silage management zone data) for employment as the source terms for RAM (ESI, 2000) simulations. The question is, are the small loss loads observed in the ceramic cups attributable to a significant load being lost by denitrification in the subsoil or because a significant proportion of nitrate is by-passing the matrix and moving directly to groundwater? The high groundwater nitrate concentrations would seem to suggest that there is a large load of nitrate being added to the groundwater system and implies minimal denitrification in the subsoil. The fact that the cups do not reflect this substantial nitrate loss loading suggests the cups are not sampling the entire load. This is taken to be further evidence for preferential flow to groundwater. Of course there are other loss terms in the nitrogen cycle such as volatilisation (refer to section 2.3.5) but gains from the far more significant mineralisation process counter other losses in the overall balance of things (see section 2.3.2). The nitrogen source terms for RAM simulations were those that were obtained from NCYCLE simulations (Scholefield *et al.*, 1991).

6.6.2.2. NCYCLE Simulations

The NCYCLE model was employed to estimate the amount of nitrogen available to be lost from the root zone (see section 3.8.1, 3.9 and Appendix A). This is a model that uses 1-year time-steps to provide the amount of nitrogen (kg/ha) lost through leaching and also the peak nitrate concentration in the drainage water leaving the root zone for the year under investigation. Experiments at North Wyke, on which the NCYCLE model is based, demonstrate that the peak nitrate is usually associated with the first 25mm drainage.

The data input requirements of NCYCLE have been outlined in Appendix A. The model was run for the four different management zone scenarios in operation on Curtin's farm (nitrogen loading data from chapter five, Tables 5.7 & 5.8). As previously noted in section 5.1.1, the four different management zones concern grazing only, dirty water and grazing, one cut silage and grazing, and two cut silage and grazing. Detailed NCYCLE model output results for each management zone is presented in Appendix T and a selection of results are presented, along with other data, in Table 6.19.

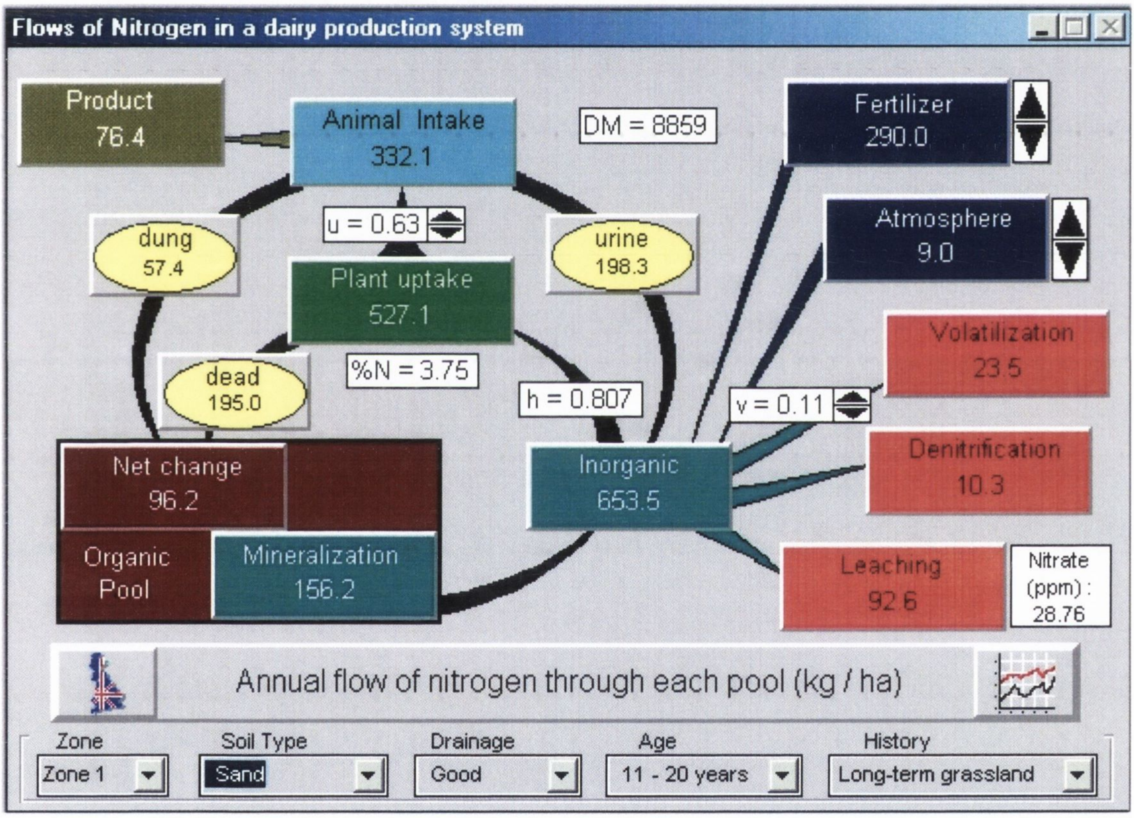
It can be observed from the individual fields' detailed loadings data, in Appendix Q, that although there may be some differences in inorganic nitrogen loading rates to each field, when management options are collated and averaged together the differences between each field within that management zone are of little significance, given the inherent uncertainties in the system anyhow. Within NCYCLE (Scholefield *et al.*, 1991) there is no way to specify a stocking rate, merely because the model is herbage driven. NCYCLE model developers worked with the rationale that there is a relationship between fertiliser application rate and stocking rate, therefore the stocking rate is duly considered (Del Prado, *pers. comm.*, 2003).

The appropriate site parameters were selected as follows:

- Climatic Zone = 1
- History = Long term grassland
- Age = 11-20 years
- Production System = Dairy Cattle
- Soil Type = Sandy soil

- Drainage Classification = Good drainage Classification

The above factors allow the NCYCLE simulation to be initiated. Further inputs, in the simulation window, concern fertiliser input and adjustment of volatilisation and plant uptake factors. The model value for nitrogen removal in animal product, although not available for user-modification, allows useful validation of the relevancy of changing factors that are open to user intervention. An example simulation window of NCYCLE is presented, in Figure 6.47, for a 290 kg N/ha fertiliser application rate. The model output is in graphical format and the nitrogen load lost by leaching is predicted to be 92.6 kg/ha and the predicted farm average, peak, root-zone nitrate concentration is 28.76mg/l NO_3-N.



Flows of Nitrogen in a dairy production system

Annual flow of nitrogen through each pool (kg / ha)

Zone: Zone 1
Soil Type: Sand
Drainage: Good
Age: 11 - 20 years
History: Long-term grassland

Figure 6.47 Representative NCYCLE simulation output window. Simulation shows loss terms for an inorganic nitrogen fertiliser application rate of 290kg/ha for the site parameters of Curtin's farm.

Table 6.19 NCYCLE model outputs for four fertiliser application rates for the different management zones of Curtin's farm (2001) in association with observed peak subsoil and groundwater concentrations monitored in each management zone.

Agricultural Management Zone	**Average Fertiliser Applied (kg N/ha/yr)**	**NCYCLE Output Areal Predicted Leached Rate (kg N/ha/yr)**	**Ceramic Cups Derived* Areal Zone Average Leached Rate (kg N/ha/yr)**	NCYCLE Output **Root-zone Predicted Peak Concentration (mg/l NO_3-N)**	**Ceramic Cups Observed Average Peak Concentration$^+$ (mg/l NO_3-N) [location –month]**	**Groundwater Observed Actual Peak Concentration (mg/l NO_3-N) [location –month]**
Grazing only	206	62	24	**20**	**23.5** [Field 13 – Feb. '02]	20 [Field 13 – Dec. '01]
Dirty Water & Grazing	240	74	63	**24**	**22** [Field 12 – Jan '02]	25 [Field 12 –Nov. '01]
1 Cut Silage & Grazing	320	100	10	**32**	**6** [Field 3 – Oct. '01]	Spring Peak
2 Cut Silge & Grazing	340	110	48	**34**	**23** [Field 15 – Dec. '01]	7 [Field 15 – Jan. '01]

*Estimated using data supplied by farm-scale subsoil investigation led by M. Ryan (Teagasc/EPA research report in press) using average concentrations from 24 ceramic cups per management zone (see Appendix N) and antecedent effective rainfall data generated in my work (see section 5.5.1).

[+] This is the observed peak prior to first spring application of nitrogen fertiliser, after which higher concentrations may have been observed.

6.6.2.3. NCYCLE Validation

NCYCLE performed reasonably well when the model output peak nitrate concentration was compared to observed peak concentrations, in the subsoil ceramic cups and also in the underlying groundwater, for specific fields within an agricultural management zone (Table 6.19). However in some incidences, i.e. for some instrumented fields, when the observed winter peak was significantly lower than the model output the spring peak matched NCYCLE peak output better. However, spring peaks could have been influenced by spring applications of fertiliser and for that reason the spring peaks were not included in the validations presented in Table 6.19.

It is worth remembering that NCYCLE output refers to the amount of nitrate leaching below the root-zone (approximately 0.4m deep). In this evaluation the output from NCYCLE was firstly compared with observed nitrate at 1m-depth in the soil profile. Lower nitrate concentrations at the 1m-depth than in the root-zone might be expected. The column on the right hand side of Table 6.19 shows the observed peak groundwater nitrate concentration at Curtin's farm. For the dirty water and grazing treatments the NCYCLE model output and groundwater peak match, for those particular piezometers. This suggests direct loss to the groundwater environment from the root zone and little dilution in the groundwater that is sampled in the piezometers.

With respect to predicted and calculated areal nitrogen loading loss, the loads calculated from the concentrations returned from the ceramic cups at 1m depth are much less than the NCYCLE simulation output for the root zone in two-thirds of the management zone scenarios (Table 6.18). Only the dirty water treatment loads compare well with NCYCLE load simulations. Because the model performs reasonably well with regard to predicted peak nitrate concentrations, it is assumed that initial concerns over the diminutive calculated loading rates, which were returned from the ceramic cup instrumentation, are substantiated. One reason for the apparent poor correlation between the simulated and calculated loads (for the 1m depth instrumentation) is that Teagasc determined the latter from average nitrate concentration data from 24 ceramic cups in each treatment. I obtained better correlation when I selected the peak observed ceramic cup concentration data, for a specific field in each management zone, for comparison with the in NCYCLE simulated peak output for that management scenario (Table 6.19). Examination of the entire data set for the ceramic cup instrumentation reveals that some cups returned either so few samples or so many zero nitrate concentration results, in contrast to other very active cups in the same field. The poorly responsive cups skewed the dataset when 24 cups in each management scenario were averaged. For illustrative purposes, the first four columns of Table 6.19 have been reproduced in Table 6.20 and a further column added representing calculated loadings from specific fields (not averaged by treatment).

Table 6.20 NCYCLE output loading data compared with two methods of determining leached load from observed subsoil nitrate concentration data.

Agricultural Management Zone	**Average Fertiliser Applied (kg N/ha/yr)**	**NCYCLE Output Areal Predicted Leached Rate (kg N/ha/yr)**	**Ceramic Cups Derived* Areal Zone Average Leached Rate (kg N/ha/yr)**	**Ceramic Cups Derived$^+$ Areal Field Average Leached Rate (kg N /ha)**
Grazing only	206	62	24	**45** **[Field 13]**
Dirty Water & Grazing	240	74	63	**85** **[Field 12]**
1 Cut Silage & Grazing	320	100	10	**16** **[Field 6]**
2 Cut Silge & Grazing	340	110	48	**81** **[Field 15]**

*Data supplied by farm-scale subsoil investigation led by M. Ryan (see footnotes of Table 6.19).

$^+$Data selected from a specific field in each management zone (see discussion at top of page).

Table 6.20 shows that selection of the maximum, rather than averaged data from fields, results achieves closer agreement with NCYCLE simulations. The one exception is that one-cut silage and grazing management zone. Given that NCYCLE performed well with respect to simulating peak nitrate concentration it was assumed that the loading output from NCYCLE is more valid than the ceramic cups data.

6.6.3. Groundwater Modelling

6.6.3.1. RAM Simulations

The RAM model (ESI, 2000) was applied in stages to simulate nitrate leaching through the subsoil to the groundwater body, and then transport it to other piezometer locations and eventually to Downing's Bridge public supply borehole.

6.6.3.2. Testing RAM at Curtin's Farm

It was possible to represent the hydrogeological system at Curtin's farm graphically using the RAM windows graphing programme within Microsoft EXCEL. This facility is user-friendly and allows the conceptual model to be easily communicated to the RAM internal model structure. Multiple contaminant sources, interlinking pathways and complex geology can be represented in a 'Tier 4' RAM analysis, which is the most complex available within RAM and this level of analysis was applied in this study. The RAM programme takes the user-defined graphical model and creates individual EXCEL worksheets for data input pertaining to contaminant flow for each pathway. Because RAM is a hydrogeological model it is built on the concept of infiltrating recharge and the hydraulic controls on water migration; transport distances and travel times (controlled by hydraulic conductivity). All input requirements for RAM simulation have been outlined in Appendix A.

Initially, the model was applied to the simple scenario of nitrate transport to BHC.1 because this is the first piezometer on the farm in terms of incoming groundwater flow direction. There are two sources of nitrate abstracted from each monitoring location; the nitrate already present in the groundwater and the nitrate leaching from the subsoil draining in the general area. The nitrate already present in the groundwater was assigned as 5mg/l, which is observed in the general area (refer to chapter 4, section 4.2.8 and Appendix D). This assumption is felt to be valid considering minimum groundwater concentrations, observed in the summer months, are approximately 5 mg/l nitrate at this location, BHC.1. Input parameters to RAM were those obtained from field investigations that have been reported reproduced in Table 6.17. Source loads were inputted to RAM (NCYCLE values to the subsoil and background nitrate concentrations to incoming groundwater), hydrogeological parameters and dimensions were assigned (both of contributing subsoil and groundwater body), and recharge flow rates to the pathways were inputted to the relevant data sheets of RAM (water balance input to the soil system and groundwater flow rates to the groundwater pathway).

The user must specify the potential transformation processes in operation within each pathway. The available transformation process options were (i) No Processes; (ii) Advection, Dispersion, Retardation and Dilution; or (iii) Dilution only. Simulation results are returned by selection of a drop down menu ('Run Mode') on the RAM toolbar. Simulation output from RAM was compared with observed groundwater nitrate concentrations. Simulation results are returned for user-selected periods in the future, e.g. 1, 2, 5, 10, 20 years.

After the initial RAM testing for the first monitoring piezometer on Curtin's Farm, more complex situations were applied. Firstly, groundwater flow and nitrate transport from BHC.1 to BHC.2 was simulated. The graphical front end of RAM that was built to simulate flow from BHC.1 to BHC.2 is shown in Figure 6.48, for example.

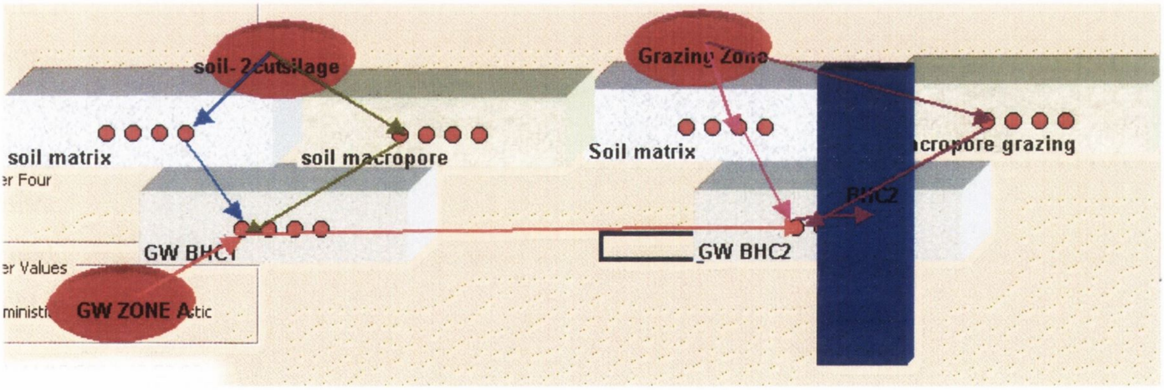


Figure 6.48 Graphical Model built within RAM for intermediary step modelling of the hydrogeological system at Curtin's farm.

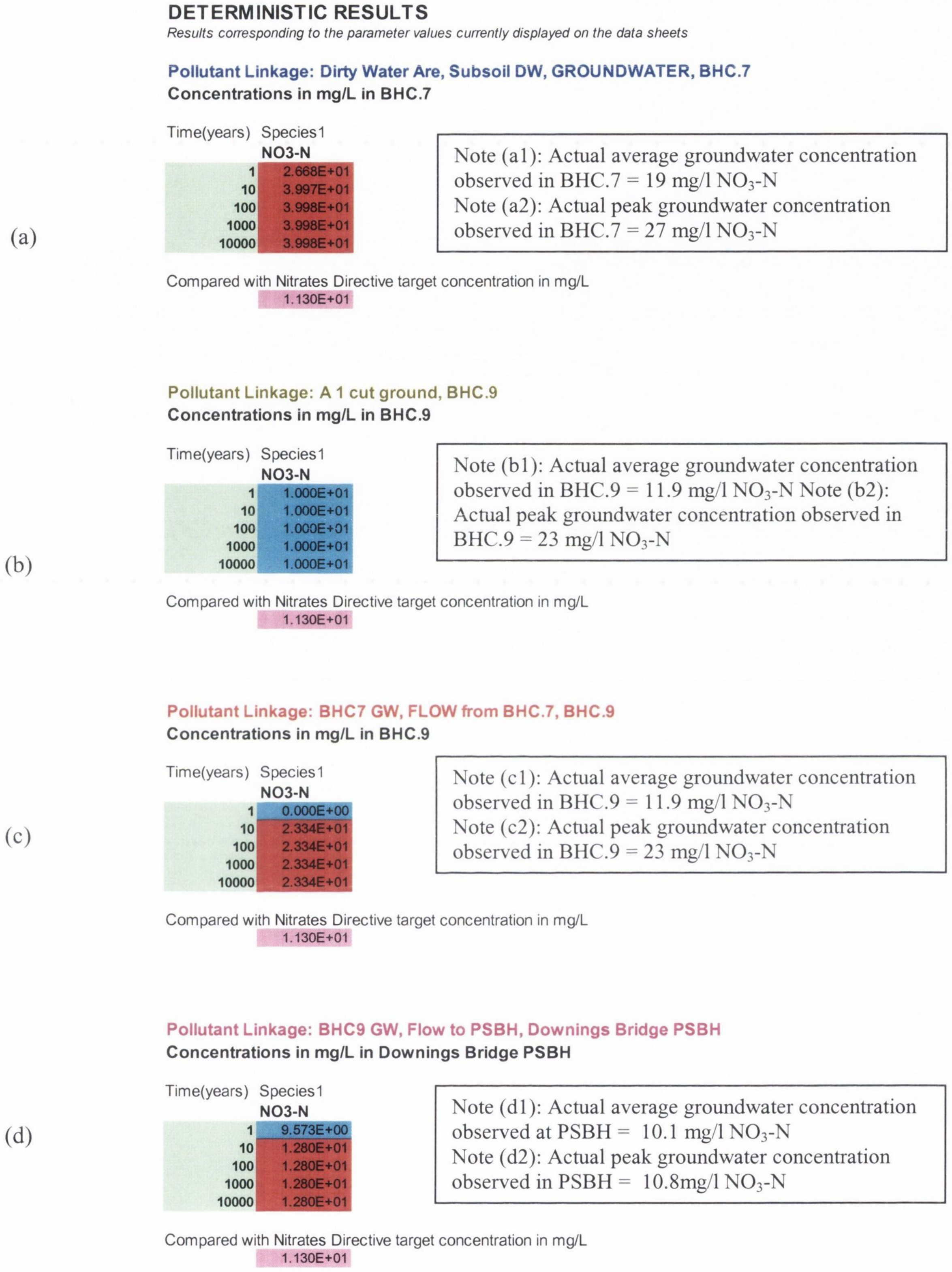
Further model application within RAM was based on the water table elevation maps for the farm (section 6.2.2) and confirmed groundwater flow and directions that had been determined during the tracing experiment (section 6.5). A third RAM model was applied, and tested, to simulate groundwater flow and nitrate transport from BHC.7 to BHC.9. This third model allowed a certain degree of inverse modelling to investigate the hydrogeological pathway between groundwater exiting the farm in the BHC.9 area and groundwater abstracted from the Downing's Bridge Public Supply borehole. APPENDIX V contains details of RAM model applications.

6.6.3.3. RAM Simulation Results

Some representative final data output sheets for the simulations described above are collated in Figure 6.49 (a-d). The final RAM model applied, which simulated flow from BHC.7 to BHC.9 and then to the eventual target at Downing's Bridge, reasonably accurately predicted peak groundwater nitrate concentrations in BHC.7 to be 26mg/l NO_3-N on an annual basis (see RAM output data in Figure 6.49a and added validation notes). Although this is a slight overestimation, it is a reasonable output: the actual annual average groundwater nitrate concentration at BHC.7 was 19mg/l NO_3-N.

Potential preferential flow in the subsoil was accommodated by simulating flow through two pathways (see Figure 6.48 for subsoil pathways). The fact that the groundwater flows through the secondary permeability of the limestone and not through the rock mass must be accommodated in the model. The model requires the physical dimensions of the rock to be defined prior to simulation. Therefore, if I merely inputted the actual measured hydraulic conductivity value for this pathway, the model would be misled. Instead, a lower hydraulic conductivity value was assigned, which is referred to as an Equivalent Porous Media approach. Reasonable simulations of nitrate migration to BHC.9 were achieved; a concentration of 10 mg/l NO_3-N at BHC.9 was predicted (see Figure 6.49(b), which agrees with observed average groundwater concentrations (11.9mg/l NO_3-N at BHC.9).

A shortfall of the model is that it is not possible for one borehole to act as a source for another and so once a step of the simulations has allowed determination of concentration at a target, then the results obtained for that target must be inputted to a new source and so on and so forth.



DETERMINISTIC RESULTS

Results corresponding to the parameter values currently displayed on the data sheets

(a)

Pollutant Linkage: Dirty Water Are, Subsoil DW, GROUNDWATER, BHC.7

Concentrations in mg/L in BHC.7

Time(years)	Species1 NO3-N
1	2.668E+01
10	3.997E+01
100	3.998E+01
1000	3.998E+01
10000	3.998E+01

Compared with Nitrates Directive target concentration in mg/L

1.130E+01

Note (a1): Actual average groundwater concentration observed in BHC.7 = 19 mg/l NO_3-N

Note (a2): Actual peak groundwater concentration observed in BHC.7 = 27 mg/l NO_3-N

(b)

Pollutant Linkage: A 1 cut ground, BHC.9

Concentrations in mg/L in BHC.9

Time(years)	Species1 NO3-N
1	1.000E+01
10	1.000E+01
100	1.000E+01
1000	1.000E+01
10000	1.000E+01

Compared with Nitrates Directive target concentration in mg/L

1.130E+01

Note (b1): Actual average groundwater concentration observed in BHC.9 = 11.9 mg/l NO_3-N Note (b2): Actual peak groundwater concentration observed in BHC.9 = 23 mg/l NO_3-N

(c)

Pollutant Linkage: BHC7 GW, FLOW from BHC.7, BHC.9

Concentrations in mg/L in BHC.9

Time(years)	Species1 NO3-N
1	0.000E+00
10	2.334E+01
100	2.334E+01
1000	2.334E+01
10000	2.334E+01

Compared with Nitrates Directive target concentration in mg/L

1.130E+01

Note (c1): Actual average groundwater concentration observed in BHC.9 = 11.9 mg/l NO_3-N

Note (c2): Actual peak groundwater concentration observed in BHC.9 = 23 mg/l NO_3-N

(d)

Pollutant Linkage: BHC9 GW, Flow to PSBH, Downings Bridge PSBH

Concentrations in mg/L in Downings Bridge PSBH

Time(years)	Species1 NO3-N
1	9.573E+00
10	1.280E+01
100	1.280E+01
1000	1.280E+01
10000	1.280E+01

Compared with Nitrates Directive target concentration in mg/L

1.130E+01

Note (d1): Actual average groundwater concentration observed at PSBH = 10.1 mg/l NO_3-N

Note (d2): Actual peak groundwater concentration observed in PSBH = 10.8mg/l NO_3-N

Figure 6.49 Representative data output tables for 2001-2002 RAM application/model simulations of (a) NO_3-N leaching to BHC.7; (b) NO_3-N leaching to BHC.9; (c) lateral NO_3-N transport from BHC7 to BHC.9; and (d) lateral NO_3-N transport from BHC.9 to Downing's Bridge public supply borehole.

The simulations suggested that the rapid transport and throughputs of the groundwater system at Curtin's would result in only a 3mg/l increase in groundwater nitrate concentrations at the Downing's Bridge target in 10 years. Originally I questioned this result because the observed trend at the Downing's Bridge target demonstrates continuously increasing groundwater nitrate concentrations for the last twenty years. However, on reflection nitrogen addition rates remain stable within RAM's forecasting simulations and so the results are reasonable. A useful feature of the model is that it requires the appropriate legislative standard to be defined (e.g. The Nitrates Directive, EEC, 1991a). If the simulation results breach specified regulation limits, the breach is highlighted automatically in the output sheet (see Figure 6.49). Appendix T contains all hydrogeological simulation results.

6.6.4. Scenario Testing

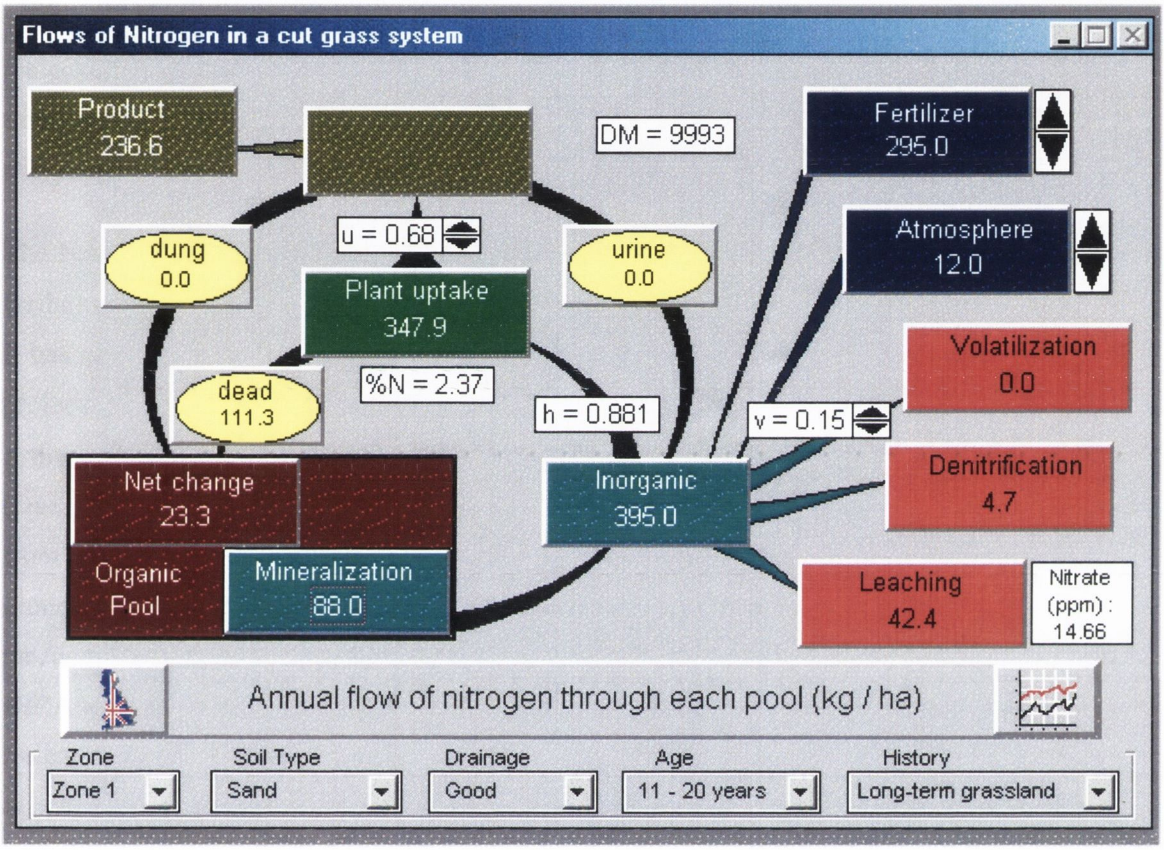
The environmental impact of reducing nitrogen loading was examined using NCYCLE. Simulation results for these reduction scenarios can be found in Appendix T. Because NCYCLE does not simulate organic nitrogen loading, but assumes a simple relationship between fertiliser nitrogen applied and organic loading, it was only possible to simulate reduction in loadings, without specifying source of that nitrogen loading. The results of the load reduction scenarios were as follows:

- Halving the applied nitrogen loading to each system would result in a 45-60% reduction in leached nitrogen load.
- Higher reductions are associated with higher application rates.

These simplistic results are expected from the model: the model is built to a simple structure but this is valid because it is acknowledged in the sphere of nitrogen cycling in grassland that increasing fertiliser application rates increases risk of leaching and to a certain extent the relationship is linear (Jarvis, 1999a). Therefore, scenario testing simulation results are as expected.

Also, NCYCLE allows simulation of 'cutting only' systems. Results of these simulations allow evaluation of the effects of grazing animals on nitrate leaching. The NCYCLE simulation output for a cutting only treatment receiving 290kg N/ha fertiliser application and set for Curtin's farm site conditions are shown in Figure 6.50. The model predicts a load lost by leaching to be 42 kg

N/ha and the predicted peak subsoil porewater nitrate concentration to be 14.66 mg/l NO_3-N, which is 15mg/l NO_3-N less than the predicted peak concentration under a grazed system receiving the same fertiliser application rate (see Figure 6.47).


Flows of Nitrogen in a cut grass system

Product 236.6
DM = 9993
Fertilizer 295.0
u = 0.68
dung 0.0
urine 0.0
Atmosphere 12.0
Plant uptake 347.9
%N = 2.37
Volatilization 0.0
dead 111.3
h = 0.881
v = 0.15
Net change 23.3
Inorganic 395.0
Denitrification 4.7
Organic Pool
Mineralization 88.0
Leaching 42.4
Nitrate (ppm) : 14.66
Annual flow of nitrogen through each pool (kg / ha)

Zone: Zone 1
Soil Type: Sand
Drainage: Good
Age: 11 - 20 years
History: Long-term grassland

Figure 6.50 NCYCLE predictions for a 'cut only' system for 290 kg nitrogen application rate.

6.6.5. Recommendations For Future Nitrate Leaching Modelling Strategy

The modelling strategy selected and tested in the work presented herein is necessarily simplistic and not labour intensive. It is a strategy based on the principle that dairy farming requires a user-friendly medium for assistance with compliance to the Nitrate Directive (EC, 1991a). The NCYCLE (Scholefield *et al.*, 1991) and RAM (ESI, 2000) combination simulates annual peak groundwater nitrate concentration reasonably well but further model development and validation will be necessary for wider geographical application.

The observed groundwater nitrate response at Curtin's farm has a clear temporal dimension (see section 6.4). I believe that, on a national scale, more detailed temporal nitrate trend modelling would be beneficial towards further clarifying critical loading periods, hydrological transport processes and periods of relatively higher risk. My findings with respect to the large variations in organic nitrogen loadings deposited/applied to different spatial regions on an intensive dairy farm, the consequent variable responses in groundwater nitrate concentrations, evidence of preferential flow, and the significance of the GSI groundwater vulnerability methodology deserve further analysis, on a national scale.

The Nitrogen Risk Assessment Model for Scotland, NIRAMS, (Dunn *et al.*, 2003a & b) warrants further attention. This national scale surface water nitrate model has only recently been released. It has not been fully documented in this review because details were published at the end of this project. NIRAMS employs a very simple approach based on NLEAP leaching potential and hydrological soils classifications, built within a GIS system. The approach has been validated (Dunn et. al, 2003b) for nitrate$^-$ concentration in ungauged surface waters but the water is routed from land surface through groundwater to the surface water body and so some validation for groundwater is inferred. NIRAMS is currently being applied in Northern Ireland with regard to meeting Water Framework and Nitrates Directives obligations (Dunn, pers comm., 2003). NIRAMS is a model that may have a future role to play with respect to national scale modelling in Ireland. Its operational framework appears similar to that already established in Ireland by Daly *et al.* (2002) to model national phosphorus loss to Irish rivers. Neither NIRAMS, nor the existing Irish phosphorus model (Daly *et al.*, 2002), currently has specific hydrogeological components, and therein is the advantage of the RAM (ESI, 2000) model tested in my work. NIRAMS does, however, demonstrate that the principles of risk assessment and nitrate$^-$ leaching risk have been successfully linked in other countries.

As yet, no national approach to modelling nitrate transport has been attempted in Ireland. Daly *et al.* (2002) delineated areas at risk from phosphorus runoff through the use of GIS to develop an empirical phosphorus model for Irish surface waters. Essentially, the data-set availability for surface waters facilitated model development, validation and calibration. Maps and databases were produced using information based on the integration of a wide range of existing Irish databases. The parameters were extracted and derived from independent data sets from Teagasc (soil P levels), the Department of Agriculture (fertiliser usage and agricultural census data) and Met Eireann (long term rainfall and estimates for runoff). The independent data were used to model river phosphorus loads in conjunction with remotely sensed data (Corine landcover database). Validation was based on water phosphorus concentrations and stream flow data collected for thirty-five river sub-catchments (dependent variables; obtained from the EPA and OPW). The input parameters were combined using statistical techniques and equations were derived to predict phosphorus levels in catchments not used for model development. In contrast, there is a scarcity of continuous, long-term time-series Irish groundwater data relevant for modelling the resource. Irish groundwater data tends to be collected at purpose built public water supply boreholes and if these boreholes breach drinking water standards pumping and monitoring may cease. Therefore the pre-requisite time-series data may not be available for the very areas which exhibit nitrate trends requiring modelling. However, it is my feeling that the national scale phosphorus model of Daly *et al.* (2002) could be built upon for nitrogen loss modelling. After all, the Water Framework Directive (EC, 2000) encourages consideration of integrated water resources.

Potential national data sources available for modelling nitrate loss in Ireland include:

- Fertiliser Usage Survey (Teagasc)
- General Soil Map of Ireland (Gardiner and Radford, 1980)
- Agricultural Census data (CSO)
- Long-term rainfall patterns (Met Eireann)
- Groundwater nitrate concentrations (EPA, GSI etc.)
- Hydrogeological data (GSI)
- Hydrological survey data (OPW, EPA)
- Existing intrinsic groundwater vulnerability maps (GSI)
- Landcover patterns (CORINE landcover database)

The hydrogeological data available from the GSI combines aquifer and vulnerability maps, which have been derived from bedrock and subsoil geology, depth to bedrock, and hydrogeological data. For modelling purposes, the above national scale information would be supported by the detailed research data for nutrient loss mechanisms at scales appropriate to the issue under investigation. The field investigation carried out in this body of work would form part of the available dataset.

6.7. Summary & Discussion of Field Monitoring Results

Intrinsic Site Characteristics

At Curtin's farm the subsoil is thin (0-4m thickness, but at least 2m at each groundwater monitoring location) and the subsoil is classified either as a SAND or SANDY GRAVEL (BS 1377, 1990). Subsoil hydraulic conductivities are relatively high, in general, but the topsoil layer was more compacted, in general, with the exception of the dirty water irrigation area.

The low incidence of water-strike suggests that broken rock only contains flowing groundwater, which confines the flow and facilitates little dilution of groundwater nitrate by inflowing groundwater. Measured groundwater hydraulic conductivity (10^{-3} – 10^{1} m/day) fall within the range offered by Brassington (1998) for the secondary permeability of limestone bedrock; 10^{-5} – 10^{1} m/day. The average groundwater table elevation beneath Curtin's farm throughout the two-year monitoring period was 30m AOD (25m bgl).

Groundwater Vulnerability

According to the GSI vulnerability assessment methodology (Fitzsimons *et al.*, 2003) the groundwater vulnerability rating is 'extreme' (see sections 5.3.4 and 6.1.1.5). Groundwater nitrate concentrations observed beneath Curtin's farm reflected this. Results from a similar experiment at Johnstown castle add further validation to the vulnerability concept in the context of nitrate leaching to groundwater risk assessment. Thick soil cover and low permeability soils at Johnstown Castle result in a low vulnerability rating that is substantiated by low groundwater nitrate concentrations.

Groundwater Recharge Determinations

The recharge and non-recharge seasons were clearly defined by cumulatively plotting effective rainfall (RF_{eff}) over the time period of the study. Daily effective rainfall was determined using data from the Met Eireann weather station at Moorepark, the FAO evapotranspiration model (FAO, 1998) and soil moisture deficit accounting (Aslyng, 1965). Recharge to the groundwater begins in October of each year and continues until May or June. While all piezometers reacted with similar trends, the magnitude of the response was quite different in some piezometers as is to be expected for inhomogeneous field conditions. Water levels in all the piezometers were observed to decline steadily throughout the summer period (July to September) and so I conclude that the effective rainfall calculation method is validated for determination of total meteorological loading to the groundwater system. One shortcoming of the effective rainfall methodology is that it does not account for preferential flow or rainfall intensities. Both of these issues are important for contaminant transport at the storm-event scale.

Groundwater Level Response

The response of the groundwater to meteorological loadings is most clearly observed with the onset of recharge each winter. In each hydrological year, piezometer water levels demonstrated a significant response to RF_{eff} within one month of the onset of recharge. The initial stages of the winter recharge season have been shown to cause substantial rise in groundwater levels. Similarly rapid water table responses to recharge are reported for another Waulsortian unit in Cork (Fitzsimons *et al.*, 2003). It is difficult to discern the temporal effects of additional recharge. The magnitude of the initial surge on the system clouds the influence of any further recharge additions. Water level recovery, after the intense initial pressure on the system, seems to prevail over the influence of further recharge. Effective rainfall affects an increase in groundwater levels, at 25-28m bgl, within a short period on Curtin's farm. Within one month of the heavy block of winter recharge, observed to be 200mm in the wettest winter month in both years, groundwater levels rise by up to 8m, on average. After the massive winter peak in groundwater levels the influence of further recharge on groundwater levels is difficult to discern unless >50mm RF_{eff} falls within a two-week period. In that case, a 0.5-1.5m rise in water levels is observed.

Groundwater Nitrate Response

Analysis of nitrate concentrations during recharge periods in comparison to periods of little or no recharge showed that concentrations have a strong relationship to recharge events (i.e. hydraulic loading). At most monitoring locations effective rainfall transported nitrate to the groundwater body (section 6.4.5.1). Generally, it is observed that there is a clear groundwater nitrate response to meteorological loading. Groundwater nitrate concentrations were observed to rise in response to significant rainfall events in spring and summer but fell proportionately with autumn and winter recharges (see Figure 6.13 and section 6.4.1 for further discussion). The initial decrease in concentration is a result of less source material being available in proportion to the amount of water that enters the system (Peterson, et al., 2002). However, the initial diluting effect of recharge not sustained and groundwater quality was observed to be detrimentally impacted by nitrate recharge by matrix flow.

There was a marked difference in groundwater nitrate concentration depending on piezometer location. The groundwater nitrate response was discernible in correspondence to differing agricultural practice in different locations on the farm. The highest nitrate concentrations were observed beneath the dirty water treatment area where organic nitrogen loadings were higher than at any other location on the farm. There was a decline in groundwater nitrate concentrations in the second year that is probably a combined result of farm management practices and meteorological conditions. In the second year, almost fifty percent more effective rainfall fell in the winter, acting to dilute nitrate as it was flushed from the soil. The timing of the recharge was also important. In the first year, nitrate deposited in the soil throughout the grazing season resided until January 2002. In the second year, the residence time of deposited nitrogen was much shorter.

Nitrate concentrations in the groundwater monitored beneath Curtin's farm are elevated with respect to local groundwater nitrate status. Groundwater nitrate concentrations were nearly always above the EU Drinking Water Directive (EC, 1998) MAC of 11.3mg/l NO_3-N. Additionally, the observed maximum ammonium concentrations in the groundwater at most boreholes are extremely high and 77% of the monitoring locations reveal peak concentrations that breach the EPA IGV (EPA, 2003a). These results highlight a significantly vulnerable groundwater.

Literature providing groundwater nitrate concentrations related to dairy farming practice in a karstified hydrogeological setting was difficult to find. Most groundwater studies concern the regional scale and therefore the agricultural land-use is mixed, cropland being a popular focus of much international literature. With respect to comparing the groundwater nitrate concentrations observed at Curtin's farm with the findings of others who have studied similar hydrogeological environments, Peterson *et al.* (2002) investigated the movement of nitrate through a karst spring basin in an agricultural catchment. They observed average concentrations at the point of spring discharge to be 4.09 mg/l and 5.07 mg/l NO_3-N during storm and non-storm flow, respectively. These concentrations are low with respect to both the 11.3 mg/l NO_3-N MAC (EC, 1998) and the observed range of groundwater nitrate concentrations beneath Curtin's farm (ranging up to 31 mg/l NO_3-N). However, Peterson *et al.* (2002) register concern over their findings and conclude that agricultural activities are having a detrimental impact on their vulnerable karst aquifer, given that the background concentration of their aquifer is 1 mg/l NO_3-N. Available background groundwater concentrations in north Cork average <5mg/l NO_3-N (see section 4.2.9) and therefore, the high groundwater nitrate concentrations observed at Curtin's farm require that agricultural activity in vulnerable environments be more controlled.

Sanchez-Perez *et al.* (2003) researched nitrate leaching through the subsoil and in the groundwater body. However, their hydrogeological setting and scale of investigation were very different to that at Curtin's farm. They studied a Spanish quaternary aquifer, of an average thickness of 5m, covering an area of 90 km^2, with a 0 to 1.5m deep water-table which, at times of recharge, rose to contribute nitrate to the subsoil. Another crucial difference was that the predominant land-use was irrigated cropland. Nonetheless, the groundwater concentrations presented by Sanchez-Perez ranged from 50 to 200 mg/l as NO_3 (equivalent to 11.3 to 45 mg/l as, NO_3-N, approximately). Although this does not represent leaching from grassland it does show that leaching concentrations can reach high levels.

Loadings Driving Groundwater Response

Detailed loadings data were generated from daily records kept at Curtin's farm. Nitrogen loadings from inorganic fertiliser applications, dirty water irrigation, slurry application and grazing animals' depositions in the field were considered. These loadings were converted to the same rate format (kg/ha) so that the temporal response of the groundwater system to all nitrogen loadings could be examined. Graphs were created to show both meteorological and agronomic loadings and the groundwater elevation and nitrate response.

The most significantly discernable temporal response was that to meteorological loading. It became clear that the most discernable influence, temporally, was the pattern of effective rainfall and nitrogen loading occurring relatively closes together. However, given the unsuitability of defining a groundwater nitrate protection strategy based on weather prediction, as a working methodology for dairy farm managers, a simpler load response relationship was investigated.

On an annual time-scale, there was found to be a positive correlation between the grazing intensity at the farm field scale and the average nitrate concentration observed in groundwater samples extracted from piezometers in the same plots in the following recharge period (R^2=0.91). Using the GSI vulnerability assessment methodology, it is the nature of the cover that determines intrinsic vulnerability but the observed relationship between grazing intensity and nitrate response in groundwater at 25-30m bgl shows that increased grazing intensity increases the potential for nitrate delivery to the groundwater.

Substantiating the Effect of Grazing Intensity on Groundwater Quality

In grazed pastures the potential for nitrate leaching increases significantly (Di *et al.*, 1998). Whitehead (1995) reports that as the intensity of grazing is increased, there is increased consumption of the herbage available, which results in a larger proportion being returned to the soil via animal excreta. Sapek (2000) found that intensively used pastures with excessive grazing intensity was one of the "hot spots" responsible for farm input to groundwater pollution by solutes, especially nitrogen, phosphorus and potassium.

McGechan & Topp (2004) found higher nitrate loss from grazed fields compared to fields receiving slurry and cut for silage. They also found that nitrate leaching was exacerbated by the effects of cows congregating (for water or shelter) and by excretions deposited at times of low plant uptake. Others (Puckett *et al.,* 1999) have concluded that animal production did not significantly contribute to groundwater contamination in their investigation area. However, cropland comprised 73% of their study area and their model simulations were validated with only one sampling event, which was carried out in June-July.

Zebarth *et al.* (1998) studied a similarly classified 'vulnerable aquifer' overlain by well-drained soils in Canada to conclude that their results highlight the potential of intensive animal production to affect negatively groundwater quality. They report groundwater nitrate concentrations in the range of 10.7 to 16.6 mg/l NO_3-N at 25m bgl, which are similar to those recorded at Curtin's farm. Rodvang *et al.* (2004) report average groundwater nitrate concentrations in the range of 12.5 to 17.4 mg/l NO_3-N at 8m depth in their aquifer and conclude that piezometers located in areas of high agricultural intensity contain significantly higher nitrate than in areas of lower agricultural intensity.

Lysimeter studies predominate the recent nitrate leaching from grassland literature (e.g. Di *et al.*, 1998; Silva *et al.*1999; Loiseau *et al.*, 2001; Decau *et al.*, 2004). Each of these recently published lysimeter studies report their principal findings to be the deleterious effect of grazing animals on nitrate loss from grassland. Their findings substantiate the grazing days relationship identified in my work. Loisseau *et al.* (2001) conclude that grazing management is likely to be the main factor driving nitrogen leaching under grazed swards. Silva *et al.* (1999) measured peak concentrations of 120mg/l NO_3-N at 0.9m depth beneath a urine patch. Decau *et al.* (2004) found that low winter drainage and grazing management resulted in a higher impact on waters' nitrate status than nitrogen fertiliser management; the impact of grazing was found to be more important than fertilisation at rates up to 300 kg N/ha (Curtin's farm average nitrogen fertiliser application rate was 290 kg N/ha).

Agricultural Signature in the Groundwater

The agricultural signature in the groundwater beneath Curtin's Farm is strong. In terms of general hydrochemistry, most piezometers yielded Electrical Conductivity (EC) values between 800 and 900μS/cm, which are within the EPA IGV (EPA, 2003a) standards. However, one piezometer, BHC.4, consistently breached the EPA IGV for groundwater EC, 1000μS/cm, during the monitoring period. Median phosphorus concentrations at

BHC.4 are also elevated with respect to those observed at other locations. Generally the groundwater beneath the farm conforms to the Drinking Water Standards (DELG, 2000) potassium limit of 12 mg/l K and the IGV value of 5 mg/l K. However, BHC.3 and BHC.4 consistently breach the higher 12mg/l K concentration. There may be some leakage to BHC.3 & BHC.4 from the adjacent farmyard but the underground slurry tanks cannot be deemed the entire source of the problem because potassium concentrations are highest in the summer. Results presented in section 6.4.6.5 highlight the effect of groundwater solute concentrations being influenced from multiple sources and directions is at these monitoring locations. Point sources of contamination at the farmyard do affect groundwater quality in the immediate vicinity of the yard. However, groundwater flow directions and the tracing experiment show that the farmyard is not the only source of contamination on the farm. Intensive animal grazing, stores of nutrients in the soil and dirty water irrigation, coupled with a free draining soil and vulnerable hydrogeological conditions, affects groundwater quality at Curtin's farm.

In the course of soil fertility investigations, for agronomic purposes, potassium levels in the topsoils of Curtin's farm were observed to be approximately 80 mg/l K in the grazing and silage areas, but in the dirty water treatment area topsoil potassium levels measured 200-300 mg/l K (see chapter 4, Figure 4.2). Groundwater concentrations ranging from 90-3597 mg/l K were observed by Sapek (2000) in the vicinity of farmyards and manure storage areas, but she also observed maximum groundwater concentrations of 952 mg/l K beneath pastures on sandy shallow soils.

Dirty water irrigation occurs every day on this farm, and on other dairy Irish dairy farms. Dirty water is implicated as a contaminant source that requires more thoughtful management because in autumn 2002 there is a definite potassium contamination incidence in many piezometers. The potassium content of irrigated dirty water is high: Ryan (1990) reported concentrations greater than 200mg/l K in analysed dirty water from a similar Irish dairy farm. Sandy soils, such as those at Curtin's, have little capacity to retain potassium by cation exchange (Whitehead, 1995) and the extremely high topsoil potassium concentrations in the dirty water irrigation area would suggest that any capacity to retain potassium has already been reached. Bohlke (2002) suggests that observations of potassium, phosphorus and sulphate in groundwater must indicate an agricultural signature and that macropore flow and/or excessively high irrigation rates must be investigated. BHC.1 is deemed to be representative of groundwater flowing into the farm and was not impacted by the dirty water irrigation under scrutiny. Groundwater potassium concentrations were consistently below the IGV 5mg/l standard at BHC.1. The potassium contamination event was first detected in BHC.7, after dirty water was irrigated in August in the plot in which BHC.7 is located (Plot 12BLUE), and then in all other piezometers around BHC.7. This potassium migration was detected at a time when there had been no calculated effective rainfall recharge to the system in the previous three months. However, over 60mm of rainfall had occurred and perhaps some recharge occurred that was missed by the monitoring programme. There were only two potassium contamination incidences at BHC.7, the second occurred in March 2003, again one month after dirty water irrigation in the plot. The water table elevation maps and tracing experiment suggest groundwater radiates from this area and so this borehole is one that allows clearest interpretation of hydrochemical analyses results in terms of overlying land use and management practices.

Bromide Tracing Experiment

The tracing experiment involved eight ceramic cups at the 1m-depth in the subsoil and one groundwater piezometer, all in the same plot, in the dirty water irrigation area. The tracer tests highlighted that the time of travel for solutes from ground's surface, through the subsoil, to the groundwater body was in the order of months, approximately 44 days to peak groundwater concentration, under spring recharge and a single dirty water irrigation rate of 15mm. Bromide was transported in the groundwater, approximately 200m horizontally, and observed to peak in these other piezometers two months before the bromide arrived at 1m-depth in most of the ceramic cups in the subsoil of the field in which the tracer was applied.

The bromide tracing experiment, conducted in the spring season, suggests that the horizontal groundwater velocity was ~8m/day in the central farm area. Other Irish karst groundwater research (e.g. Coxon & Drew, 1986; Drew *et al.*, 1995; Coxon & Drew, 2000) suggests higher groundwater velocities. However, those investigations were carried out in conduit karst in the west of Ireland.

The tracer experiment proved that dirty water irrigated in the central farm area moves quickly to the groundwater body at 28m bgl and is transported to some other neighbouring piezometer monitoring points. However, groundwater-monitoring data suggest that, simultaneous to this dirty water influence, the loadings of nitrogen from grazing animal's depositions impact groundwater nitrate concentrations in the immediate vicinity of piezometers.

Dual Mechanisms of Solute Transport

Tracing experiment results suggest that bromide moved preferentially to the groundwater body and was more quickly transported horizontally through karstified bedrock than vertically through the subsoil matrix. This does not prevent piston flow; it merely supersedes it initially. Iqbal & Krothe (1995) certify that solute transport may proceed simultaneously in two different modes: one by complete displacement of existing soil water, piston flow, and the other by short-circuiting through the vertical soil column, commonly referred to as by-pass or preferential flow.

Research on Irish karst systems in county Kerry concluded that soil matrix and preferential flow both influence karst water chemistry: soil matrix flow being dominant during dry periods, whilst preferential flow through soil macropores being important during recharge (Tooth & Fairchild, 2003). Macropores are pores with an effective diameter of more than 0.05mm (Whitehead, 1995). Peterson *et al.* (2002) found that solute transport through macropore flow played a major role in elevated nitrate groundwater concentrations observed within a karstified system. However, in my observations preferential flow incidences were assumed to be the cause of observed dilution in groundwater nitrate concentrations, at BHC.2 and BHC.7, when that dilution was associated with rapid water table increases in response to rainfall recharge. The dilution persisted for a short period only. I believe that preferential flow contributes recharge to groundwater that has by-passed the soil matrix and so does not carry nitrate with it: contaminants transported by preferential flow must be available at the soil surface. However as previously mentioned, the initial diluting effect of recharge by-passing the soil matrix was not sustained and groundwater quality was observed to be detrimentally impacted by nitrate recharge by matrix flow.

Groundwater Phosphorus Concentrations

A phosphorus signature was observed in response to recharge events at numerous locations in both years studied. A factor to consider is phosphorus concentrations in the soils of Curtin's farm (see chapter four, section 4.2.3.1 and Figure 4.3). Although phosphorus is strongly adsorbed onto positively charged soil particles, it has been shown to leach from freely draining soils that are phosphorus over saturated. However, phosphorus may have moved preferentially to the groundwater body. Groundwater phosphorus concentrations were observed to respond in a completely opposite fashion to observed nitrate trends under potential preferential flow conditions in that water table peaks were sometimes associated with phosphorus peaks at some locations at Curtin's farm.

Dills & Heathwaite (1996) suggested preferential flow as a mechanism for phosphorus to bypass the soil's natural sorbing capacity. Phosphorus movement due to oversaturation of the soil matrix with phosphorus has been observed in free draining soils of coarse texture (Haynes & Williams, 1992b; Ozanne *et al.*, 1961; Richards *et al.*, 1998). Chen *et al.* (1996) demonstrated leaching of phosphorus from sandy soils with high permeability, conditions which exist at Curtin's farm. In those cases, phosphorus was assumed to move with infiltrating water that percolates through the soil matrix. However, I propose that the groundwater phosphorus observations in my work are indeed a result of preferential flow because of the apparent close relationship between effective rainfall and subsequent rapid groundwater level increases, in association with the observed phosphorus and ammonium concentration peaks in the groundwater.

Further Evidence of the Potential for Preferential Flow

Groundwater ammonium peak concentrations were sometimes observed in association with nitrate concentration troughs at Curtin's farm. McGechan & Topp (2004) observed ammonium transport, from previously marked urine patches, by preferential flow, which was activated by urine deposited on wet ground. This provides further support to my analysis of ammonium (and phosphorus) moving preferentially to groundwater monitoring at Curtin's farm (see section 6.4.6.7). The significance of hydrological control on preferential flow was also underpinned by the work of Kulli *et al.* (2003) which found that while compaction might decrease the surface permeability in upper soil layers, it is rainfall (or sprinkler) intensity which dictates the role of macropore flow in contaminant transport scenarios. Although it is popularly thought that preferential flow is a phenomenon restricted to clay soils, the phenomenon has been observed in the unsaturated zone of layered silt and sand (Derby & Knighton, 1997) and in a sandy unsaturated zone (Kung, 1990a & b).

Preferential flow paths can explain the seemingly anomalous results of some studies where greater concentrations of solute are observed at depth than in more shallow layers (Fetter, 1999). Kung (1990a & b) monitored solute concentration through soil layers in a sandy unsaturated zone and observed higher concentrations at depth, which was attributed to preferential flow. Others also reported higher solute concentrations at depth than in upper soil layers (Sanchez-Perez, 2003; Gibbons *et al.*, 2003) but did not make the link with preferential flow.

Agricultural Impact on Groundwater Quality

Bohlke (2002) suggests that indirect effects of infiltration of agriculturally contaminated water with high ionic strength or acidity include increasing weathering rates. Rates of leaching may therefore be enhanced by physical and biological changes in the subsoil caused by increased acidity and the ionic strengths of agriculturally impacted recharge. These results suggest that it is inappropriate to maintain the same land usage year after year for dirty water application. Continuous use of an area for dirty water irrigation may change the structure of the soil. Also, slurry areas should be rotated: the decay series of slurry demands that if the same land is used in successive years, then rates must be reduced (Whitehead, 1995). Excessively high levels of phosphorus in the topsoils of the dirty water and slurry areas of Curtin's farm substantiate these recommendations. However, because groundwater nitrate concentrations were observed to be influenced by multiple sources and upgradient directions it was not possible to confidently assess the impact of slurry alone on groundwater quality at Curtin's farm.

Reducing Nitrate Leaching

A turn of the century review of nitrate leaching reported that the key to reducing nitrate leaching is by preventing the accumulation of mineral nitrogen in the soil profile before the leaching season starts, which can be achieved by an integrated approach with regard to nitrogen applications, crop harvest and post-harvest livestock management in grazed pastures (Di & Cameron, 2002). The most current computer simulations of the effect of grazing animals on nitrate leaching from dairy farming conceptualise the stocking density as doubled over the grazing area, since half the farm is typically shut off for hay and silage (McGechan & Topp, 2004). This strategy galvanises the reality of the significant localised effect of grazing animals. Acknowledgement of the vulnerability of grazing areas, coupled with analysis of the most intrinsically vulnerable areas of any farm, will ensure that risks can be minimised and, therefore, dairy farming optimised.

The US Geological Survey (USGS) has been working quite extensively in characterising groundwater quality as part of the National Water Quality Assessment (NAWQA). Nolan (2001) related nitrogen sources and aquifer vulnerability to nitrate in shallow groundwaters of the US. He employed a multivariate logistic regression model and found that vulnerability of groundwater to contamination by nitrate depends not on a single factor but on the combined, simultaneous influence of factors representing nitrogen loading sources and aquifer susceptibility characteristics, which is not a new contribution to our understanding of nitrate leaching but merely adds statistical validation to the vulnerability concept. Much of the USGS work stresses the long time lag between nitrogen application at the surface and its delivery to the groundwater body. Contrastingly, my work has demonstrated the rapid response of groundwater at Curtin's farm to hydrological and agronomic loadings, which is essentially good news for dairy farming in vulnerable conditions. The significance of a rapidly responding hydrogeological system is that all improvements in management, specifically grazing intensity and rotation over wider areas of the farm, should shortly result in an observable improvement in groundwater quality.

CHAPTER SEVEN CONCLUSIONS

A principal objective of this work was to assess the groundwater nitrate concentrations beneath grasslands' and its response to dairy farming agricultural practice. The main area chosen was an intensive dairy farm in north Cork, in Ireland, on freely draining subsoil over a karst groundwater body. Four distinct management zones operate on a typical dairy farm namely, grazing only pasture, a dirty water treatment area that is managed in rotation with grazing, a one-cut silage growing area and a two-cut silage growing area, each of which are grazed after silage production.

- The results of this thesis provide further evidence of this link between agricultural practice in dairy farming and nitrate groundwater concentrations in Ireland. More importantly, the work provides evidence of subsurface preferential flow. Solute transport was observed to move through the subsoil by two flow mechanisms, preferentially and through the soil matrix, to groundwater.

Groundwater Response

- The response of groundwater in this karstified hydrogeological environment under grassland does confirm the designation of the area as having a regionally important aquifer of extreme vulnerability, and monitoring results highlight the need for careful management measures.

- Analysis of nitrate concentrations during recharge periods in comparison to periods of little or no recharge showed that concentrations have a strong relationship to recharge events (i.e. hydraulic loading).

- Groundwater nitrate concentrations were observed to rise in response to significant rainfall events in spring and summer but decreased, initially, with autumn and winter recharges. However, despite the initial decrease in groundwater nitrate concentrations caused by winter recharges dilution effects, groundwater nitrate concentrations were observed to increase again in spring.

Response to Agronomic Management

- Detailed nitrogen loadings analysis demonstrated that nitrogen fertiliser application rates vary only by 50 to 60 kg N/ha/yr in different agronomic management zones on

Curtin's farm. Inorganic nitrogen application rates ranged from 290 to 340 kg N/ha/year in the first year (2001-2002). Inorganic nitrogen application rates were slightly lower on average, in the second year, ranging from 248 to 310 kg N/ha/year. The farm area weighted inorganic fertiliser application rate was 305 kg N/ha/yr in the first monitoring year (2001-2002) and 290 kg N/ha/yr in the second year.

- Total organic nitrogen loading rates varied significantly in each management zone. In each year, the average total organic nitrogen loading rate is highest in the area dedicated to dirty water treatment relative to the other three zones: the dirty water treatment area received more than double the organic nitrogen loading rate of the grazing only area. The dirty water treatment zone receives organic nitrogen from grazing animals and dirty water. The average organic nitrogen load contributed by grazing animals was calculated to be 179 kg N/ha/yr and 198 kg N/ha/yr in the grazing only and dirty water treatment zones, respectively, in the first year (2001 – 2002). However, the additional organic nitrogen load contributed by dirty water irrigation results in almost doubling the total organic nitrogen load to 378 kg N/ha/yr in the dirty water treatment zone. In the second monitoring year, an average organic nitrogen loading rate of 471 kg N/ha/yr was calculated for the dirty water treatment zone. The significance of these figures with respect to the Nitrate Directive (EC, 1991a) is noteworthy in that the Directive decrees a maximum organic nitrogen loading rate of 170 kg N/ha/yr. Groundwater nitrate concentrations were observed to be highest under the dirty water treatment area. The high organic nitrogen loading in his zone facilitated more intensive animal grazing, with respect to all other zones.

- Area weighted average organic nitrogen application rates suggest values of 216 kg N/ha/yr and 248 kg N/ha/y in the first and second years, respectively (see Tables 5.7 & 5.8). However, area weighted values mask local effects of organic nitrogen loading rates in the area of the dirty water treatment zone because the dirty water area represents a small area of the farm (only 14% of the total farm area).

- Curtin's farm currently operates at a stocking rate of 2.4 Livestock Units per hectare (LU/ha). The Nitrate Directive (EC, 1991a) organic nitrogen limit of 170 kg N/ha implies a 2 LU/ha limit.

- The timing and rate of nitrogen applications are one of the determining factors in nitrate leaching. The potential exists for large leaching losses following nitrogen fertiliser applications in spring. In some instances, groundwater ammonium, nitrite and nitrate concentration trends suggest that grazing activity and fertilisation in spring, followed by effective rainfall events, had a significant impact on groundwater nutrient concentration response. This response was weather dependent. Given that the weather is uncontrollable, the only management option is to reduce the nitrogen load available for potential loss.

- The impact of late winter applications of nitrogen fertiliser was also observed to be detrimental to groundwater quality when effective rainfall occurred after inorganic fertiliser was applied.

- The groundwater nitrate response was discernible under small areas of differing agricultural practice. In other words, high concentrations were generally observed under

    - high nitrogen rather than low nitrogen inputs and

    - out of season nitrogen inputs.

Groundwater Nutrient Concentration Response

- Groundwater nitrate concentrations beneath Curtin's farm were nearly always above the EU Drinking Water Directive (EU, 1998) & Nitrate Directive (EEC, 1991a) parametric limit of 11.3mg/l NO_3-N.

- Nitrate concentrations in the groundwater monitored beneath Curtin's farm are elevated with respect to local background groundwater nitrate status. Background groundwater concentrations in north Cork average <5mg/l NO_3-N (see section 4.2.9) and therefore, the high groundwater nitrate concentrations observed at Curtin's farm require that agricultural activity be more controlled in such vulnerable areas.

- The observed peak concentrations of ammonium in the groundwater at most boreholes are extremely high and 77% of the monitoring locations revealed peak concentrations that breach the EPA (EPA, 2003a) Interim Guide Value (IGV).

- In the 2001-2002 hydrological year, groundwater nitrate concentrations at ~28m bgl varied from 7 to 25 mg/l NO_3-N, depending on the location of the borehole within the

50ha farm. In the following hydrological year, the observed spatial variation in groundwater concentration was 4 to 23mg/l NO_3-N.

- Point sources of contamination at the farmyard do affect groundwater quality in the immediate vicinity. However, groundwater flow directions and the tracing experiment show that the farmyard is not the only source of contamination on the farm. Intensive animal grazing, stores of nutrients in the soil and dirty water irrigation, coupled with a free draining soil and vulnerable hydrogeological conditions, are the stronger factors affecting groundwater quality at Curtin's farm.

- The agricultural signature in the groundwater beneath Curtin's Farm is strong at some locations. Phosphorus, potassium, ammonium and nitrite peaks were observed in groundwater at over 25 m below ground level, which suggests a highly vulnerable hydrogeological setting.

- Incidences of groundwater contamination were identified in response to dirty water irrigation periods. However, the rapid response of the system ensured that the K:Na status of the groundwater returned to acceptable standards in the succeeding recharge period. Again this highlights the responsiveness of the hydrogeological system. Knowing that the system responds quickly indicates that changes in management practice will result relatively rapidly in observed better groundwater quality.

Driving Mechanisms

- With respect to identification of the loadings that most significantly influence groundwater nitrate concentrations – effective rainfall, or hydraulic loading, and the intensity of animal grazing are identified the main drivers on the system.

- The most useful integral measure of the nitrogen loading may be the number of grazing animals (stocking density), since a strong correlation has emerged between grazing intensity at the field scale and observed average concentration of nitrate in the groundwater below, in the succeeding recharge period.

- Grazing animals are likely to cause large leaching losses because of the highly concentrated excretions deposited on the soil. Urinations are applied under significant hydraulic loading, which aids the vertical migration of the nitrogen in the urine, especially in the context of dual porosity subsurface flow. The importance of the contribution of nitrogen loading by grazing animals should not be ignored. The organic nitrogen-loading rate is therefore a crucial factor in managing nitrogen loss to groundwater. This finding validates the requirements of the Nitrate Directive (EC, 1991a) to restrict grazing intensity in vulnerable areas.

- The hydraulic loading, be it recharge from dirty water irrigation, recharge as rainfall or cattle urinations, is a key factor that determines nitrate delivery to ground water. Nitrogen applications in excess of plant growth requirements increases the risk of leaching but recharge has been shown to be the driver ultimate of leachate generation.

Tracing Experiment Results & Preferential Flow

- Surface applied bromide was observed to migrate though 2.5m of subsoil to the groundwater body, at 28m below ground level, in less than three weeks. Indeed bromide was observed in the groundwater body before it was observed in most subsoil ceramic cups installed at 1m below ground level. Bromide migrated 200m horizontally in the groundwater body before peak concentration was observed in the ceramic cups. Therefore, strongly confirming subsurface preferential flow and rapid hydrogeological response times.
- Maximum vertical travel velocity to the groundwater body was ~1.66m/day. Groundwater horizontal velocity was calculated to be ~8m/day.
- Groundwater phosphorus and ammonium peak concentrations, in association with water level increases, are further evidence of the fact that on some occasions contaminant transport is by preferential or by-pass flow.
- The effect of preferential flow on groundwater nitrate concentrations is quite opposite to the phosphorus response because nitrate is not readily available at the soil surface; it is within the soil matrix that nitrate is generated through the nitrogen cycle. However, subsequent to preferential flow, matrix flow acts to transport nitrate to the groundwater body.
- The observed initial decrease in groundwater nitrate concentrations and subsequent slow increase after recharge also suggests dual mechanism solute transport through the subsoil. The proposition is that the intense winter recharges surge the system because some of the recharge arrives quickly at the water table, due to by-passing of the soil

matrix and so has a relatively low recharge concentration that acts to dilute groundwater concentrations (of some constituents). Hence the overall decrease in groundwater nitrate concentrations. Subsequent slow percolation through the soil matrix, in spring, results in nitrate enriched recharge to the groundwater body that does not significantly impact water table elevation but does cause increases in groundwater nitrate concentrations.

Role of Hydrometeorological Loadings

- Despite similar peak groundwater nitrate concentrations in both years, in the second year there was a marked reduction in observed nitrate concentrations. Winter effective rainfall in the second year was double that recorded in the first year, which means that the same available nitrate loss load was diluted, potentially two-fold. The responsiveness of the system is thereby demonstrated: the nitrate response in the groundwater is characterised by relatively recent recharge.

- The hydrometeorological balance presented in this work has been developed to represent recharge and non-recharge conditions on an annual basis. However, the role of preferential flow under specific hydraulic loadings (e.g. storm events, dirty water irrigation or cattle urinations) will require further manipulation of the methodology.

Modelling Results

- The modelling strategy presented in this work is necessarily simplistic and not labour intensive. It is a strategy based on the principle that dairy farming requires a user-friendly medium for effective assistance in compliance to the Nitrate Directive (EC, 1991a).

- The risk assessment concept for groundwater assessment was further progressed by successful testing of the hydrogeological risk assessment model RAM (ESI, 2000) for the karstified hydrogeological system at Curtins farm.

- The NCYCLE nitrogen loading model (Scholefield *et al.*, 1991) and networking routing RAM (ESI, 2000) model combination simulates annual peak groundwater nitrate concentration reasonably well in the studied area but further model development and validation will be necessary for wider geographical application.

- The agronomic NCYCLE model (Scholefield *et al.*, 1991) was validated as an adequate methodology for source term definition of peak nitrate leachate concentration from the root zone, on an annual basis. However, current further development of NCYCLE should result in a model that more accurately represents the average areal nitrate load lost.

- Simulation results suggest that NCYCLE alone may not be sufficient as a predictor of groundwater response as the hydrogeological system has a strong role in modifying nitrogen concentrations. The ultimate integrator of nitrogen concentrations is the groundwater and the key receptor may be remote from the individual farm (e.g. estuaries).

- RAM facilitated user-friendly representation of the hydrogeological pathways governing nitrate leaching to groundwater. The karst hydrogeology was easily represented by control of the groundwater pathway dimensions. Although RAM requires hydraulic conductivities to be specified those obtained in the field investigations of this study, and subsequently employed in model simulation, were similar to those suggested in the literature.

- The observed groundwater nitrate response at Curtin's farm has a clear temporal dimension. Future development of modelling nitrate leaching to groundwater and nitrate leaching risk should incorporate a seasonal dimension. This level of computation will require use of GIS. If a GIS system were set up then it would seem more feasible to attempt to use a finer resolution model for simulating nitrate load available for leaching.

Groundwater Vulnerability

- The Groundwater Survey of Ireland (GSI) groundwater vulnerability and protection methodology was applied to two Teagasc study farms and was further validated.

- As previously mentioned, monitoring results highlight the extreme vulnerability of groundwater beneath Curtin's farm.

- Groundwater nitrate values are very low at all monitoring locations at Johnstown Castle in Wexford. The nitrate concentration of groundwater monitored at Johnstown castle corresponds with expected background values even though two thirds of the instrumented plots on the conventional dairy farm receive nitrogen loadings similar to those applied on Curtins farm in north Cork. However, because the groundwater is protected by thick subsoil of low permeability at Johnstown Castle, it is protected from nitrate contamination. The Johnstown castle results also demonstrate that the hydrogeological controls on solute leaching, such as the nature of the subsoil, ploughing history and amount of artificial under-drainage are factors as, or even more, important than applied nitrogen fertiliser.

Summary & Implications for Agricultural Practices

- My work has demonstrated the rapid response of groundwater concentrations at Curtin's farm to hydrological and agronomic loadings in hydrogeologically vulnerable conditions. This has beneficial implications for dairy farming in that the significance of a rapidly responding hydrogeological system is that all improvements in management, specifically grazing intensity and grazing rotation over wider areas of the farm, should result relatively quickly in an observable improvement in groundwater quality. Moreover, the results indicate that regionalisation of organic nitrogen loading limitations, in light of intrinsic hydrogeological and meteorological conditions, might form more prudent policy under the Nitrate Directive (EEC, 1991a) and the Water Framework Directive (EC, 2000).

- Generally the delivery of nitrate to groundwater below any particular site is dependent on the thickness and hydraulic conductivity of subsoil as well as the timing and magnitude of nitrogen loading and effective rainfall. Mixing or dilution by additional sources also affected downgradient groundwater concentrations.

- The nitrate concentrations found in the groundwater indicate that farming practices as conducted on an intensive dairy farm, such as Curtin's farm in 2001 and 2002, need to be modified in order to ensure future compliance with the Nitrate Directive (EEC, 1991a) in vulnerable areas.

Dairy Farming Issues

- Slurry applications at Teagasc recommended rates and according to Good Farming Practice, applied during the growing season, do not result in significant nitrate leaching, which is to say that the EU Drinking Water Directive (EU, 1998) Maximum

Admissible Concentration (MAC) of 11.3mg/l NO_3-N was not persistently breached in the silage growing zones.

- Nitrogen fertiliser rates should be reduced to take full account of the nitrogen loading from dirty water applications. Whitehead (1995) suggests that irrigation increases nitrogen uptake, which yields to higher grass yields. This scenario facilitates more intensive grazing in irrigated areas, which must be avoided.

- Teagasc soil-tests were found to be a useful indicator of soil enrichment, which signified increased risk of nutrient loss to groundwater, in these free draining soils.

- Rotation of dirty water and slurry spreading areas should be strongly considered. Evidence of increased leachate risk, attributable to irrigation with high strength agricultural recharge, was found during these field investigations of subsoil hydraulic conductivity. These findings were substantiated by the literature (e.g. Bohlke, 2002).

- The literature suggests that the main aim should be to restrict the amount of nitrogen in the rootzone at the end of the growing season (Garwood & Ryden, 1986; Steenvoorden, 1989; Addiscott et al., 1991; and Whitehead, 1995). Whitehead (1995) suggests a greater integration of cutting and grazing, especially the cutting for silage late in the season of swards that have been grazed intensively earlier in the season. Modification of the dietary intake of animals and, on areas where there is a known risk of nitrate leaching, taking cattle off the land earlier in Autumn are other suggestions for reducing risk of nitrate leaching (Addiscott et al., 1991).

Recommendations

1. Longer term monitoring of nitrate response in groundwater to agronomic practices should be undertaken to further substantiate the key controlling factors as identified in this work.

2. For better validated prediction of nitrate response in groundwater to organic nitrogen loadings, the modelling strategy should be further developed and tested against field evidence from a wider geographical area.

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